Chiranjib Kumar Gupta

Chemical Metallurgy

Chemical Metallurgy: Principles and Practice. Chiranjib Kumar Gupta

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Principles and Practice

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Foreword

Dr. C. K. Gupta is a very distinguished colleague of mine. I have been familiar with his professional career over a long period. A very large number of research papers, reviews, and several books authored by him bear ample testimony to the diverse and wide-ranging contributions he has made to date to the field of chemical metallurgy. I was indeed very happy to accept the invitation from him to write a foreword for the present volume entitled, "Chemical Metallurgy – Principles and Practice", being published by Wiley-VCH Verlag, Germany.

This volume provides in one place a self-contained and adequately detailed coverage of the chemical metallurgy of the major metals, common as well as less common. It has been brought into being as an exceedingly well-structured treatise. The presentation has been organised in seven chapters. The first chapter gives a general appraisal of the whole field of chemical metallurgy. The coverage also includes a brief account of resources. The next two chapters are devoted to thermodynamics and kinetics and to processing of minerals. The remaining three chapters deal, respectively, with pyrometallurgy, hydrometallurgy, and electrometallurgy. The last chapter attends to energy and environmental considerations. Physicochemical principles provided for the various unit operations and description of the key details of the processes deserve special mention as being among the attractive features of this volume. One must also additionally note the emphasis laid on the less common metals in the presentation. This is decidedly an additional special feature of the book. Chemical metallurgy of the less common metals described with pertinent principles involved has not been done earlier in one place as has been accomplished in this publication. The abundance of illustrations and the comprehensive collection of carefully selected references appended to each chapter add to the value and enhance considerably the overall strength of the book. On the whole, the presentation displays an imaginative and competent handling of the subject matter and really reaches out to the readers.

The volume deals with a very wide technical field and will be of interest and relevance to many disciplines, particularly metallurgy, chemical engineering, and chemistry. It will undoubtedly be a valuable addition to the list of available books dealing with chemical metallurgy. At the same time, this volume will be very useful to professionals working in the area of extractive and process metallurgy. The present book has had the benefit of Dr. Gupta's wide and long-standing experience in the field in full measure and will certainly be greatly valued by those to whom it is addressed. I wish this publication all success and hope it will be as useful as the other books which Dr. Gupta has authored.

India, May 2003

B. Bhattacharjee
Director of Bhabha Atomic Research Centre
and Member of Atomic Energy Commission

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Preface

As the title, “Chemical Metallurgy: Principles and Practice” implies, this text blends theory with practice covering, of course, a good deal of descriptive items on hows and whys of extraction and processing of metals and materials. While the processes for the extraction of the common metals have been provided in sufficient detail, I have tried to go in equal depth, if not more, to provide focus on the less common metals. I have, however, avoided lengthy descriptions of current commercial practices as these change rapidly. Rather, selected examples have been presented to illustrate the various principles dealt with in the text. It is expected the readers will supplement this text with appropriate examples of current practices. All along I have made an effort to lead the treatment to a point where the readers will find the transition to more advanced and specialized metallurgical engineering textbooks, texts, and monographs with emphasis on chemical metallurgy quite easy.

This book altogether contains seven chapters. In Chapter 1, I have endeavored to organize the text with a view to acquainting the readers with a miscellany of relevant information and preparing them for going into the contents of the subsequent chapters. Chapter 2 deals with mineral processing, which usually takes the position as the principal front-end operation in the overall process flowsheet for metal extraction. Chapter 3 pertains to thermodynamics and kinetics which provide unequivocally a sound basis for the understanding of the processes. The next three chapters delve into pyro-, hydro-, and electro-metallurgy, in that order. Chapter 7 addresses certain representative issues concerning energy consumption and environmental pollution aspects especially pertinent to chemical metallurgy operations.

It is difficult for an author to praise the virtues of his own book. However, just to say a few words, I may add that, as pointed out, I have systematized the organization of the text in the chapters by presenting the process principles first and then following up with process practice. I have in my opinion adopted a lucid style – readable, interesting, intelligible, and informative – for a wide and varied audience. It has on the whole been a delightful experience for me to produce and place this book for the readership it will fetch. May I end by saying that I earnestly believe the book will provide an interesting reading and knowledge, and will certainly be highly successful in putting the readers into the fascinating world of preparative metallurgy, into the arduous journeys through which different metals and materials traverse to come into their useful beings and finally make themselves available in the service of man. A carefully selected reference list and a good number of clear illustrations may be treated as additional features which should not be lost sight of. All these presentations have not been carried out without incorporating the backing of the principles involved and this very element should go to provide additional attractions and spice, so to say, for the book.

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Appreciation

No reader of this book can fail to recognise how much I owe to others who have written earlier in this field. To the authors and the editors of the references cited in this volume I express my heartfelt thanks. A book is very much a team project. I am truly indebted to my colleagues, Tapan Kumar Mukherjee, Ashok Kumar Suri, N. Krishnamurthy, and Pradip Mukhopadhyay, whose counsels I sought and whose opinions and advice, so generously given, have largely determined the scope and character of what I have written. All have greatly brought life to the project in the form of unique insights in chemical metallurgy.

Prof. Kenneth N. Han of South Dakota School of Mines and Prof. Paul Duby of Henry Krumb School of Mines have had occasions to review this work. They provided knowledge, insight, and plain common sense to guide me during the process of development of this work. I wish to record my deepest gratitude to them. In the same breath, my deepest appreciation goes to Pradeep Mukhopadhyay, who has patiently gone through the writing and spared me in no way to keep mistakes at bay. Despite all the thorough inputs from many quarters, if errors have still remained they are all my own responsibility, of course, and I hope readers who find them will communicate them to me or the publisher. This would go a long way to provide a very valuable chance to carry out necessary amendments in the future.

It is a pleasure to acknowledge the devoted services of Poonam Khattar, to whom work connected with the mechanics of manuscript preparation extending to producing computer-generated art work has become a labor of love. I also wish to mention Yatin Thakur who has continued to be associated with me in commendably executing draughtsmanship duties.

Finally, I express my appreciation to all the members at Wiley-VCH, particularly to Claudia Barzen, Maike Petersen, and Martin Ottmar for helping me in many ways right from the inception to the finishing of this publication.

This volume, which is the most significant undertaking in my authorship career in metallurgical literature, could not have been attempted and brought to completion without the understanding and patience of my wife, Chandrima, and my son, Chiradeep. Their sacrifices were great; my gratitude to them is profound. Throughout the preparation of this book, I have derived strength and inspiration from the work and the percepts of my late father, Probodh Chandra Gupta. It is with a sense of warm affection, great humility, and profound respect that I am dedicating this work to his memory.

Illustrations may be treated as additional features of the book which should not be lost sight of. I have taken care to see that all these presentations have the backing of the principles involved and this very element should go to provide additional attractions and spice, so to say, for the book.

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Acquaintance

1.1
Introduction

The subject of metallurgy broadly divides itself into physical metallurgy, mechanical metallurgy, chemical metallurgy, mineral dressing, powder metallurgy and engineering metallurgy.

Physical metallurgy is concerned with the scientific study of materials. Phase transformations, recovery and recrystallization, precipitation hardening, structure–property correlations, characterization of microstructure by microscopy (optical, electron and field-ion), are some specific examples among the many topics covered under physical metallurgy.

The importance of metals and alloys largely lies in their unique mechanical properties involving the combination of high strength with the ability to undergo plastic deformation. Their plasticity makes them amenable to various mechanical working methods (drawing, rolling, pressing, forging etc.). Plasticity can make strong materials tough and enable them to endure long service, even under very exacting conditions. Mechanical metallurgy addresses all these aspects of the behaviour of metallic as well as other materials. Testing mechanical properties, establishing relations between these properties of materials and their design and selection, assessing and predicting materials performance during service are some of the important areas that come under the purview of mechanical metallurgy. This branch also involves with mechanical working of metals and alloys in solid state. For example, mention may be made of rolling, forging, drawing and extrusion.

Chemical metallurgy, according to one definition, is the branch of metallurgy that deals with the extraction of metals from naturally occurring compounds and their refinement to levels of purity suitable for commercial use. The starting raw materials, however, in many cases are not restricted to naturally occurring compounds. Nor in all cases are the end products desired as metals. The chemical treatments quite often depend upon the prior physical processing to which the relevant materials have been subjected. In acknowledgement of these facts it is only proper that both physical and chemical treatments are considered together in the total scheme defined for materials processing. There exist a very large variety and range of treatments and many possible combinations of these which may be used in chemical metallurgy processes. The chemical metallurgy coverage extends further to deal with all the chemical properties of metals, including those pertaining to the formation of alloys by uniting one metal with other metals or nonmetals.

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Physical metallurgy has obvious links with mechanical metallurgy. It also has close links with chemical metallurgy. It helps in obtaining a scientific understanding of the various chemical metallurgy processes and can assist in designing new processes or modifications of existing processes. The linkage between physical metallurgy and chemical metallurgy has grown with time. This has helped considerably in replacing the empirical or the “trial and error” mode of development with more logical and science based modes. For example, a newly found ore resource can be studied by such powerful physical metallurgy tools as x-ray diffraction, electron microscopy and electron probe microanalysis, and with the knowledge thus gained about the resource, it is possible to make very useful predictions in a number of fronts. Once the type and the nature of the minerals present in a given resource are studied and analysed, it is entirely possible to make useful predictions on the processing of the resource. Refractory minerals would need highly corrosive leachants and aggressive conditions of leaching such as those obtained at elevated temperatures and pressures as in autoclaves. If the structural features show the substitution of one element at the lattice sites of another then separating these elements by physical methods is not possible.

The area of mineral dressing concerns itself with the starting operations and involves crushing and grinding either for purposes of liberation of the desired substances that are physically entrapped with others or for making them adoptable for further processes. Once liberated, they normally go through such physical beneficiation processes as magnetic separation, electrostatic separation, screening, flotation, to name some, to produce a beneficiated product usually called a concentrate and chemical metallurgy normally takes over from then onwards.

Powder metallurgy is concerned with production and processing of powdery forms of metals and materials and of solid industrial products therefrom.

Engineering metallurgy mainly deals with the processing of metals and materials in the molten condition. Foundry, metal joining and other related areas appear to come under its coverage.

These branches, individually as well as collectively, have enabled metallurgy to play a very important role in modern science and technology. The outstanding importance of metals as constructional materials is, in fact, the reason why metallurgy, by itself, is an extensive and self-contained subject. It has, however, gone very much beyond the confines of any rigid classification. On the whole, the subject of metallurgy, besides its own constituent disciplines, as described herein, draws heavily from a number of others. With inputs from physics, chemistry, chemical engineering, instrumentation technology, design engineering and so on, metallurgy today has shaped into a truly multidisciplinary and interdisciplinary character.

It is only natural that chemical metallurgy is given a further introductory elaboration at this beginning stage although a good portion of it will either be repeated or be dealt with in a more detailed way as the text advances in the subsequent chapters.

The extraction of metals fundamentally relies on their availability in nature. Three terms are important while one refers to availability. One is the crustal abundance and the other two are the terms: resources and reserves. The average crustal abundance of the most abundant metals, aluminum, iron and magnesium, are 8.1%, 5.0% and 2.1% respectively. Among the “rare” metals titanium is the most abundant, constituting 0.53% of the Earth’s crust. No metal can be economically extracted from a source in which its concentration is the same as its crustal abundance. Fortunately, geochemical processes have resulted in significant selective concentration of the elements in certain portions of the Earth's crust. These portions are called ore reserves or resources, depending on whether their processing is economical currently or is expected to be so at some future date. With the passage of time more and more of what are presently considered as resources will become reserves. High grade reserves or ore bodies, containing a high concentration of the desired metal, have been selectively mined and processed in the past and at the present time there remain very few, if any, of such ore bodies. Those presently available are low in grade and complex in composition. In the future the grade will decrease further and the complexity will increase, making metal recovery from such sources a much more difficult affair.

The poor grade and the complex composition of the ores being processed currently cause mineral processing to be a major operation in the metal extraction scheme. Physical and chemical characterization of the minerals becomes very important as these characteristics determine the processing scheme to be used. Magnetic and electrical properties have been extensively used in mineral beneficiation, using electromagnetic and electrostatic separators. Surface properties of minerals determine the basis for their beneficiation using flotation.

The processing of ores or primary resources for metal extraction is constrained by two major factors. One is their limited supply and availability and the other is the large energy consumption involved in their processing. An option to circumvent these constraints is to resort to recycling of metals or secondary resource processing. Recycling of scrap usually consumes only a fraction of the energy needed for metal extraction from the ore. No new ore is consumed in recycling and the process causes much less pollution of the environment. These attractive features have generated serious interest in recycling in recent times and the interest will certainly grow in the days to come. This area has received detailed attention in the chapter on energy and environment.

The route by which an ore ends up as a metal suitable for commercial use is mapped in diagrams known as extraction flowsheets. These comprise a judicious assembly of the unit processes that lead to a working scheme. A flowsheet is always amenable for upgradation by improvements both in the unit processes and in their sequencing. The developments in chemical metallurgy pertain to these improvements. Much development can be expected in the coming decades in chemical metallurgy on account of the efforts needed to extract purer metals from leaner and more complex ores with minimum energy expenditure, while causing minimum environmental pollution. These demands will keep research on improved and new extraction processes alive and make extractive metallurgy an important and dynamic branch of metallurgy, as in the past.

This book "Chemical Metallurgy: Principles and Practice" contains all together seven chapters. Chapter 1 embodies a content meant to acquaint the readers on a selection of topics of considerable relevance to chemical metallurgy. Chapter 2 deals with mineral processing, Chapter 3 with thermodynamics and kinetics, Chapter 4 with pyrometallurgy, Chapter 5 with hydrometallurgy, Chapter 6 with electrometallurgy, and Chapter 7 with energy and environment. The book, as its title implies, presents chemical metallurgy practice mandatorily taking the pertinent principles involved at different stages into account.

1.2
Materials

It is a well recognised fact that classification of the vast array of materials is an important part of the study of materials. The grouping or classification of materials is to be based on a scheme. Among the different basis of classification schemes known so far the well accepted ones are: (i) nature of atomic bonding, (ii) electrical conductivity, (iii) magnetism. Taking these into account, almost all the major materials can be shown to fall under the following categories: ceramics and glasses, polymers, composites, semiconductors, thermocouples, ferroelectrics and piezoelectrics, magnetic materials and metals.

The present writing on classification of materials may additionally be drawn to another fundamental aspect and this is about a very well known scheme of classification or a way of grouping of elements. It is the periodic classification of elements. Graphical portrayals of the periodic classification of elements are familiar as periodic tables. The table represents an arrangement of elements in order of the increasing atomic number in horizontal rows, known as periods. The columns of the table are known as groups. The elements in any group have similar chemical properties. Each group is assigned a number, written at the top of the vertical column. The numbering system used so far has varied since its formal form given from the time of Mendeleev. A numbering uses a combination of roman numerals and the letters A or B to label each group while another recommends that the 18 groups be numbered consecutively from left to right, 1 to 18. The numbering scheme, the later one, for the groups will be used in the present text.

The elements in two groups at the far left (1, 2) and the six groups at the far right, as group 13 through 18 are called the representative elements or main group elements and those in the central region labelled as B (3–12) are the transition elements. The two series, the first one, the lanthanides (cerium, Ce, through lutetium, Lu) are the elements that follow lanthanum (La) in period 6, and the second one, the actinides (thorium, Th, through lawrencium, Lr) are the elements that follow actinium (Ac), in period 7, are known as inner transition elements. These two series of elements do not belong to any of the groups labeled at the top of the table. It is possible in a broad sense to classify elements as metals or nonmetals. The diagonal line or stairway that can be drawn from the left to the lower right of the periodic table can be looked upon as dividing metals from nonmetals. Elements below and to the left of this line are metals. Included among the metals are (i) all of the elements in group 1 (except H) are known as alkali metals and those in group 2 are known as alkaline Earth metals; also Al (but not B) in group 13, (ii) all of the transition metals, (iii) the elements to the right of the transition series in groups 13 (Ga, In, Tl), 14 (Sn, Pb), and 15 (Bi) (collectively, these elements are called as post-transition metals), and (iv) the lanthanides and actinides (the inner transition metals). Elements above and to the right of the diagonal line are classified as nonmetals. It may be noted that along the diagonal line in the periodic table there are several elements that are difficult to classify exclusively as metals or nonmetals. These elements are boron, silicon, germanium, arsenic, antimony, and tellurium. Their properties are in between the metallic and nonmetallic classes. They are often together called as metalloids.

1.3
Some Characteristics of Metals

1.3.1
General

It is obvious from the text described in the last paragraph of the preceding section that periodic table is replete with elements that are metals. It turns out that three fourths of all naturally occurring chemical elements are metals and that each metal occurs in a multitude of minerals from which it can be won and put into the service of man. Some members in the family of metals have been specially classified as rare metals group. The members belonging to this family come from almost all the groups of the periodic table. They are classified into five categories: light rare metals, refractory rare metals, scattered rare metals, rare Earth rare metals and radioactive rare metals (Figure 1.1). It can be seen in this figure that rhenium figures in two groups. It is a typical scattered metal. However, on account of its properties, it may also be classified as a refractory metal.

1.3.2
Electronic Structure

Detachment of an electron from an atom and taking it into the form of positive ion requires an expenditure of energy which is the ionization energy or the ionization potential. The first ionization energy is the energy change for removal of the outermost electron from a gaseous atom to form $a + 1$ ion. In general, in the case of the main group elements, ionization energy decreases moving down in the periodic table and increases going across, although there are several exceptions. A consequence of the outer electrons in a metal atom being quite far from the nucleus is that they are weakly bound to it. This weak binding is reflected in the low values of the ionization energy. This is why metals readily part with their valence electrons, playing the role of reducing agents. The magnitude of the ionization potential can be taken as a measure of the extent of the metallicity of an element. The smaller the potential, the easier it is to detach an electron from an atom and the stronger are the metallic properties of the element.

A common feature of metal atoms is that they are generally larger in size in comparison with nonmetal atoms. A characteristic of nonmetals is that their atoms have the ability to attach electrons to themselves, leading to the formation of anions. The opposite is true for the metals and as told they alter to cationic forms when their removable electrons leave them.

The higher the valency of a metal, the greater will be the number of electrons in the outermost shell. Now, since the positive charge residing in the nucleus remains unaltered by the removal of electrons, its attractive influence will progressively increase with the removal of each successive electron. It follows that when there are a number of electrons in the outermost shell, the removal of electrons will progressively tend to be more and more difficult as each electron is taken out.

The larger the atomic volume of an atom, the less strongly will the positively charged nucleus be able to hold the electrons in the outermost or the valency shell. In other words,

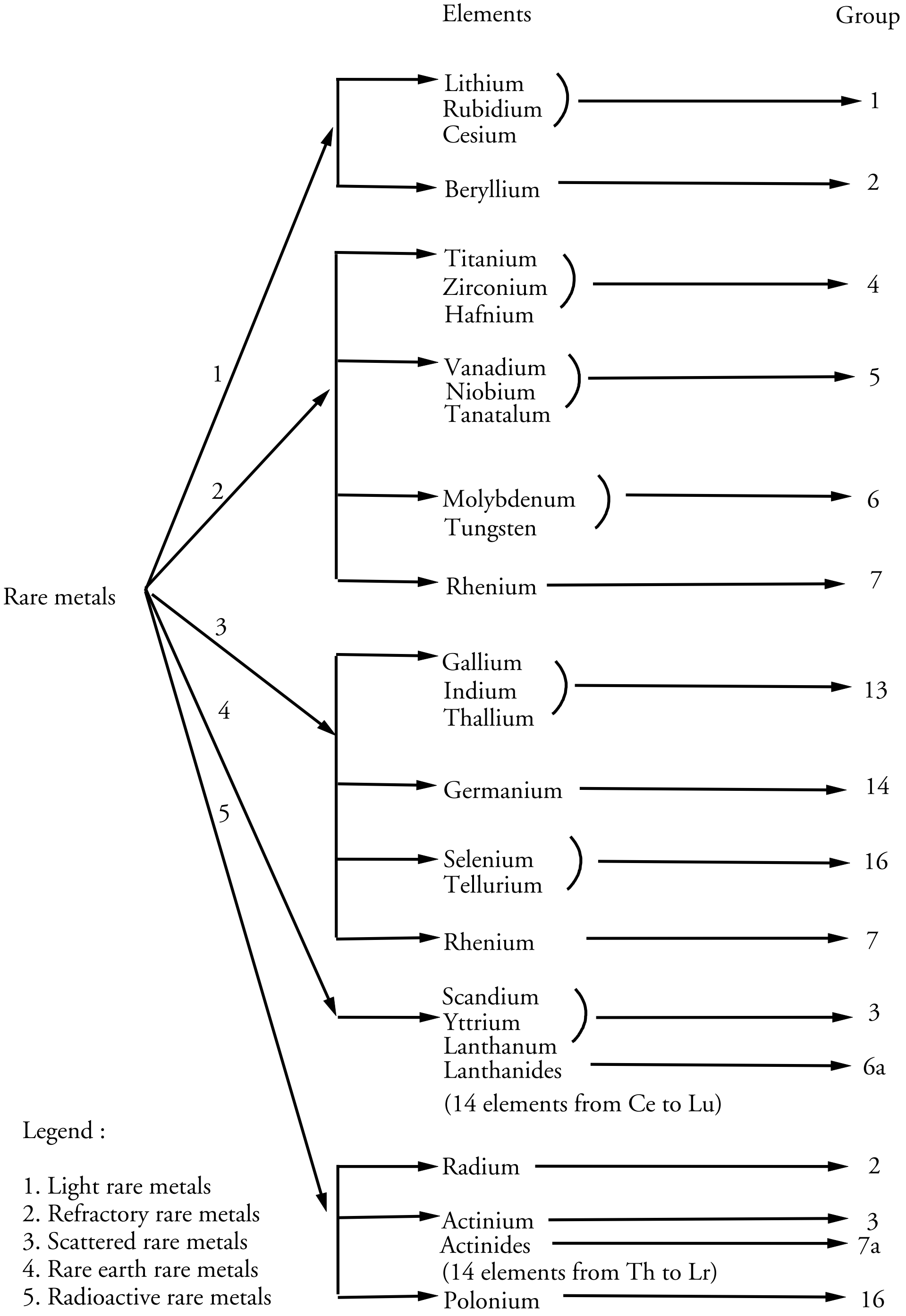


Figure 1.1 Classification of the rare metals (*a* = period).

the more easily will such an atom lose one or more electrons to become an ion. Such is the case with the atoms of a large number of metals.

Although it is possible, by the loss of several electrons, for certain metal atoms to form polyvalent cations upto a maximum valency of four (e.g., tin forms the tetravalent stannic ion, Sn^{4+}), the formation of polyvalent anions is extremely difficult since for the acquisition of each additional electron the attractive force exerted by the nucleus on each individual electron becomes progressively smaller. It is for this reason that the maximum valency for a simple anion is found to be two.

The metallic structure essentially consists of atomic nuclei and associated core electrons, surrounded by a sea of free electrons. The high electrical conductivity of metals is derived from the presence of these free electrons. In addition to high electrical conductivity, the free electrons provide the metals with good thermal conductivity as well. The electrical resistivity of a metal increases with temperature.

Metals are noted for their high reflectivity and optical opacity. Both these properties are explainable in terms of the behaviour of the free electrons. They oscillate in the alternating electrical field of the incident light beam, absorbing energy at all wave lengths; this makes the metals opaque. The oscillating electrons give out light rays and in this way produce the reflected beam, accounting for the high reflectivity.

Metals are immune to radiation damage by ionization. This is also a consequence of the free electron structure. Fast charged particles and ionizing rays can knock off electrons from the atoms they encounter. In metals, the positive vacancies so formed are immediately filled up by the electron gas, leaving no sign of damage apart from a small amount of heat.

1.3.3
Crystallography

All metals in common with many ceramics, some plastics and most minerals, are crystalline. The crystalline state is one in which the constituent atoms or molecules are arranged in a regular repetitive and symmetrical pattern in space. The study of the characteristics of crystals is known as crystallography. The properties of metals and other crystalline materials are greatly dependent on their crystal structures and on the imperfections or crystal defects that they may contain. A second reason for studying crystal structures is that each crystalline substance (elements/compounds) possesses a definite crystal structure. Thus, the crystal structure provides a means of distinguishing between various compounds or elements, even in cases where they are chemically identical. For example, gamma iron and alpha iron are both allotrophic forms of the element iron, and have the same chemical constitution but different crystal structures. In the study of crystal structures of metals the unit cell constitutes the basic unit of a crystal structure. A unit cell is a small grouping of atoms or molecules which, if repeated indefinitely in three dimensions produce a crystal of macroscopic dimension. The unit cell, therefore, exhibits all the properties of the large crystal. Thus, it is only required to known the structure of the unit cell in order to be able to specify the structure of the whole crystal.

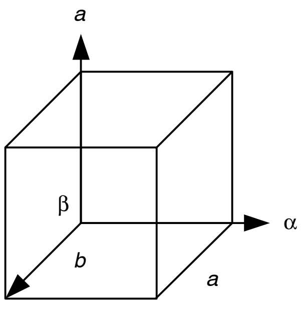
1.3.3.1 Crystal Systems

One of the concepts in use to specify crystal structures the space lattice or Bravais lattice. There are in all fourteen possible space (or Bravais) lattices.

The points of each of the space lattices can be best addressed by making reference to a set of three coordinate axes which define the directions of the three edges of the unit cell. These edges may or may not be of equal length, and may or may not be inclined at equal angles to one another. On the basis of the lengths of the unit cell edges and their inclination with respect to each other it is possible to define seven crystal systems. If these lengths are denoted by a, b, and c and the interaxial angles are denoted by α, β, and γ the crystal systems can be differentiated in the manner described in Table 1.1.

Space lattices and crystal systems provide only a partial description of the crystal structure of a crystalline material. If the structure is to be fully specified, it is also necessary to take into account the symmetry elements and ultimately determine the pertinent space group. There are in all two hundred and thirty space groups. When the space group as well as the interatomic distances are known, the crystal structure is completely determined.

Table 1.1 Crystallographic systems.



System	*Crystallographic elements*		*Examples*
	Areas	*Angles*	
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	CuF_2, ZnS, NaCl, Pt, Fe, Diamond, Pb, KCl, Cu, Ag, Au, AgCl, As
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	$CaWO_4$, SnO_2, Sn, TiO_2, $PbWO_4$, $PbMO_4$, $CuSO_4 \cdot 5\ H_2O$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	$ZnSO_4$,$PbCO_3$,KNO_3,$BaSO_4$, $MgSO_4$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$; $\beta \neq 90°$	$Na_2SO_4 \cdot 10\ H_2O$ $CaSO_4 \cdot 2\ H_2O$, $Na_2SO_4 \cdot 10\ H_2O$
Triclinic	$a \neq b \neq c$	$\alpha = \beta = \gamma \neq 90°$	$CuSO_4 \cdot 5\ H_2O$, H_3BO_3, $K_2Cr_2O_7$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$; $\gamma = 120°$	Beryl, Be, graphite Mg Zn Cd, HgS, Ca; apatite, CuS, pyrrhotite
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite, magnesite, quartz, ice, Sb, Bi, millerite, cinnabar, corundum

Since the atoms in a crystal are arranged in a regular manner, it is evident that planes can be defined which will contain many atoms. The simplest of such planes are those defined by any two axes of the coordinate system used to define the crystal system. Other planes will, of course, be more complex; their occurrence, however, should be obvious. The importance of these planes becomes evident while discussing the features and properties of a crystal such as its orientation, and the twinning and the slip systems associated with it. It is, therefore, important to have some system of nomenclature which will distinguish these planes and define their orientation. The system of nomenclature traditionally used is that of Miller indices. As mentioned earlier, it is convenient to define three coordinate axes to describe the crystal system. Starting at the intersection of these axes and proceeding along any one of them, identical points will be encountered at periodic intervals; the smallest of these intervals in each direction describes the unit cell. To find out the Miller indices of a plane, it is required first to find its intercepts on the three coordinate axes X, Y, and Z in terms of multiples or fractions of the unit cell edge lengths, a, b, and c, the values of which are known as the lattice parameters. If a plane is parallel to one of the axes, the corresponding intercept is considered as infinite. The reciprocals of the values of these three intercepts are then considered, and these reciprocals are reduced to the three smallest integers having the same ratio. These integers, written in parenthesis, are the Miller indices of the plane. For purposes of general description, the letters, h, k and l are used to refer to these integers. The Miller indices of the plane would thus be written as (h, k, l). In an example, where a plane intersects the X-axis at four units, the Y-axis at infinity, and the Z-axis at two units, the intercepts are 4, ∞, 2, so that the reciprocals of the intercepts are ¼, 0, ½; when multiplied by 4, these give the Miller indices 1, 0 and 2 and the plane is represented as (1 0 2), corresponding to $(h\ k\ l)$ of the general case. As a consequence of the reduction to the smallest integers, parallel planes will have the same indices. It may be pointed out that the coordinate axes extend to both the positive and the negative directions from the point of their intersection (which may be taken as the origin), so that negative indices are also possible.

Direction indices are also frequently used in crystallography to specify the direction or the orientation of a line in the crystal. If a point is moved from the origin (the intersection of the coordinate axes) to some other position in the crystal by means of translations paral-

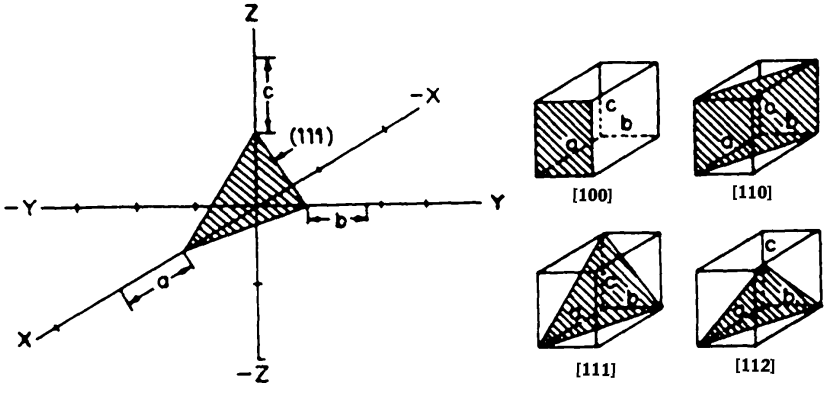


Figure 1.2 Miller indices of some important planes.

lel to the coordinate axes, the direction indices of the line connecting the origin and the final translated location will be given by the numbers *x*, *y* and *z*, where *x* is the number of units of *a* that the point moved parallel to the X-axis, *y* is the number of units of *b* that the point moved parallel to the Y-axis, and *z* is the number of units of *c* that the point moved parallel to the Z-axis. The values of *x*, *y*, and *z* are reduced to the simplest integers, and are presented in square brackets [*x y z*] to signify that they are direction indices. Figure 1.2 shows some of the important crystal planes with their Miller indices. In this figure, the face diagonal of the base of the parallelpiped will have the direction [110], the X-axis will have the direction [100], and the body diagonal, the direction [111].

1.3.3.2 Metallic Crystal Structures

The term crystal structure in essence covers all of the descriptive information, such as the crystal system, the space lattice, the symmetry class, the space group and the lattice parameters pertaining to the crystal under reference. Most metals are found to have relatively simple crystal structures: body centered cubic (bcc), face centered cubic (fcc) and hexagonal close packed (cph) structures. The majority of the metals exhibit one of these three crystal structures at room temperature. However, some metals do exhibit more complex crystal structures.

1.3.4
Alloying

The unsaturated nature of the metallic bond accounts for several of the typical metallic properties. It is responsible for the ability of some metals to accept small atoms, as for instance, carbon, nitrogen and hydrogen, in the interstitial spaces between the metal atoms. It also accounts for the alloying properties between metals. When two metals such as copper and nickel are mixed together, each atomic species reacts fairly indifferently to the other, because their atoms are held together by the common free electron cloud to which both have contributed. In this way it is possible to form alloys over wide ranges of composition by randomly replacing atoms of one metal by those of another. Such a "solid solution" is called a substitutional solid solution. For extensive solid solubility to occur, the two metals must be quite similar as defined by Hume–Rothery rules: (i) less than about 15% difference in atomic radii; (ii) the same crystal structure; (iii) similar electronegativity; and (iv) the same valence. If one or more of these rules get violated, only restricted solid solubility results. For example, in the aluminum–silicon system, the rules (i), (ii) and (iv) are violated and that explains why aluminum can dissolve not even about 2 atomic percent of silicon. In situations where atom sizes of the two components differ greatly, the substitution of a larger atom by a smaller atom at the lattice site of the former may not be energetically stable. In such cases a more stable configuration may be obtained when the smaller atoms place themselves in the interstitial spaces among the adjacent atoms in the host crystal lattice. This gives rise to what are known as interstitial solid solutions. Solid solutions of this type often constitute very important phases in steels.

1.3.5
Mechanical Properties

Metals in general possess some characteristic properties. However, many of these properties are not exclusive to metals but are exhibited by some nonmetals as well. Lustre, for example, is usually taken as characteristic of metals, but it is not their prerogative alone, because nonmetals like iodine and graphite also have a metallic lustre. Again, although metals possess the property of conducting electricity to a remarkable degree, the nonmetal graphite is used extensively in electrodes in electric furnaces to conduct the current to the charge or the arc. The exclusivity to metals holds when terms of reference rests on mechanical properties. Such mechanical properties as malleability and ductility, whilst are not truly possessed by all metals, are essentially recognised as metallic characteristics.

Mechanical properties per se concerns with the qualities which determine the behaviour of a material towards applied forces. The ability to support weight without rupture or permanent deformation, to withstand impact without breaking, to be mechanically formed into different shapes – all these depend upon a combination of mechanical properties characteristic of metals. Four types of behaviour of a material under stress are very important: linear or elastic behaviour, plastic behaviour, creep behaviour and fatigue behaviour.

1.3.5.1 Elastic Deformation

It is useful to get preliminary learning on the mechanical properties of materials under simple static tension. Members of engineering structures are often subjected to steady axial loads in tension. Moreover, the response of materials subjected to other types of loading also can often be explained or predicted on the basis of knowledge of their behaviour under simple tension. In addition, such behaviour is usually quite easy to study experimentally.

When a solid bar is loaded axially in tension, it elongates more and more with increasing load. The mechanism by which such elongation occurs can be visualised as a progressive increase in the separation of the atoms of the bar in the direction of loading, i.e., in the axial direction. The displacement of the atoms from their equilibrium positions results in the development of attractive forces between them; these forces balance the applied load. This elementary picture can be considered to be applicable to the initial stages of deformation of many types of materials, crystalline as well as amorphous.

If the deformation involves only an increase in the separation of atoms in the direction of loading by relatively small amounts, the atoms can return to their normal equilibrium positions when the applied force is withdrawn (i.e., the load is released). In such a situation, the axially loaded bar regains its original size and shape and the deformation is termed elastic deformation. Elastic deformation is reversible.

In the context of elastic deformation two parameters, known as stress and strain respectively, are very relevant. Stress is an internal distributed force which is the resultant of all the interatomic forces that come into play during deformation. In the case of the solid bar loaded axially in tension, let the cross sectional area normal to the axial direction be A_0. From a macroscopic point of view the stress may be considered to be uniformly distributed on any plane normal to the axis and to be given by σA_0 where σ is known as the normal stress. The stress has to balance the applied load, F, and one must, therefore have $\sigma A_0 = F$ or $\sigma = F/A_0$. The units of stress are those of force per unit area, i.e., newtons per square meter (Nm^{-2}) or pascals (Pa). The elastic deformation results in an elongation of the bar and the elongation per unit length is termed strain. If L_0 is the original length of the bar and δ is its total elongation then the strain, ε, is given by $\varepsilon = \delta/L_0$. Being the ratio of two lengths strain is dimensionless.

As the atoms are pulled apart in the direction of the applied force during elastic deformation, they are simultaneously pulled inwards; as a consequence of this, the longitudinal elongation is accompanied by a lateral contraction. The ratio of unit lateral contraction, or lateral strain, and longitudinal strain is known as Poisson's ratio. If the former is denoted by ε_y and the latter by ε_x, then $\varepsilon_y = -\mu\ \varepsilon_x$ where μ is Poisson's ratio. The negative sign indicates that one strain corresponds to contraction and the other to expansion. It is found that for most metals the value of Poisson's ratio is close to 0.33. If the bar is now assumed to be of square cross section with lateral dimension a, then $A_0 = a^2$ and $V_0 = L_0\ a^2$ where V_0 is the volume of the bar. On being subjected to axial loading its length increases by the amount $\delta = \varepsilon_x\ L_0$ while both of its lateral dimensions decrease by the amount $\mu\varepsilon_x a$. Due to these dimensional changes the volume of the bar now becomes

$$\begin{aligned} V &= (L_0 + \varepsilon_x\ L_0)\ (a\ \ \mu\ \varepsilon_x\ a)\ (a - \mu\varepsilon_x\ a) \\ &= L_0\ a^2(1 + \varepsilon_x)\ (1 - \mu\ \varepsilon_x)^2 \\ &= V_0\ [1 + \varepsilon_x(1 - 2\ \mu) + \varepsilon_x^2(\mu^2\ - 2\ \mu) + \mu^2\ \varepsilon_x^3] \end{aligned}$$

Usually ε_x is very small so that the terms containing ε_x^2 and ε_x^3 can be ignored. The unit change in volume can then be expressed as:

$$\frac{\Delta V}{V_0} = \frac{V - V_0}{V_0} = \varepsilon_x\ (1 - 2\ \mu)$$

The quantity $\Delta V/V_0$ remains positive as long as the value of μ does not exceed 0.5. In most situations $\mu < 0.5$ and thus elongation is accompanied by a dilatation or increase in volume.

In order to examine the elastic behaviour of a material in static tension, a uniform bar of the material may be loaded slowly and simultaneous observations of load and elongation made at regular intervals. The load and elongation data so obtained can be converted to stress and strain and plotted in the manner indicated in Figure 1.3 (A). Such a plot is known as a stress-strain plot. Such plots are usually linear though nonlinear plots may also be obtained in some cases as depicted in Figure 1.3 (B). However, as long as the deformation is elastic, the curve returns to the origin on unloading.

Most engineering materials, particularly metals, follow Hooke's law by which it is meant that they exhibit a linear relationship between elastic stress and strain. This linear relationship can be expressed as $\sigma = E\ \varepsilon$ where E is known as the modulus of elasticity. The value of E, which is given by the slope of the stress-strain plot, is a characteristic of the material being considered and changes from material to material.

The important elastic properties of a material undergoing deformation under static tension are stiffness, elastic strength and resilience. For a material obeying Hooke's law, the modulus of elasticity, E (= σ/ε), can be taken to be a measure of its stiffness. The elastic

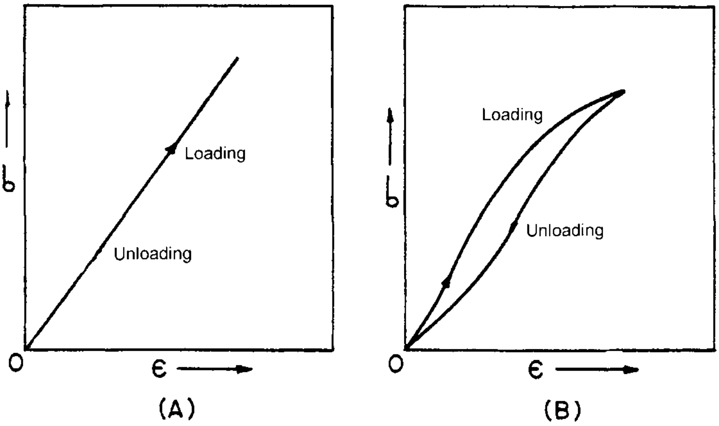


Figure 1.3 Elastic stress–strain diagram: (A) linear; (B) nonlinear.

strength of such a material is determined by the highest stress upto which its behaviour remains elastic. If the proportionality between stress and strain holds over almost the entire elastic range, which is usually the case with most materials, elastic strength corresponds to the value of stress which marks the termination of this proportionality and is known as the proportional limit, σ_{PL}. The proportional limit can be found experimentally by obtaining a stress–strain plot and carefully determining the point at which a deviation from liner behaviour is first exhibited. The elastic strength of a material is often expressed in terms of another measure, namely, its yield strength which is discussed later in this chapter.

The term elastic limit is mainly a definition. It describes a stress which, if exceeded, will influence plastic deformation. Experimentally, the elastic limit is practically unattainable because it is a limit. Either it has not been reached or it is overreached. Ideally, the elastic limit and proportional limit are the same.

The term elastic resilience pertains to the capacity of a material to absorb energy elastically. In the case of a bar elongated elastically in static tension, the energy absorbed by the bar arises from the work done by the applied force. Provided that the deformation is elastic as well as linear in nature, this absorbed energy is stored in the material of the bar in a recoverable form as strain energy which equals the work done by the applied force. If x is the instantaneous elongation and $F(x)$ is the applied force expressed as a function of x, the strain energy, U, is given, therefore, by

$$U = \int_0^{\delta} F(x)\,\mathrm{d}x$$

since $F(x) = \sigma A_0$ and $x = \varepsilon L_0$ so that $\mathrm{d}x = L_0\, d\,\varepsilon$, the expression for strain energy becomes

$$U = A_0 L_0 \int_0^{\varepsilon} \sigma\,\mathrm{d}\varepsilon$$

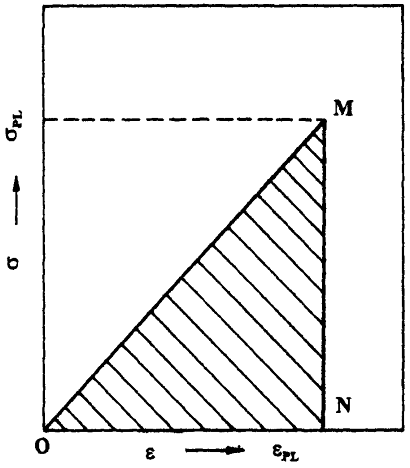


Figure 1.4 Linear elastic stress-strain relation.

since $\varepsilon = \delta / L_0$. Dividing both sides of this equality by the volume $A_0\ L_0$, one obtains

$$\frac{U}{A_0\ L_0} = \int_0^{\varepsilon} \sigma\ \mathrm{d}\varepsilon$$

This expression indicates that U, the strain energy per unit volume is given by the area under the stress–strain plot over the strain range $\varepsilon = 0$ to $\varepsilon = \varepsilon$. If Hooke's law holds, i.e., if $\sigma = E\,\varepsilon$, it follows that

$$U = E \int_0^{\varepsilon} \varepsilon\ \mathrm{d}\varepsilon = \frac{E\,\varepsilon^2}{2}$$

It can be easily shown that equivalent expressions for the strain energy per unit volume are $U = \sigma\,\varepsilon/2$ and $U = \sigma^2/2\,E$. The modulus of elastic resilience, U_r, of a material is defined as the strain energy absorbed per unit volume when it is stressed to its proportional limit. Thus,

$$U_r = \frac{E\,\varepsilon_{PL}^2}{2} = \frac{\sigma_{PL}\,\varepsilon_{PL}}{2} = \frac{\sigma_{PL}^2}{2\,E}$$

The shaded area in the stress–strain plot shown in Figure 1.4 is numerically equal to the modulus of resilience. It is to be noted that for a given value of E, U_r directly proportional to σ_{PL} while for a given value of σ_{PL}, U_r is inversely proportional to E (stiffness).

1.3.5.2 **Plastic Deformation**

Continuing the discussion on the deformation of a solid bar loaded axially in tension, it is interesting to consider the phenomena after the limit of elastic deformation is reached. As the tension on the bar increases progressively, the atoms are pulled farther and farther apart and a point is reached when deformation ceases to be reversible. This marks the end of the elastic range. Elongation no longer involves a simple pulling apart of the atoms from their equilibrium positions. Irreversible structural changes start occurring. The termination of the elastic regime is brought about by one of two possible phenomena: fracture or yielding.

Fracture initiates at some imperfection such as a crack of macroscopic dimensions. Stress concentration occurs at such imperfections. If the local value of stress at an imperfection becomes so large as to exceed the cohesive strength of the material, the atomic bonds in that region break. As this happens, the imperfection, which was originally confined to a microscopic region, rapidly spreads across the bar, resulting in complete fracture. If this happens while the overall deformation is still elastic, the material is said to behave in a perfectly brittle manner. Materials such as some ionic crystals, glass, cast iron etc. tend to be perfectly brittle. However, generally even such materials undergo some finite, albeit small extent of yielding before getting fractured. Some aspects of fracture have been dealt with in a later chapter.

Yielding is a manifestation of the possibility that some of the atoms (or molecules) in the stressed material may slip to new equilibrium positions due to the distortion produced by the applied tensile force. The displaced atoms can form new bonds in their newly acquired equilibrium positions. This permits an elongation over and above that produced by a simple elastic separation of atoms. The material does not get weakened due to the displacement of the atoms since they form new bonds. However, these atoms do not have any tendency to return to their original positions. The elongation, therefore, is inelastic, or irrecoverable or irreversible. This type of deformation is known as plastic deformation and materials that can undergo significant plastic deformation are termed ductile.

By increasing tension slowly and by taking simultaneous readings of load and elongation at regular intervals a stress–strain plot showing elastic as well as inelastic or plastic ranges can be obtained. Typical stress–strain plots for a perfectly brittle material (only elastic deformation), a material of low ductility (only a small amount of plastic deformation) and a ductile material (significant plastic deformation) are shown in Figure 1.5 (A–C).

The most common mechanism by which yielding occurs in crystalline materials is slip, in which two planes of atoms undergo a relative displacement with respect to each other so that one whole section of the crystal is shifted relative to another. For each crystal structure there are certain preferred planes on which slop can occur most readily. In general, these preferred planes are those in which the atoms are the most closely spaced. Since these planes contain the largest number of atoms per unit area, they are also the most widely separated planes because the number of atoms per unit volume of the crystal is fixed. Again, for each crystal structure there are certain directions along which slip can occur most easily. Generally these directions of easy slip correspond to those directions in the slip plane along which the atoms are most closely spaced. By way of an example, it may be mentioned that in face centered cubic crystals the (III) type planes and the [110] type directions are respectively the closed packed planes and the close packed directions; these are also the preferred slip planes and directions.

In most ductile materials it is found that as yielding progresses, an ever-increasing stress is required to produce further yielding. This is reflected in the stress–strain plot of a ductile material (Figure 1.5 C): stress always increases with increasing strain. This is the effect of a phenomenon known as strain hardening or work hardening. Like yielding, strain hardening is an important feature of plastic deformation.

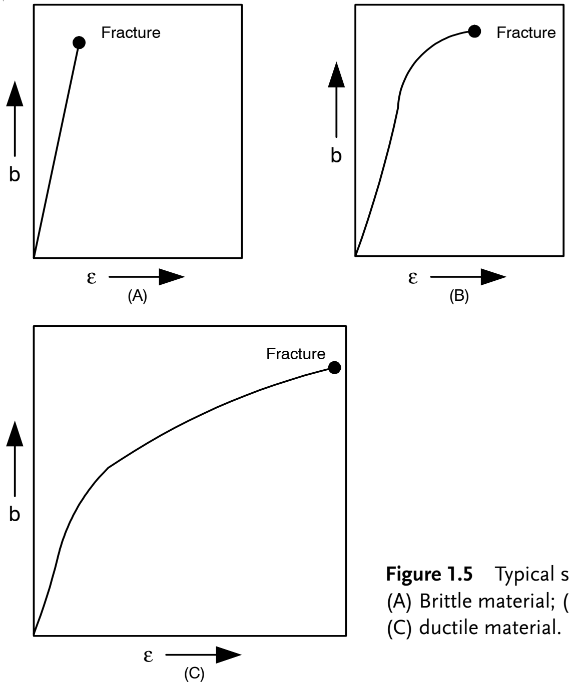


Figure 1.5 Typical stress–strain diagrams. (A) Brittle material; (B) low ductility material; (C) ductile material.

In the plastic range of mechanical behaviour the strain has two components. In addition to the irrecoverable plastic strain that results from yielding, there is also a recoverable elastic strain component. An elementary explanation for this is presented here. In order to provide the internal stresses required to balance the externally applied load the atoms must always be displaced to a certain extent from their equilibrium positions. With the progress of yielding the atoms get shifted to new equilibrium positions; however, they must move slightly away from these new positions so that the necessary interatomic forces are generated. Thus in the plastic range two distinct mechanisms – elastic and plastic – always come into play in producing strain and the total strain necessarily has two components. The elastic component normally continues to increase at a constant rate dictated by Hooke's law. The plastic component, on the other hand, increases more rapidly with increasing stress. As indicated earlier, elastic strain leads to an increase in volume. This is a consequence of the atoms being pulled away from their equilibrium positions. Plastic strain, which involves shifting of atoms to new equilibrium positions, is not accompanied by any significant change in volume.

At any given instant the process of yielding is localised at many points which are distributed throughout the material undergoing plastic deformation. The yielding of such a point is accompanied by a slight reduction in area and a concomitant increase in stress. At the same time, however, the material undergoes strain hardening and thus becomes capable of withstanding the increased stress. The next yielding occurs at a different point. On a macroscopic scale, the overall effect of this random yielding is that the strain remains uniform along the length of the bar. On a microscopic scale there is continued competition between the increased stress due to reduction in area and the increased strength brought about by strain hardening. The latter more than compensates for the former and the strain remains essentially uniform.

The rate of strain hardening decreases with increasing strain in many materials. It may so happen that beyond some value of strain the strengthening due to strain hardening is insufficient to compensate for the increased stress resulting from area reduction. When such a situation is obtained in some location of the material undergoing plastic deformation, the plastic strain continues to increase there because the rate at which stress increases is greater than the rate at which strengthening occurs at that location. This localised increases in plastic strain takes place with no increase in load. All further elongation occurs at that location and a neck or constriction starts to form there. With progress of deformation the rate of strain hardening continues to fall locally and the load bearing area continues to decrease; as a consequence, the load required to bring about further deformation becomes smaller and smaller. This process continues until rupture occurs. The situation described above is encountered in many ductile materials and is known as plastic instability. It is characterised by a maximum in the load versus elongation curve (Figure 1.6). The condition that has to be satisfied for plastic instability to occur is given by $\mathrm{d}F = 0$, or $d\,(\sigma\, A) = 0$, where A stands for the load bearing area. Since both stress and area are variables, this condition can be expressed as

$$A\,\mathrm{d}\sigma + \sigma\,\mathrm{d}A = 0$$

Here the term $A\,\mathrm{d}\sigma$ represents the increase in load due to strain hardening and is positive since $\mathrm{d}\sigma$ is positive; the term $\sigma\,\mathrm{d}A$ represents the decrease in load due to area reduction and is negative since $\mathrm{d}A$ is negative. Before the maximum load (F_{max} in Figure 1.6) is reached the absolute value of the first term exceeds that of the second term and $\mathrm{d}F$ is positive. At the maximum load these values are equal and $\mathrm{d}F$ is zero. After this point the second term dominates and $\mathrm{d}F$ becomes negative.

The plastic deformation of a member terminates with its rupture which normally occurs at the smallest section of the neck formed due to plastic instability. After being loaded into the plastic range, if the member is unloaded before plastic instability occurs then the elastic component of the strain can be recovered. This is a consequence of the atoms returning to

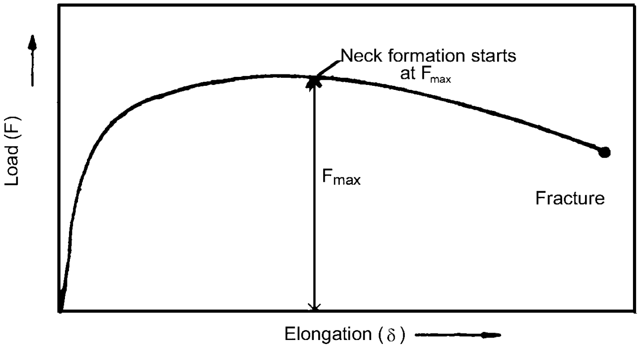


Figure 1.6 A load versus elongation diagram for a typical ductile metal, showing plastic instability.

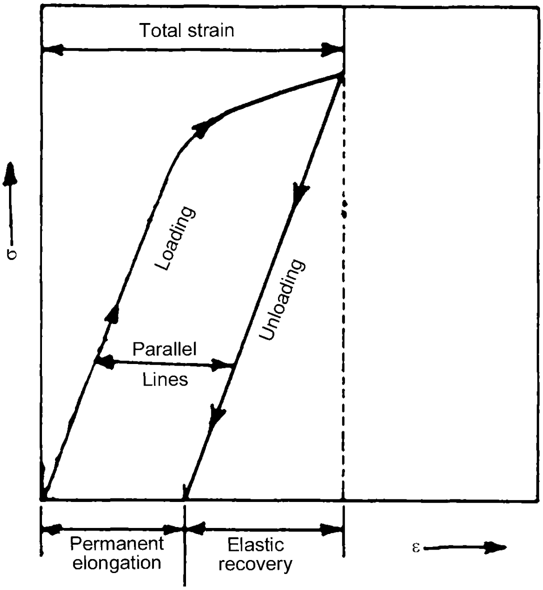


Figure 1.7 Representation of loading and unloading in the plastic range.

their relevant equilibrium positions. However, the irrecoverable plastic component of the strain is manifested as a permanent elongation (permanent set) of the member. This is illustrated in the schematic stress–strain plot shown in Figure 1.7. It is to be noted that the unloading line is parallel to the initial elastic loading line. If the member is reloaded after unloading the atoms are again displaced to the positions that they occupied before unloading and further yielding occurs on continued loading. However, as a consequence of the strain hardening associated with the first loading into the plastic range, the proportional limit exhibited during the second loading is higher than that exhibited during the first loading.

In some materials the initiation of yielding takes place abruptly and not in a gradual manner, with a good amount of plastic deformation occurring without any significant strain hardening, i.e., almost without any increase in stress. In the corresponding stress–strain plot, the point at which yielding commences is called the yield point. While in most metallic materials there is a gradual transition from elastic to plastic strain with increasing stress, in some cases, mild steel (which is essentially an iron–carbon alloy containing around 0.2% carbon) as for an example, there is a sharp discontinuity in tensile stress–strain curve (Figure 1.8). The material behaves in an elastic manner upto a certain point, A, and then suddenly yields. Point A is termed the upper yield point. The stress level necessary to continue plastic straining falls to level B, the lower yield stress, and a considerable amount of plastic strain takes place at this lower level. After this sudden yielding has occurred the stress has to be increased again to bring about further plastic strain, and beyond point C on the curve normal strain hardening occurs. If the metal is stressed to some point, D, on the curve and the stress is then removed elastic strain will be recovered along the path DO. Immediate reloading of the test piece will give elastic strain to point D with continued plastic strain beyond point D, but with no sudden yielding. However, if after stressing to

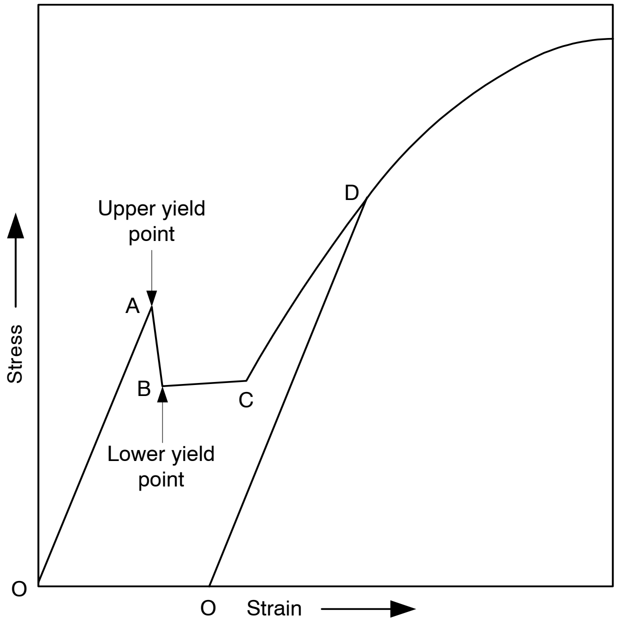


Figure 1.8
Discontinuous yielding.

point D and unloading, the sample is left at ordinary temperatures for about a week before retesting (or heated at 100 °C for about one hour) it is found that the sudden yield phenomenon returns. This is termed strain ageing.

It may be pointed out that the term yield point is sometimes erroneously used as a synonym for elastic limit and proportional limit. As it has been described in the paragraphs above it is actually a phenomenon that occurs in only a very small number of cases in tensile testing. As it has also been observed in the description that graphically and experimentally, it is an anomalous behaviour in which there is a strain occurring with no increase in stress.

The expressions for stress and strain introduced earlier in the context of elastic deformation need some modifications while dealing with plastic deformation. In the elastic range the reduction in area and the strain are generally very small. In the plastic range, however, these could be quite large. Stress and strain, when expressed as $\sigma = F/A_0$ and $\varepsilon = \delta/L_0$, where A_0 and L_0 refer to the original dimensions of the member undergoing deformation, are known as nominal or conventional or engineering stress and strain respectively. As more appropriate descriptors of the mechanical behaviour of materials terms known as true stress and true strain will now be introduced.

True stress, σ', is defined as $\sigma' = F/A$ where A is the actual area of cross section of the member corresponding to the load F.

True strain differs from nominal strain in that each increment in strain is expressed in terms of the actual length of the member at the time of the increment rather than in terms of the increment of the original length. The instantaneous nominal strain is given by

$$\varepsilon = \frac{\delta}{L_0} = \frac{L - L_0}{L_0}$$

where L is the instantaneous length. The increment in nominal strain corresponding to an infinitesimal increase in length, dL, from L to L_1 is given by

$$\mathrm{d}\varepsilon = \varepsilon_1 - \varepsilon = \frac{L_1 - L_0}{L_0} - \frac{L - L_0}{L_0} - \frac{L_1 - L}{L_0} - \frac{\mathrm{d}L}{L_0}$$

True strain, ε', is defined in such a way that the increment resulting from an increase in length by dL is based on the instantaneous length, L:

$$\mathrm{d}\varepsilon' = \frac{\mathrm{d}L}{L}$$

The total nominal strain, ε, obtained by integrating the expression for the increment, dε, is given by

$$\varepsilon = \int_0^{\varepsilon} \mathrm{d}\varepsilon = \int_{L_0}^{L} \frac{\mathrm{d}L}{L_0} = \frac{L - L_0}{L_0}$$

which is the same as the expression for the instantaneous nominal strain given earlier. The total true strain, ε', obtained by integration is

$$\varepsilon = \int_0^{\varepsilon'} \mathrm{d}\varepsilon' = \int_{L_0}^{L} \frac{\mathrm{d}L}{L_0} = \ln L - \ln L_0 = \ln\frac{L}{L_0}$$

since

$$\varepsilon = \frac{L - L_0}{L_0} = \frac{L}{L_0} - 1$$

true strain can be expressed in terms of nominal strain in the following manner:

$$\varepsilon' = \ln\frac{L}{L_0} = \ln(1 + \varepsilon)$$

At large plastic strains, the elastic strain component constitutes only a small fraction of the total strain and the volume of the deforming member can be taken to remain essentially unchanged so that one has

$$V_0 = L_0\, A_0 = L\, A$$

or

$$\frac{L}{L_0} = \frac{A_0}{A}$$

It follows that $\varepsilon' = \ln A_0/A$ for large plastic strains. The quantity A_0/A is a measure of the reduction in area due to deformation. One can define a quantity, the true reduction in area (q'), in a manner analogous to the definition of true strain:

$$q' = \int_{A_0}^{A} \mathrm{d}'q = \int_{A_0}^{A} -\frac{\mathrm{d}A}{A} = \ln\frac{A_0}{A}$$

It could be seen that for large plastic strains the true strain and the true reduction in area are identical.

In Figure 1.9 stress–strain plots of the same material, using nominal and true values, are shown. Corresponding points on the two plots are connected by broken lines. It could be noted that before the maximum load is reached the points on the true stress–true strain plot are always located to the left of the corresponding points on the nominal stress–nominal strain plot. After the maximum load is reached the regime of uniform strain is terminated and necking, with the associated localization of strain, starts. Because of the high local strains in the neck the true stress–true strain plot overtakes the nominal stress–nominal strain plot in the sense that points on the former are located to the right of the corresponding points on the latter. It should be reiterated here that nominal stress and nominal strain are approximations that are not very inaccurate in the elastic range but become more and more inaccurate with increasing strain in the plastic range. True stress and true strain correspond to the correct values in the elastic range as well as in the plastic range until the onset of necking. However, after a neck forms these also have to be regarded as approximations only since neither the stress nor the strain is uniform in any cross section in the neck. Nevertheless, they indicate average values and approximate the true situation better than nominal stress and nominal strain do.

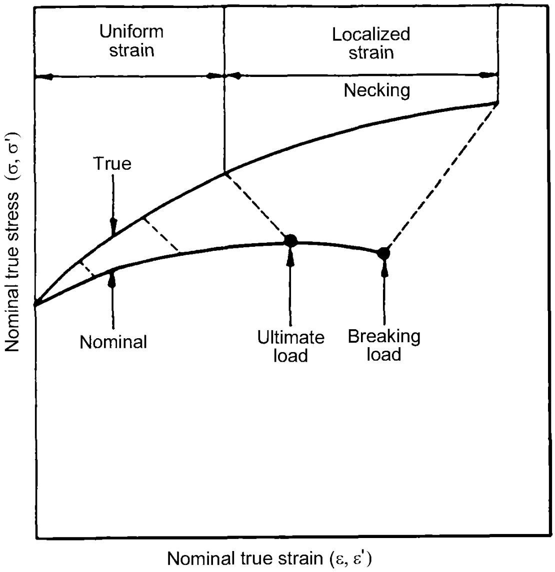


Figure 1.9 Comparison between nominal and true stress–strain.

The rate of strain hardening, $d\sigma'/d\varepsilon'$, at any given value of the true stain is given by the slope of the true stress–true strain plot at that strain and is called the modulus of strain hardening.

It has been found that in the case of many metals the observed stress–strain data approximately follow the empirical relationship $\sigma' = k_1\,\varepsilon'^n$ $(n < 1)$, where k_1 and n are constants that vary from material to material. Taking logarithms one can write

$$\log\sigma' = \log k_1 + n\log\varepsilon'$$

A plot of $\log\sigma'$ against $\log\varepsilon'$ should thus yield a straight line whose slope is n and which makes an intercept equal to $\log k_1$ on the $\log\sigma'$ axis (at $\varepsilon' = 1$). Thus the constant k_1 represents the true stress at unit true strain and is termed the strength coefficient. The exponent n is known as the strain hardening exponent.

It has been seen earlier that the condition for plastic instability can be expressed as

$$A\,d\sigma + \sigma\,dA = 0$$

Replacing σ by σ' and dividing throughout by $\sigma'\,A$, one obtains

$$\frac{d\sigma'}{\sigma'} = -\frac{dA}{A}$$

Assuming that the onset of plastic instability occurs at a fairly large value of plastic strain, one may consider the volume to remain essentially constant, so that $A\,L = A_0\,L_0$. Differentiation gives

$$A\,dL + L\,dA = 0$$

or

$$-\frac{dA}{A} = \frac{dL}{L} = d\varepsilon'$$

Thus it is seen that

$$\frac{d\sigma'}{\sigma'} = d\varepsilon'$$

or

$$\frac{d\sigma'}{d\varepsilon'} = \sigma'$$

This relationship indicates that for plastic instability to occur the modulus of strain hardening, i.e., the slope of the true stress–true strain plot, should be equal to the true stress. This result is independent of any assumed functional relationship between σ' and ε'. If the relationship $\sigma' = k_1\,\varepsilon'^n$ assumed to hold then one obtains

$$\frac{d\varepsilon'}{d\varepsilon'} = n\,k_1\,\varepsilon^{(n-1)} = \sigma' = k_1\,\varepsilon^n$$

so that

$$\varepsilon' = n$$

This relationship implies that the value of the true strain at which plastic instability sets in, i.e., necking starts to occur, is equal to the strain hardening exponent.

Some of the important inelastic properties of a material undergoing plastic deformation are yield strength, ultimate tensile strength, ductility and toughness.

The yield strength (YS) refers to the stress at which a ductile material commences to yield. It is difficult to detect the beginning of yielding very precisely and it is necessary to specify a certain measurable extent of yielding as the beginning of yielding. The value of the yield strength depends upon the selection of this amount of yielding. The yield strength can be determined from the stress–strain plot by following a simple procedure. The specified yield strain is measured along the strain axis and a straight line parallel to elastic part of the plot is drawn through the point corresponding to this offset. The stress corresponding to the point at which this straight line intersects the stress–strain plot is the required yield stress or the offset yield strength which is a measure of the commencement of yielding and of the termination of the elastic range. A very frequently used value of the offset strain is 0.2% (Figure 1.10).

In a material exhibiting a distinct yield point, the stress corresponding to the yield point may be taken as the yield strength. When both upper and lower yield points occur, generally the stress corresponding to the lower yield point is taken to be the yield strength.

In design, whenever it is intended that a member should be in the elastic range under load, the yield strength is used as the basis for obtaining a design or working stress. The working stress, σ_w, is given by $\sigma_w = \varepsilon_y/n_y$ where σ_y is the yield strength and n_y is an appropriate factor of safety. Depending on the application the factor of safety may vary over a wide range, its minimum value being unity. In engineering practice, the yield strength is usually measured in terms of nominal stress.

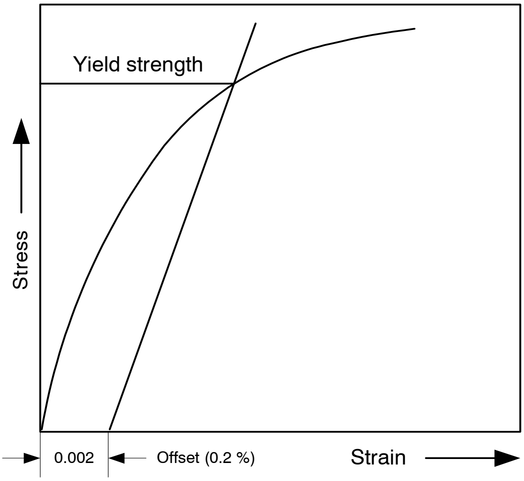


Figure 1.10 Determination of offset yield point.

The ultimate tensile strength (UTS) of a material refers to the maximum nominal stress that can be sustained by it and corresponds to the maximum load in a tension test. It is given by the stress associated with the highest point in a nominal stress–nominal stress plot. The ultimate tensile strengths of a ductile and of a brittle material are schematically illustrated in Figure 1.11. In the case of the ductile material the nominal stress decreases after reaching its maximum value because of necking. For such materials the UTS defines the onset of plastic instability.

For brittle materials the UTS is generally used as the basis for obtaining the working stress: $\sigma_w = \sigma_u/n_u$ where σ_u is the UTS and n_u is a factor of safety. The UTS may be used as a basis for arriving at the working stress even for ductile materials in situations where some permanent deformation is acceptable.

Ductility is one of the very important features of most metals. Two measures of ductility are obtained from the tension test. These are the percent elongation in a specified length of the deforming member at the time of rupture and the percent reduction in area of its smallest cross section at rupture. The percent elongation varies with length on account of the fact that the plastic strain is locally concentrated in the neck region, with relatively little strain in other parts of the member. It is, therefore, very much necessary that the length is specified while quoting the percent elongation. The main use of percent elongation as a measure of ductility is for comparing the ductilities of materials. The percent reduction in area can be found by measuring the area of cross section of the member before loading and the area of cross section of the neck after fracture. If these two are denoted by A_0 and A_f respectively, the percent reduction in area can be represented as $100\,(A_0 - A_f)/A_0$. Ductility can be expressed in terms of true stress and true strain also. One such measure of ductility gives the maximum uniform strain and is represented by the true strain at maximum load.

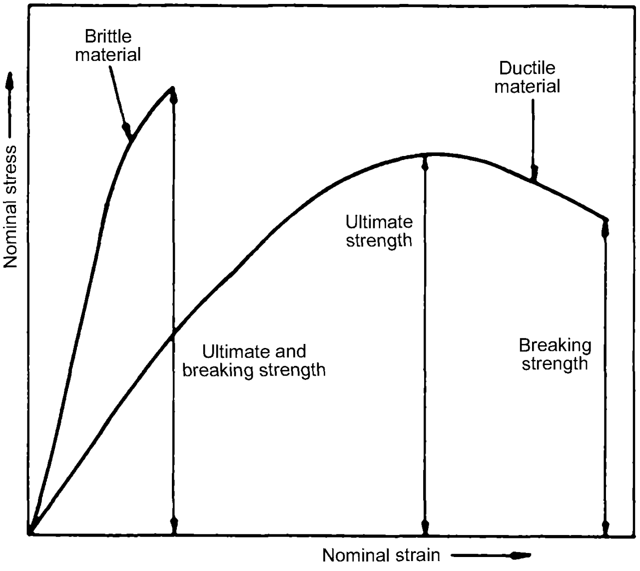


Figure 1.11 Depiction of ultimate tensile strengths of ductile and brittle materials.

Another measure is the true fracture strain which is expressed in terms of the true reduction in area at fracture and is given by, $\varepsilon = q = \ln A_0/A_f$, where the subscript f refers to fracture.

The toughness of a material indicates its overall capacity to absorb energy. Just as the modulus of resilience is measured by the strain energy absorbed per unit volume in the elastic range, the modulus of toughness is measured by the strain energy absorbed per unit volume over the entire range of deformation upto rupture and is given by

$$u = \int_0^{\varepsilon_r} \sigma \, d\varepsilon$$

where ε_r is the strain at rupture. The integral represents the total area under the stress–strain plot. If the true stress–true strain plot is used, this area corresponds to the energy per unit volume pumped into the material at the smallest part of the neck.

The time element has so far remained conspicuously absent. The deformation characteristics is ordinarily considered independent of time. If, however, the rate of straining is varied over several orders of magnitude, the true stress versus true strain curve may change as a function of the strain rate, ε_t. A relationship can be used to express σ' at a given strain ε', in terms of the strain rate, $\varepsilon' : \sigma' = k_2 (\varepsilon')^m$, where k_2 is a constant and m is the index of strain rate sensitivity. Certain interesting observations ensue from this relationship. If $m = 0$, the stress is independent of the strain rate and all strain rates yield the same true stress versus true strain behaviour. The value of m is approximately 0.2 for common metals. A material may exhibit superplastic behaviour (deform to several hundred percent of strain without necking) if m has a value in range of 0.4 to 0.9. The reason for this is that as soon as necking starts in some region, the strain rate goes up locally; this results in a rapid enhancement in the stress required to cause further deformation in that region. The deformation then shifts to another region of the material, where there is no necking. In this region the strain rate and hence the stress required for causing deformation are smaller. Some stainless steels and aluminum alloys, with a very fine grain size, show superplastic behaviour. It is on account of the fact that the value of m for glass approaches unity that a glass blower is able to pull his working material to very long rods without necking. A material behaves like a viscous liquid when the value of m approaches unity.

The behaviour of materials in static compression is in many ways similar that in static tension described above. There are, however, important differences. Stress–strain diagrams often differ for tension and compression, as does the amount of ductility exhibited by a material and the mode of failure. Behaviour in the elastic range is important for brittle materials, which are better adapted to compression than to tension. Behaviour in the plastic range is involved in hardness measurements and technological forming operations such as rolling and extrusion as well as in simple compression applications. It is in the plastic range that the differences between compression and tension are the greatest.

1.3.5.3 **Creep Deformation and Fatigue Deformation**

The effect of temperature on the mechanical properties has definite place in specification of a material for any particular application. Some materials become dangerously brittle under arctic conditions, and all metals exhibit at elevated temperatures a phenomenon called creep.

In the study of creep the usual procedure is to apply a constant stress or a constant load to a member and measure the strain as it varies with time. Figure 1.12 (A) is a creep curve plotted when done this way. Strength at normal temperatures is measured by a tensile test and in this situation the elongation is not time dependent. However, at elevated temperatures deformation under constant load progresses with time. Such deformation of a material over a period of time is known as creep, so called because the phenomenon occurs at a slow rate. A typical creep curve is a plot of strain, ε', versus time, t. After the initial elastic deformation at $t = 0$, there are three stages of creep deformation. Initially there is a rapid increase in strain and this stage is called the primary stage (primary creep). This stage is characterized by a decreasing strain rate (slope of the ε' versus t curve). This is followed by the secondary stage (also known as steady state creep) which is characterized by a linear dependence of ε' on t, i.e., by a constant strain rate. The slope of the creep curve in this stage gives the creep rate commonly used for design purposes. The final stage is that of tertiary creep in which the strain rate increases due to an increase in the true stress which results from a reduction in cross-sectional area due to necking or internal cracking. In some cases, fracture occurs in the secondary stage and the tertiary stage is absent. For the same material, a creep curve corresponding to a higher load (or stress) is displaced upwards with respect to a creep curve corresponding to a lower load (or stress). The most important properties used directly in design for creep are creep strength and creep rupture strength. They are defined as the highest stress that a material can stand for a specified length of time without excessive deformation, or rupture, respectively. Creep strength is determined experimentally in several ways. One of the simplest is to test several specimens simultaneously, at the expected operating temperature, but each under a different stress. If the length of time required to yield the allowable strain is measured for each specimen, a curve of stress vs time can be plotted (Figure 1.12 B). Tests of this kind are commonly limited to 1000 hours. From the results creep strengths may be tabulated on the basis of a specified amount of creep strain for various temperatures. When testing times or available data are limited to 1000 hours, the creep properties used in design for longer times must be based on extrapolation.

In many situations metals and alloys are exposed to cyclic rather than static or monotonic loading. For example, a turbine shaft, which carries the weight of the turbine discs and blades as well as its own, is subject to alternating states of tension and compression as it revolves. Its strength under this kind of repeated loading is much lower than its strength when it experiences the same magnitude of stationary load. Thus with regard to the behaviour of materials when subjected to dynamic loading, such as in high speed machinery and in air craft structures, the fatigue strength is of far greater importance to the engineer than the yield or the ultimate tensile strength. The deformation of the static strength of a material requires only a single or at most a few tests, whereas finding its the fatigue strength or endurance limit may involve 20 or 30 separate tests, some of which take several days to complete. A number of identical specimens are prepared and the test is carried out by subjecting a specimen to a known alternating stress until it fractures. This is repeated at differing stresses until sufficient results have been obtained to plot stress (S) versus number of cycles to failure (N), on a logarithmic scale (Figure 1.13). The curve is also called an S–N curve and shows that the decay in strength with increasing number of cycles reaches a limit. This limit is called the endurance limit or fatigue strength. In a general way fatigue strength can be defined as the stress which a material can withstand repeatedly for a given

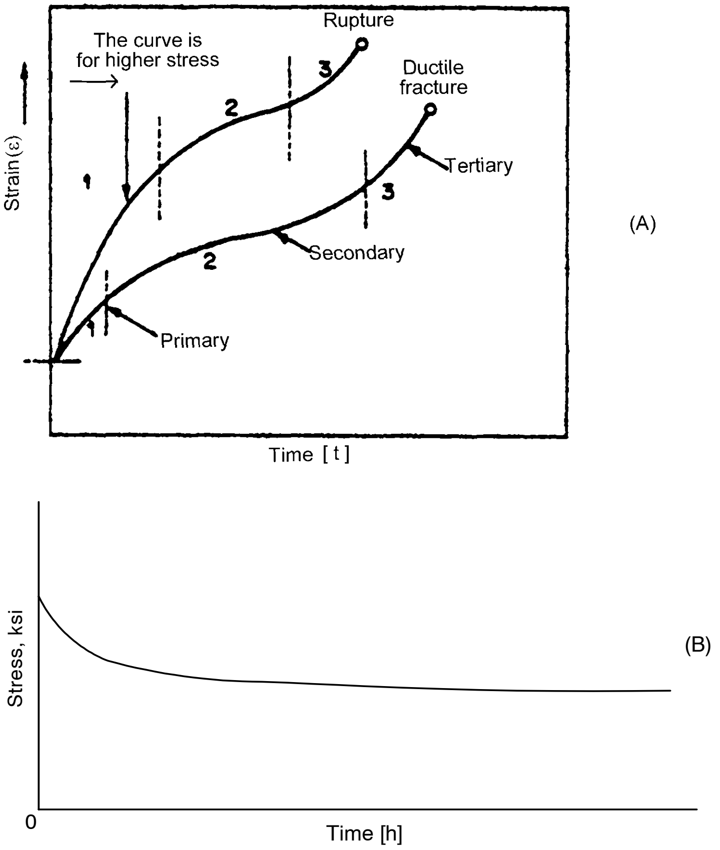


Figure 1.12 (A) Creep curve showing basic components; (B) stress versus time curve.

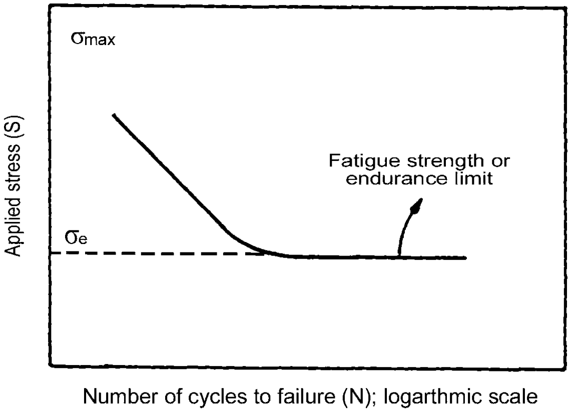


Figure 1.13 Typical fatigue curve (S–N diagram for a material having an endurance limit, σ_e).

number of cycles of stress (N). Thus, for all practical purposes, a value of stress can be chosen at which the risk of fatigue failure is negligible. Obviously fatigue strength cannot be measured directly experimentally simply because the stress must always be settled upon prior to commencing the test and it would be impossible to preselect a stress for each test piece such that its failure occurs at just N cycles. The fatigue strength is consequently found by interpolation from the S–N curve. While the occurrence of an endurance limit is the characteristic of ferrous alloys, nonferrous alloys tend not to exhibit such a distinct limit. The rate of decay in their case, however, decreases with N. For a given material, prior cold working or reduction of structural discontinuities help in increasing the resistance to fatigue failure.

1.3.5.4 **Hardness**

Hardness signifies the resistance to deformation shown by materials undergoing abrasion, cutting and indentation. As strength is also a measure of resistance to deformation, the two properties are, to some extent, related; but not all hard metals are strong, for hardness takes no account of brittleness.

Hardness is determined by hardness tests which involve the measurement of a material's resistance to surface penetration by an indentor with a force applied to it. The indentation process occurs by plastic deformation of metals and alloys. Hardness is therefore inherently related to plastic flow resistance of these materials. Brittle materials, such as glass and ceramics at room temperature, can also be subjected to hardness testing by indentation. This implies that these materials are capable of plastic flow, at least at the microscopic level. However, hardness testing of brittle materials is frequently accompanied by unicrack formation, and this fact makes the relationship between hardness and flow strength less direct than it is for metals.

In hardness testing, indentation is carried out by applying a load to a suitable indentor placed on the surface of the material. It is understandable that the material of which the indentor is to be made has to be considerably harder than the material to be indented. Hardened steel and diamond are the typical indentor materials. Depending on the material to be tested and the type of test to be employed, different combinations of load and indentor are used in hardness testing. The tests besides playing their conventional role of investigation and assessment of physical condition of the material surface with respect to abrasion and mechanical resistance also provide valuable information regarding the strength of the material when it is not possible or convenient to carry out the usual tensile tests. They are also used to investigate the effects of heat treatments, hardening and tempering, and of cold working on strength. The description given below pertains to the Brinell, Vickers, Knoop, Rockwell hardness and Shore scleroscope tests.

The Brinell test uses an indentor of 10 mm diameter hardened steel ball, and applies a load which is usually 3000 kg. The Brinell hardness number (BHN) is defined as the load, F (kilogrammes), divided by the surface area of the indentation. The expression given below describes the definition.

$$\mathrm{BHN} = \frac{2\,F}{\pi\,D\,[D - (D^2 - d^2)^{1/2}]}$$

where D is the ball diameter (millimeters), and d is the diameter of the impression (millimeters). To obviate calculation, the Brinell numbers are usually obtained from tables giving values of impression diameter and corresponding Brinell numbers.

The Vickers hardness test uses a square based diamond pyramid as the indentor which gives geometrically similar impressions under different tests. The angularity of the pyramid is 136° and loads ranging from 5 to 120 kg can be used. The diamond pyramid hardness number (DPH, or alternatively, the Vickers hardness number, VHN) is determined by dividing the load by the indented surface area. Since the load used in this test is less than in a Brinell test, indentation size is reduced correspondingly. This requires more elaborate techniques for measuring indentation dimensions, and also implies that the surface of the material must be suitably prepared, for example by polishing it. For these reasons, the Vickers hardness test is not as extensively used as the Brinell test. However, the variations in load allowed by the Vickers test enables assessment of the hardness of materials with widely varying plastic flow resistances. The DPH also has dimension of stress and is related to flow behaviour in a manner similar to the BHN. However, because there is no plastic deformation of the diamond, this test may be used for very hard materials. As in the case of the Brinell test, the hardness is given by load divided by the surface area of indentation. The hardness is quoted in Vicker's pyramid hardness numbers (VPN, DHN, or H_D) and is represented mathematically as

$$H_D = \frac{2\,F\,\sin\theta/2}{d^2}$$

where F = applied load, θ = angle between opposite pyramid faces, and d = mean length of indentation diagonals. For a standard pyramid angle of 136 °C

$$H_D = \frac{1.854\,F}{d^2}$$

Brinell and Vicker's hardness numbers are comparable upto value of about 300. For higher hardness materials than this the Brinell values are slightly lower than H_D numerals for the same material.

The Knoop test is a microhardness test. In microhardness testing the indentation dimensions are comparable to microstructural ones. Thus, this testing method becomes useful for assessing the relative hardnesses of various phases or microconstituents in two phase or multiphase alloys. It can also be used to monitor hardness gradients that may exist in a solid, e.g., in a surface hardened part. The Knoop test employs a "skewed" diamond indentor shaped so that the long and short diagonals of the indentation are approximately in the ratio 7 : 1. The Knoop hardness number (KHN) is calculated as the force divided by the projected indentation area. The test uses low loads to provide small indentations required for microhardness studies. Since the indentations are very small their dimensions have to be measured under an optical microscope. This implies that the surface of the material is prepared approximately. For those reasons, microhardness assessments are not as often used industrially as are other hardness tests. However, the use of microhardness testing is undisputed in research and development situations.

An alternative to the measurement of the dimensions of the indentation by means of a microscope is the direct reading method, of which the Rockwell method is an example. The Rockwell hardness is based on indentation into the sample under the action of two consecutively applied loads – a minor load (initial) and a standardised major load (final). In order to eliminate zero error and possible surface effects due to roughness or scale, the initial or minor load is first applied and produce an initial indentation. The Rockwell hardness is based on the increment in the indentation depth produced by the major load over that produced by the minor load. Rockwell hardness scales are divided into a number of groups, each one of these corresponding to a specified penetrator and a specified value of the major load. The different combinations are designated by different subscripts used to express the Rockwell hardness number. Thus, when the test is performed with 150 kg load and a diamond cone indentor, the resulting hardness number is called the Rockwell C (R_C) hardness. If the applied load is 100 kg and the indentor used is a 1.58 mm diameter hardened steel ball, a Rockwell B (R_B) hardness number is obtained. The facts that the dial has several scales and that different indentation tools can be filled, enable Rockwell machine to be used equally well for hard and soft materials and for small and thin specimens. Rockwell hardness number is dimensionless. The test is easy to carry out and rapidly accomplished. As a result it is used widely in industrial applications, particularly in quality situations.

The Shore scleroscope test is a dynamic hardness test in which a small diamond pointed hammer weighing 2.5 g is allowed to fall freely from a height of 250 mm down a glass tube graduated into 140 equal parts. The height of the first rebound is taken as the index of hardness. This test is particularly useful for the testing of the very hard metals, also for insitu testing of parts such as dies, gears and the surfaces of large rolls. The test leaves no visible impression.

Since the hardness test involves a substantial component of plastic deformation, hardness values are linked with tensile strength and not with yield strength when correlation between hardness and tensile properties are carried out. This appears to be a relationship between the hardness and tensile properties are carried out. There appears to be a relationship between he hardness of a metal and its tensile strength, but no general application has been found to exist. However, the following empirical relationship appears to hold fairly well for most steels, other than heavily cold worked steels or austenitic steels.

$$\text{T.S. } (\text{MN/mm}^2) = 3.4\ H_D$$

is given by 1.854 P/D^2, where P is the load in kilograms applied to produce the indentation, and D is the average of the measured diagonals of the indentation, expressed in mm. Since the hardness test, by the very manner it is performed, involves a substantial component of plastic deformation, hardness values are linked with tensile strength and not with yield strength when correlation between hardness and tensile properties is carried out.

1.3.5.5 **Toughness**

The term toughness was referred to earlier in the context of tensile testing. The impact energy in a way is an analog of toughness. An impact test is essentially a high speed tensile test. In a matter microseconds, the material is taken through the elastic range partially into the plastic region, then cleavage should take place. If too much plasticity is present, a valid measure of the impact energy is not obtained, since the energy that is responsible for fracture is spent in performing plastic work. A brittle nature of failure is essentially the objective of the test, although some plastic deformation will necessary take place. The most common laboratory measurement of impact energy is by the Charpy test. The principle of the test is straightforward. The energy necessary to fracture a test sample piece is directly calculated from the difference in the initial and the final heights of the swinging pendulum of the Charpy machine. The test sample is notched. The notch essentially acts as a stress concentrator and thereby exerts a control over the fracture event. The sample is subjected to elastic deformation, plastic deformation and finally fracture, in succession, as if a tensile test proceeds rapidly to completion. The impact energy derived from the Charpy test correlates with the area under the stress–strain curve obtained in a tensile test. The impact data are sensitive to (i) the type of the notch, (ii) the nature of stress concentration at the notch and the crack tips, and (iii) the test temperature. Face centered cubic (fcc) metals and alloys generally show ductile fracture. However, body centered cubic (bcc) metals and alloys show a significant variation in the fracture mode with temperature. In general, they fail in a brittle manner at relatively low temperatures and in a ductile manner at relatively high temperatures. The fracture surface corresponding to a high temperature ductile failure has a dimpled appearance with a number of cuplike projections of the deformed metal. Brittle fracture is characterized by cleavage surfaces. In the case of a failure that has occurred at a temperature close to the transition temperature, the fracture surface has a mixed appearance. The ductile-to-brittle transition temperature (DBTT) is of considerable practical significance. The metals and alloys that show such a transition lose toughness and become susceptible to catastrophic failure below this transition temperature. It is worthwhile to consider an example in this context. It is known that a large fraction of structural steels have the bcc structure and because of this, the ductile–brittle transition temperature is an important design criterion in structures where these steels are used. The transition temperature for this class of steels generally occurs between –100 and +100 °C. Low carbon steels that are ductile at room temperature can become brittle when exposed to a lower temperature ocean environment. This accounted for several disastrous failures of Liberty ships during World War II. Some of these ships broke into halves.

In conclusion, it may be mentioned that the characterization of the mechanical behaviour of materials has many facets. Different methods of testing pertain to different aspects and conditions. The tensile properties, as determined by the tensile test, correspond to slowly applied single load applications. Rapidly applied and cyclic load applications respectively provide the impact and the fatigue properties. Hardness is an analog of the tensile strength which a tensile test measures. The creep test pertains to mechanical behaviour under long term loading at elevated temperatures.

1.4
Resources of Metals

1.4.1
General

Present account provides a preliminary knowledge of the processes leading to mineral formation. The coverage is amply illustrated. The account has also made references to resources other than the land based ones. Thus figures the oceanic resources. These particular ones and some others that have appeared in the presentation, however, are of no major consequence as commercial resources of metals at present. Metals extracted from naturally occurring resources are commonly known as primary metals and those derived principally from scrap, as for example, as secondary metals. Primary metal production is by far the largest involvement of chemical metallurgical operations. It is to be noted that the classification into primary and secondary is no way a reflection of the quality of the metal. There is neither any laid down criterion or certification nor any examination or test, chemical or metallurgical or otherwise, which can be treated as the determining factor for a metal to be identified as primary or secondary. It is perhaps simply a historically used expression that has been in place to distinguish between the metals that have originated from the natural resources or habitat, so to say, and those that have not. Secondary metal industry, however, is a very well recognized industry. Just as an example mention may be made of the fact that some of the best quality stainless steels are made almost entirely from scrap. Scrap is in every sense an extremely important and valuable source of metals. One can go even more a step ahead to add that in some specific situations it is placed really in high esteem as far as goes its position to augment, correct and fulfill supply and availability status of particularly of those metals which are not abundant or in the wanting list in a country.

1.4.2
Earth's Crust

The Earth has geospherically been described in terms of five major zones. These are: (i) atmosphere (extending to approximately 250 km above the Earth's surface; general chemical feature: N_2, O_2, H_2O, CO_2, inert gases; general physical feature: gas), (ii) hydrosphere (thickness: 0–11 km; general chemical feature: saline and fresh water; general physical feature: liquid), (iii) lithosphere (thickness: 1200 km; general chemical feature: common silicate rocks; general physical feature: solid), (iv) chalcosphere (mantle) (thickness: 1700 km; general chemical feature: high content of sulfides of the heavy metals; general physical feature: solid), and (v) siderosphere (core) (thickness: 3500 km; general chemical feature: iron–nickel melt; general physical feature: liquid). The Earth proper is then composed of a central core (siderosphere), the surface crust (lithosphere), and an intermediate layer between them called the mantle (chalcosphere).

The atmosphere contains no minerals (although it is the source of nitrogen for ammonia-based fertilizers, and of argon used for many industrial purposes), while the major part of the mantle and the core are inaccessible (the depth of the deepest mine exploited till now is approximately 5200 m). The hydrosphere accounts for the major part of the production of magnesium and sodium. The crust and the uppermost part of the upper mantle, together called the lithosphere, is the principal reservoir serving as the supplier of a majority of the metals and materials. The lithospheric matter is continuously being recycled through the process of plate tectonics, a process responsible not only for the changes in the configuration of continents and oceans through the geological ages, but also for bringing several mantle constituents to near the surface of the crust.

Present attention is focussed on the lithosphere which is the solid part of the Earth's crust. Details as regards its components and composition are shown in Table 1.2. It is

Table 1.2 Components and average composition of the lithosphere.

Components		*Average composition*	
Rock type	***Weight (%)***	***Oxide***	***Weight (%)***
Igneous rocks	95.00	SiO_2	59.07
Shale	4.00	Al_2O_3	15.22
Sandstone	0.75	FeO	3.71
Limestone	0.25	Fe_2O_3	3.10
		CaO	5.10
		Na_2O	3.71
		MgO	3.45
		K_2O	3.11
		H_2O	1.30
		TiO_2	1.03
		CO_2	0.35
		P_2O_5	0.30
		MnO	0.11
	100.00		99.56

found to consist mainly of igneous rocks as seen from the data provided on the components. The data on composition show that 99.5% of the solid, outer crust of the Earth, is made up of 13 elements. These elements taken in the order of their abundance are (see Table 1.3): O_2, Si, Al, Fe, Ca, Na, K, Mg, Ti, P, H_2, C and Mn, which are combined in different ways to form silicates and oxides and smaller amounts of carbonates, phosphates, and other compounds. The carbonates are found almost entirely in the sedimentary rocks. S, Cl_2, organic C, and F_2 (in decreasing order) jointly make about 0.2% and the metals, Ba, Rb, Cr, Sr, V and Zr (in decreasing order) jointly make about another 0.2%. All other metals together make the remaining 0.1%. Table 1.3 conveys two noticeably important facts. One is that some metals that are generally considered rare are actually present in good amounts in the lithosphere. The example of titanium is considered. It is the ninth most abundant element in the solid crust, although it is by and large regarded as rare. The same is true of Ba and Rb. These and some others are widely distributed through the crust. Second striking fact which the table shows is that many of the daily and commonly used metals such as Cu, Pb, Zn, Sn, Au, Ag and Pt are actually rare. It is thus obvious that before any metal can be gainfully extracted from the Earth, it must have been highly concentrated by geological processes leading to formation of economically important ores. This fact has also been brought out elsewhere in the text. While on the subject it may be added that some specific man-made processes may be very significantly instrumental to bring about a concentration of an exceedingly rare metal. The example of tellurium metal may be considered. Its relative abundance in the lithosphere is only 0.2 parts per million. Its concentration during the various processes of copper smelting and refining enriches to such an extent that its commercial recovery as a by-product of the copper industry works out to be remunerative.

A classification of mineral deposits has been proposed which recognizes the importance of concentration (or grade) as well as of geological occurrence. According to this classifica-

Table 1.3 Relative abundance of the elements in the lithosphere.

Element	**%**	***Element***	**%**	***Element***	**%**	***Element***	**%**
Actinium	$3 \cdot 10^{-14}$	Europium	$1 \cdot 10^{-4}$	Neodymium	$1.7 \cdot 10^{-3}$	Scandium	$5 \cdot 10^{-4}$
Aluminum	8.13	Fluorine	$8 \cdot 10^{-2}$	Neon	–	Selenium	$9 \cdot 10^{-6}$
Americium	–	Francium	–	Neptunium	–	Silicon	27.72
Antimony	$1 \cdot 10^{-4}$	Gadolinium	$5 \cdot 10^{-4}$	Nickel	$8.0 \cdot 10^{-3}$	Silver	$2 \cdot 10^{-6}$
Argon	–	Gallium	$1.5 \cdot 10^{-3}$	Niobium	$2.4 \cdot 10^{-3}$	Sodium	2.83
Arsenic	$5 \cdot 10^{-4}$	Germanium	$7 \cdot 10^{-4}$	Nitrogen	–	Strontium	$1.5 \cdot 10^{-2}$
Astatine	–	Gold	$1 \cdot 10^{-7}$	Osmium	–	Sulfur	$5.2 \cdot 10^{-2}$
Barium	$4.3 \cdot 10^{-2}$	Hafnium	$4.5 \cdot 10^{-4}$	Oxygen	46.6	Tantalum	$2.1 \cdot 10^{-4}$
Beryllium	$6 \cdot 10^{-4}$	Helium	–	Palladium	$1 \cdot 10^{-6}$	Technecium	–
Bismuth	$2 \cdot 10^{-5}$	Holmium	$1.15 \cdot 10^{-4}$	Phosphorus	0.12	Tellurium	$1.8 \cdot 10^{-7}$
Boron	$1.0 \cdot 10^{-3}$	Hydrogen	0.14	Platinum	$5 \cdot 10^{-7}$	Terbium	$2 \cdot 10^{-4}$
Bromine	$2.5 \cdot 10^{-4}$	Indium	$1.0 \cdot 10^{-5}$	Plutonium	–	Thallium	$3 \cdot 10^{-5}$
Cadmium	$1.5 \cdot 10^{-5}$	Iodine	$3 \cdot 10^{-5}$	Polonium	$3 \cdot 10^{-14}$	Thorium	$1.1 \cdot 10^{-3}$
Calcium	3.63	Iridium	$1.0 \cdot 10^{-7}$	Potassium	2.59	Thullium	$2.0 \cdot 10^{-5}$
Carbon	$3.2 \cdot 10^{-2}$	Iron	5.00	Praseodymium	$5 \cdot 10^{-4}$	Tin	$4.0 \cdot 10^{-3}$
Cerium	$2.5 \cdot 10^{-3}$	Krypton	–	Promethium	–	Titanium	0.44
Cesium	$3.2 \cdot 10^{-4}$	Lanthanum	$1.7 \cdot 10^{-3}$	Protactinium	$8 \cdot 10^{-11}$	Tungsten	$1.0 \cdot 10^{-4}$
Chlorine	$4.8 \cdot 10^{-2}$	Lead	$1.5 \cdot 10^{-3}$	Radium	$1.3 \cdot 10^{-10}$	Uranium	$4 \cdot 10^{-4}$
Chromium	$2.0 \cdot 10^{-2}$	Lithium	$6.5 \cdot 10^{-3}$	Radon	–	Vanadium	$1.5 \cdot 10^{-2}$
Cobalt	$2.3 \cdot 10^{-3}$	Lutetium	$7.5 \cdot 10^{-5}$	Rhenium	$1.0 \cdot 10^{-7}$	Xenon	–
Copper	$7.0 \cdot 10^{-3}$	Magnesium	2.09	Rhodium	$1 \cdot 10^{-7}$	Ytterbium	$1.5 \cdot 10^{-4}$
Curium	–	Manganese	0.10	Rubidium	$3.1 \cdot 10^{-2}$	Yttrium	$1.0 \cdot 10^{-3}$
Dysprosium	$2 \cdot 10^{-4}$	Mercury	$5 \cdot 10^{-5}$	Ruthenium	–	Zinc	$8.0 \cdot 10^{-3}$
Erbium	$1.5 \cdot 10^{-4}$	Molybdenum	$2.3 \cdot 10^{-4}$	Samarium	$3 \cdot 10^{-4}$	Zirconium	$2.2 \cdot 10^{-2}$

Abundancy range	***Element***
Over 10%	O (46.6); Si (27.7)
1–10%	Al (8.1); Fe (5.0); Ca (3.6); K (2.6); Na (2.8); Mg (2.1)
0.1–1%	C; H; Mn; P; Ti
0.01–0.1%	Ba; Cl; Cr; F; Rb; S; Sr; V; Zr
0.001–0.01%	Cu; Ce; Co; Ga; La; Li; Nb; Ni; Pb; Sn; Th; Zn; Yt
1–10 ppm	As; B; Br; Cs; Ge; Hf; Mo; Sb; Ta; U; W; and most of the rare Earths
0.1–1 ppm	Bi; Cd; I; In; Tl
0.01–0.1 ppm	Ag; Pd; Se
0.001–0.01 ppm	Au; Ir; Os; Pt; Re; Rh; Ru

tion elements fall into two broad groups: one of geochemically abundant elements and the other of geochemically scarce elements.

Figure 1.14 shows a typical distribution for the geochemically abundant elements in crustal rocks. It could be seen that the proportion of the volume of material available for exploitation increases in geometrical progression as grade falls in arithmetical progression. In a sense, therefore, there is no finite limit to the availability of such elements, however, dilution with host rock implies that revenue would be insufficient to cover the fixed cost of extraction.

The dividing line between a grade which is amenable to economic exploitation and one which is uneconomic would depend on the cut off used and this, in turn, would be a func-

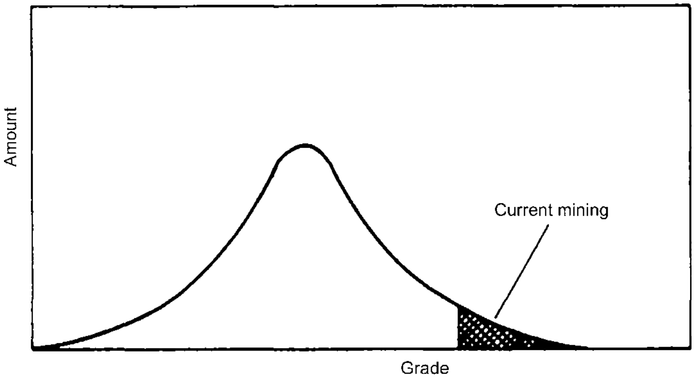


Figure 1.14 Curve showing the typical distribution of the geochemically abundant elements.

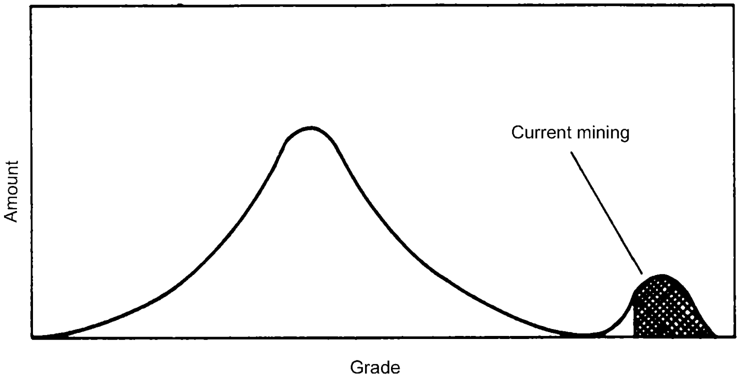


Figure 1.15 Curve showing the typical distribution of the geochemically scarce elements.

tion of product prices, operating cost and the return expected from the initial capital cost of the project. Important examples of mineral deposits corresponding to geochemically abundant elements are those associated with oxides. These include magnetite (iron and vanadium), bauxite (aluminum), and ilmenite (titanium). These are, in general, exploited in high tonnage bulk mining operations.

A typical distribution for the geochemically scarce elements is shown in Figure 1.15. These are usually present as atomic substitutes in refractory silicate minerals. However, geological processes lead to their preferential concentration in sulfides.

1.4.3
Minerals and Ores

It is extraordinary difficult to provide a sufficiently precise, yet concise, definition of the term mineral that will entirely be satisfactory from all points of view. However, the term mineral has been described in several ways. As used by the mineralogist the term may refer to a naturally occurring solid inorganic matter with distinctive physical properties and atomic structure, and a composition that can be represented by a chemical formula. As used by the mineral economist, the term may refer to a commercially traded product, derived from a naturally occurring, nonliving, organic or inorganic, solid, liquid or gaseous substance. As used in the description of resources, the term refers to a naturally occurring, nonliving, organic or inorganic, solid, liquid or gaseous substance that has a known or potential use.

Minerals have two broad divisions: metalliferous minerals and nonmetallic industrial minerals. Generally, the latter are associated with low unit value while the products obtained from the former have relatively a higher unit value. In both types of mineral deposit, the mineral of interest should occur in concentrations adequate to support its extraction in an economically viable operation. This, in turn, depends strongly on the prevailing market price for the product. Nonmetallic industrial minerals include those separated from source rocks such as diamonds and asbestos. They also include monomineralic deposits by themselves, such as beds of gypsum, salt and sulfur. Other nonmetallic minerals which the industry uses are feldspar, quartz, mica, spodumene, gemstones, fluorite, barite, magnesite, and many others. Of these, spodumene and magnesite can as well be regarded as metalliferous because they are also mined to extract lithium and magnesium respectively. A distinction must be made between industrial minerals and industrial materials. The latter are used as such without any processing. Examples of these are soapstone, pumice, limestone, and shale, which are rocks, and clays such as kaolin, which are mixtures of hydrous aluminum silicates derived from the weathering of rocks.

Many minerals are somewhat variable in their chemical composition because an element may be substituted for another. Such atomic or ionic substitution takes place because a mineral usually crystallises from natural solutions that contain other atoms or ions in addition to those necessary to form the particular mineral. Consequently, some foreign atoms or ions often get incorporated in its structure. In fact, this is a fairly common phenomenon among minerals. There are basically two ways by which substitution between two or more ions of similar size and similar charge can take place and both these involve solid solutions. In the first, a certain ion or ions may substitute for another only in limited amounts (the extent of substitution being usually quite small). In the second, substitution of one ionic species for another may occur very extensively, forming solid solution series. Regardless of which type of substitution takes place, there is no change in the atomic structure of the mineral. The mineral sphalerite, ZnS, provides an example of the first type of substitution. In this mineral, iron (Fe) substitutes for some of the zinc (Zn). The formula of such a mineral would be written as (Zn,Fe)S, to indicate that Fe substitutes for Zn. Occasionally, other elements such as manganese (Mn), in addition to Fe, may substitute for Zn. The formula then would be written as (Zn,Fe,Mn)S to indicate this substitution. The ideal formula for sphalerite, ZnS, corresponds to the situation where there is no Fe and Mn substitution. An example of the second type is seen in the mineral group called the olivines. In this group, iron (Fe) and magnesium (Mg) may substitute for each other in unrestricted amounts. The main components of this group are forsterite, Mg_2SiO_4, and fayalite, Fe_2SiO_4 (these two minerals being the two end members of the olivine group). Substitution may degrade the value of a mineral as an ore as in chromite, where aluminum substitutes for chromium ($FeO(Cr,Al)_2O_3$), or may enhance it, as in the case of tetrahedrite, an important source for silver, where silver partly replaces copper ($(\mathrm{Cu,Ag})_{12}\mathrm{Sb}_4\mathrm{S}_{13}$). It may be pointed out that substitution alone does not account for the presence of one or more metals in certain minerals. An example is the presence of cobalt (Co) and arsenic (As) in cobalite, CoAsS. The absence of parenthesis in the formula for cobalite, CoAsS, implies that cobalt (Co) and arsenic (As) both are primary elements in the structure and do not substitute for each other.

Certain minerals may be mined and processed for more than one purpose. For instance, bauxite, on the one hand, can be utilized for making bricks or abrasives and, on the other, is used for the production of aluminum. It is often found that many nonmetallic minerals are associated with metalliferous minerals. As an example mention may be made of galena, the main mineral source of lead, which is found very frequently to be associated with fluorite ($\mathrm{CaF_2}$) and barytes ($\mathrm{BaSO_4}$), both of which are important industrial minerals.

A single metal may be extracted from several minerals. Thus there are many minerals of copper, such as chalcocite, bornite, chalcopyrite, cuprite, native copper, and malachite; one or more of these may occur in an individual deposit. Also, more than one metal may be obtained from a single mineral; stannite, for example, yields both copper and tin. A mineral deposit, therefore, may yield several metals from different minerals.

Mineral deposits that are essentially as originally formed are called primary or hypogene. The term hypogene also indicates formation by upward movement of material. Those deposits which have been changed by weathering or other superficial processes are secondary or supergene deposits. It is the secondary minerals that prospectors encounter and during the early days of mining operation it makes up the ore from which metals are won. However, such surface reactions are usually not deep and secondary minerals give way in depth to the primary ore in which all great mines of world operate.

Some mineral products are employed essentially in the form in which they are mined, with only shaping, crushing, cleaning or other treatments that do not change their compositions. Coal, in most of its uses, is a typical example. Most minerals are processed, however, to yield usable products – metals, chemicals or other materials from which most of the items of utility are derived. As regards coal, it may be pointed out that it is often referred to as a mineral, but unlike a true mineral, it has no fixed chemical formula.

It is important that a clear understanding of the distinction is presented between mineral and ore deposits. A mineral is a naturally occurring, homogeneous solid element or compound, of definite composition, having an ordered atomic structure and, thus, in a crystalline condition. The solid materials of the Earth which is customarily recognised as rocks are aggregates of one or minerals. The definition of ore goes as a naturally occurring aggregate of minerals from which one or more metals may be extracted with profit or with hope of profit. Economic factor dominates in the definition and this being so it may be stated that all ore deposits are mineral deposits but the opposite is not true. A mineral deposit of yesteryears which is not an ore deposit may become one today or in future years. This, of course, depends upon number of other factors. An ore is not just an aggregate of minerals, but must contain metallic minerals in such form and abundance that the metals can be profitably extracted, as indicated in the definition. A mineral such as molybdenite ($\mathrm{MoS_2}$) is always molybdenite, but a mineralised rock containing molybdenite may or may not be a molybdenum ore. The economics of extraction depends on a number of factors. Some of these are: the fraction of the valuable metal in the ore, the form in which the metal occurs (i.e., the nature of the mineral in the ore), the fraction of impurities in the ore, the physical condition of the ore, the location and the magnitude of the ore deposits and their proximity to transport facilities, the accessibility of the deposits and the market price of the metal. Geographic setting is an important consideration in the evaluation of a mineral deposit. For example, an iron ore deposit in a remote place would not be subject to the same economic determinants as an iron ore deposit in an industrialised area. Both ore bodies may have potential for development, but the remotely located deposit would need to be larger, much higher in grade and much better suited to low cost mining in order to be competitive. In consideration of local geography, site conditions might allow or disallow otherwise suitable methods of development, mining and processing. Thus an ore in a particular region in a country may not have been regarded as an ore had it been located in another region in that country. The criteria of recognition of a deposit as an ore body also vary from country to country.

Another important consideration pertains to the metal content of the deposit. A deposit with a content of iron of about 20% can have little value as an iron ore since there are several deposits with 30–50% iron. Earlier, a copper ore with a minimum of 5% copper was regarded or accepted as a copper ore. However, today, thanks to advancements in technology, rocks with as little as 0.5% copper are mined and processed economically despite the fact that the price of copper, in comparison with those of some other metals, might be showing a downward trend. It is possible that in the future, other resources, which are not considered to be worth exploiting today (such as the manganese nodules or the clays), would become acceptable ores for manganese, copper, nickel, cobalt, and aluminum.

Traditionally rocks like quartzite, limestone, dolomite etc. are not called ores even though, in addition to their other uses, they may also be used as raw materials for the production of silica, calcium and magnesium. On the other hand, zircon should definitely be called an ore as it is mined and processed as a raw material for the production of zirconium. Sea water, which contains about 0.13% magnesium, may serve the purpose of a raw material for the production of magnesium. In fact, sea water is an inexhaustible source of magnesium. It has been estimated that working on only 1% of this resource would allow the production of 20 million tonnes of magnesium per year for 10 million years. This is an unique situation which is not encountered in the case for many metals. Despite all this, however, sea water does not entitle itself to be recognized as an ore since its other uses are far more important. So, for a resource to be recognized as an ore, its alternative uses have also to be considered; if these are much more predominant than its role in producing the metal, it is not counted as an ore.

A description of minerals remains incomplete without the mention of gangue minerals. These are the nonmetallic materials, usually worthless, associated with a deposit. The gangue, customarily, includes only nonmetallic minerals, but in technical usage it also includes some metallic minerals, such as pyrite, which are discarded as worthless. Certain gangue materials, however, may at times be collected as by-products and put to use. For example, fluorspar may be utilized as flux, quartz in abrasives or concrete, pyrite for yielding sulfur, and limestone in fertilizers or as flux. A gangue mineral which is considered to be worthless today may prove to be of value tomorrow. The dividing line between ore minerals and gangue minerals is determined by economics, an aspect given prominence in the definition provided for an ore. A typical lead–zinc ore, as for example, may contain the minerals galena (PbS), sphalerite (ZnS), pyrite (FeS_2), siderite ($FeCO_3$), and quartz (SiO_2). Among these, galena and sphalerite are the minerals which are ores while pyrite, siderite, and quartz are not so. They are gangues. As yet no process has been developed by which it is possible to extract iron economically from the pyrite and the siderite present in such an ore. A huge deposit of relatively pure siderite, however, might be considered to be a valuable ore of iron. If the pyrite associated with the lead–zinc ore referred to earlier happens to contain precious metals like gold and others, then it would, in its own right, come to be classified as an ore mineral.

No description of ores is deemed complete without making reference to metal associations and by-products. A few ores, such as those of gold and tin, may often contain only one worthwhile ore mineral; others, notably those of copper, may contain just one recoverable metal although it may be present in several mineral forms. Most ores, however, contain more than one recoverable metal. These may be present as different minerals, or sometimes, one metal may be in solid solution within the ore mineral of another. Silver, for instance, is frequently found dissolved in lead and copper minerals; in fact, the principal source of silver is obtained as a by-product from refining these metals after they have been smelted from their ores. Molybdenum, on the other hand, occurs as a specific by-product mineral associated with certain copper ores and must be separated from the copper minerals prior to smelting. In many ores, such as those of lead and zinc, two metals may be present as coproducts of roughly equal value. Such metal associations are not haphazard; they occur in specific geological climates, and a metal may have different associations under different geological conditions. Examples of associations are given in Table 1.4. Some minerals may have more than one metal in solid solution. The silver content of lead, for instance, depends on the presence of bismuth, as silver cannot be in solution without it. Molybdenum sulfide, itself a by-product, has its own (dissolved) by-product rhenium. Like rhenium, many minor metals have no source other than the yields as by-products; as examples of such metals reference may be drawn to cadmium, indium, tellurium, selenium and hafnium.

Minerals are well regarded as national assets. Extensive use of mineral resources forms the physical basis of a high standard of living not only in the developed but also in the developing countries. A strong positive correlation exists, for example, between the per

Table 1.4 Metal associations.

Main product	*Coproduct or by-product as a separate mineral*	*By-product in solid solution*
Lead	Zinc	Silver, Bismuth
Zinc	Cadmium	Cadmium, Germanium, Gallium, Indium
Copper	Molybdenum, Cobalt, Zinc + Lead, Gold Uranium, Antimony, Copper	Gold, Silver, Tellurium, Selenium
Gold	Copper, Platinum, Cobalt	Silver
Nickel	Tungsten, Copper	
Tin		Tantalum
Molybdenum	Lead, Copper, Gold	Rhenium
Silver		

capita national income and the per capita consumption of energy and of key mineral commodities in any given country. Minerals that are essential for the economic progress as well as the defence requirements of a country and which are in short supply, or that are found predominantly in certain areas of the world from where they must be imported, are known as strategic minerals. The minerals that belong to this category vary from country to country and from time to time.

Mineral resources are nonrenewable resources, in contrast to renewable resources such as surface water and timber, which are or can be replenished naturally or artificially. The geological processes by which most mineral deposits form take a very long time. They can, in no way, be thought to replenish deposits extracted from the ground and dispersed by use. However, it is important to recognize that mineral resources are extendable with the help of advancing technology that develops uses for sources that were not readily usable or exploitable before, allows hidden deposits to be discovered, and enhances the efficiency of recovery and of use.

Conservation of mineral resources is a particularly important issue that should engage attention. Conservation means the utilization of the deposit in such a manner that the maximum amount of mineral is mined and ultimately utilized. Leaving out lower grades of minerals and mining only higher grades for the sake of immediate monetary gain should be discouraged. Higher grades deplete very rapidly. A long life of mine and mill can be assured by mixing mined material of higher grades with that of lower grades to yield an acceptable average grade for daily processing in a mill. Advancements in mining techniques have made economic mining of low grade deposits possible. This trend will continue and in the future large volumes of low-grade deposits that are not mined today will be exploited. Along with this, one should not lose sight of the emphasis on maximum utilisation of mined ore, by exploiting and finding applications for all by- and co-products.

1.4.4
Rocks and Ore Deposits

All ore mineral deposits lie in or on solid rocks of which the Earth's crust is predominantly composed. The geological processes which are responsible for the formation of rocks also form the ore bodies associated with them. For the formation of an ore body, the metal or metals concerned must be enriched to a considerably higher level than their normal crustal abundance. The degree of such enrichment below which the extraction cost makes the processing of the ore uneconomical is termed the concentration factor. Typical values of the concentration factor for some of the common metals are given in Table 1.5.

Three main modes of the formation of rocks are recognized: (i) igneous, (ii) sedimentary and (iii) metamorphic. The geological processes leading to the formation of these rock groups are interrelated and are cyclic in operation; these are conceptually illustrated in Figure 1.16. The igneous, sedimentary and metamorphic processes also lead to the formation of different types of ore deposits which, like the rock groups, are interrelated with one type changing into another with changes in the physico-chemical conditions. Two genetic groups within each group can be recognized: primary or syngenetic, formed at the same time as the enclosing rock, and epigenetic, formed as a result of later introduction into the enclosing rock.

Table 1.5 Concentration factors of common metals.

Metals	*Average crustal abundance (%)*	*Average minimum exploitable grade*	*Concentration factor*
Aluminum	8	30	3.75
Iron	5	25	5
Copper	0.005	0.4	80
Nickel	0.007	0.5	71
Zinc	0.007	4	571
Manganese	9.09	35	389
Tin	0.0002	0.5	2500
Chromium	0.01	30	3000
Lead	0.001	4	4000
Gold	0.0000004	0.0001	250

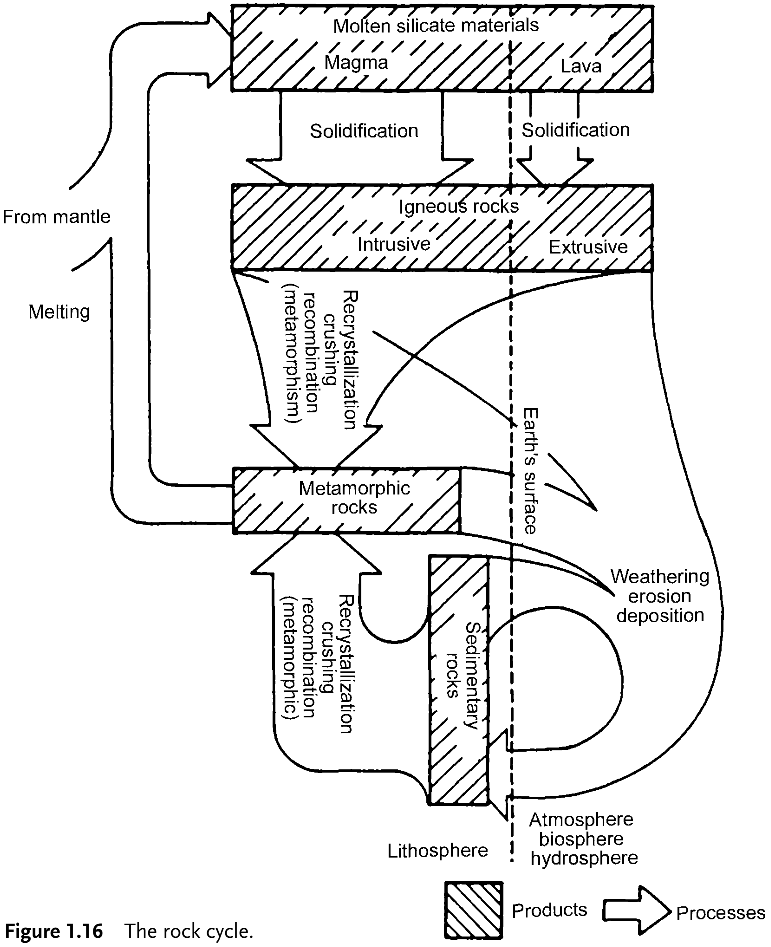


Figure 1.16 The rock cycle.

1.4.4.1 **Igneous Processes of Rock and Ore Formation**

Igneous rocks are formed by the solidification of the magma which includes, besides the molten rock material, a number of dissolved gases. If the solidification takes place completely deep within the Earth's crust, without reaching the surface, the resulting rocks are called intrusive or plutonic rocks. If, on the other hand, it takes place on reaching the surface of the Earth, the resulting rocks are called extrusive or volcanic rocks. Mineral deposits are associated with both these types of igneous rocks. The solidification process is very complex and, depending on the conditions of temperature and pressure, rate of cooling and presence of dissolved gases, a large number of rock types are formed with entirely different chemical compositions.

A large fraction of igneous rocks belongs to one of the three kinds: basalt, granite and intermediate. Corresponding to these, three major types of magmas are commonly suggested. These are: basaltic (mafic or basic), granitic (felsic or acidic) and andesitic (intermediate) magmas. Mafic magmas are generated in the upper mantle by partial melting of mantle rocks; granitic magmas by partial melting of rocks of the continental crust; and andesitic magmas by partial melting of subducted oceanic crust, or by mixing of melted crustal material and basaltic magmas.

Broadly speaking, only ten elements make up nearly 99% of the mass of the magma and the igneous rocks. These are oxygen, silicon, aluminum, iron, calcium, sodium, potassium, magnesium, titanium and hydrogen. The remaining elements of the periodic table, constituting the balance 1% of the mass, and containing many of the common and well known metals, account for the minor and trace element contents of the rocks, and generally occur in a dispersed state. However, during certain stages of the solidification of the magma, these have a tendency to be heterogeneously distributed and locally concentrated, forming the ore deposits. The volatile components of the magma, particularly hydrogen, fluorine, chlorine and sulfur, play a very significant role in the sequence of crystallization of the magma and in the formation of valuable mineral deposits.

The igneous processes which give rise to ore deposits are broadly classified into three types: (i) magmatic concentrations and segregations, (ii) contact metasomatism, and (iii) hydrothermal processes.

Magmatic concentrations form either by simple crystallisation or concentration during the formation of igneous rocks. Depending on the state, time and nature of concentration, these may be further classified as (i) early magmatic, (ii) late magmatic, and (iii) immiscible segregations. Some important types of deposits of magmatic concentrations are shown in Table 1.6.

Early magmatic concentrations may take the form of disseminations, segregations, or injections. The minerals contained in them have crystallised before the formation of the rock forming constituents of the enclosing rocks. Disseminations have resulted from simple crystallisation of a deep seated magma. Diamond bearing kimberlite pipes and corundum bearing rocks are examples of disseminated type early magmatic deposits. Early magmatic segregations are concentrations of valuable minerals that have taken place as a result of gravitational settling of early formed crystals during crystallisation differentiation of the magma, within the magmatic chamber. Most of the layered chromite deposits and platinum group elements concentrations associated with them are examples of early magmatic segregations. Magmatic injections have resulted from the moving away of the magmatic

Table 1.6 Important types of magmatic concentration ore deposits.

Type	*Description*	*Example*
1. Early magmatic		
A. Dissemination	Disseminated crystallisation without concentration	Most diamond bearing kimberlite pipes
B. Segregation	Crystallisation, differentiation and accumulation	Bushveld chromite; still water complex; Sukinda chromite
2. Late magmatic		
A. Residual liquid segregation	Crystallisation from and accumulation in residual magma	Bushveld titanomagnetite
B. Residual liquid injection	Same as above, followed by injection	Most pegmatite and carbonatite veins
3. Immiscible liquid		
A. Segregation	Immiscible liquid segregation and accumulation	Sudbury Cu–Ni; Insizwa, South Africa
B. Injection	Same as above, with injection	Norwegian nickel deposits
4. Porphyry copper deposits	Cu–Mo disseminations in granodioritic porphyritic rocks	Utah copper; The Ruth, Nevada; Climax, USA

segregations from the original place of accumulation into the surrounding rocks by injection. Most of the massive titanomagnetite, magnetite and some of the chromite deposits owe their origin to this process.

Late magmatic concentrations have come into being by crystallisation of mobile residual magmas formed toward the close of the magmatic period. The ore minerals so formed are later in origin than the rock forming minerals of the enclosing rock – a feature which is in sharp contrast to the early magmatic concentrations. They may occur both in the forms of segregations and injections. Segregations are normally associated with mafic igneous rocks; the famous iron and titanium ore bodies of Bushveld and Adirondack are examples of late magmatic segregations. There are two important types of residual late magmatic injections – the pegmatites and the carbonatites.

Pegmatites have resulted from injection of late magmatic and residual fluids of granitic composition, enriched in water, volatile components (phosphorus, fluorine, chlorine, sulfur, boron, etc.), low melting point silicates (albite, mica) and a broad spectrum of rare and exotic metals. They generally occur in the form of dykes and lenticular intrusive bodies. Many economically important pegmatite bodies average hundreds of metres in length and a few tens of metres across. While simple pegmatites contain essential quartz and feldspar (albite, microcline) and accessory mica, and tourmaline, complex zoned pegmatites are characterised by high concentrations of minerals of rare metals in the form of crystals of high purity. The important classes of rare mineral pegmatites with examples are given in Table 1.7. Pegmatites constitute the main source for beryllium (beryl, bertrandite), lithium (lepidolite, spodumene, amblygonite, petalite), cesium (pollucite) and niobium–tantalum

Table 1.7 Rare metal pegmatite deposits.

Pegmatite type	***Typical mineral association***	***Economic potential***	***Examples***
Rare Earth	Allanite Monazite Gadolinite Fergusonite Euxenite	REE, Y, U	Kobe, Japan Barringer Hill, Texas Ytterby, Sweden Shatford Lake, Manitoba
Beryl	Beryl Columbite-tantalite Triplite Triphyllite	Be, Nb-Ta	Ural Mts., Russia Mayers Ranch, Colorado Dan Patch, South Dakota
Complex	Spodumene Beryl Tantalite Lepidolite Ambylgonite Topaz	Li, Rb, Cs, Be, Ta, Sn, Ga	Manono, Zaire Hugo, South Dakota Tanco, Manitoba Londonberry, Australia Marlagalla, India
Albite-spodumene	Spodumene Tantalite Beryl Cassiterite	Li, Sn, Ta, Be	Kings Mt., N. Carolina Volta Grande, Brazil
Albite	Tantalite Cassiterite Beryl	Ta, Sn	Tin Dyke, Manitoba Hengshan, China Bastar, India

(columbite–tantalite, fergusonite, samarskite). Rare metals like rubidium, gallium and scandium are also extracted from pegmatitic sources. Pegmatites contain economic concentrations of the rare Earths (monazite, xenotime, allanite), tungsten (wolframite, scheelite), molybdenum (molybdenite), uranium (uraninite) and thorium (thorianite). Pegmatites are the main sources for high purity industrial minerals like sheet mica, ceramic and dental feldspar, optical quartz, fluorite and semiprecious stones like beryl, chrysoberyl and topaz. Important world examples of economically important pegmatites are Tanco (Manitoba, USA), Manono deposit (Zaire), Greenbushes deposit (Australia), Bancroft (Canada), Kobe (Japan), Urals (Russia) and Singhbhum (India).

Carbonatites are late magmatic dyke formed from residual liquids generated during extreme differentiation of basaltic magma derived from the mantle. They essentially consist of crystalline calcitic and dolomitic carbonates and are enriched in alkalies. Important metallic concentrations associated with carbonatites are niobium (pyrochlore), titanium (ilmenite and titanomagnetite), rare Earths (bastnasite), zirconium (zircon and baddeleyite), copper (chalcopyrite), and phosphorus (apatite). Important carbonatite deposits of the world along with the major ore minerals produced from them are given in Table 1.8. It may be mentioned in passing that apatite is by far the most important mineral produced from carbonatites, notably in Brazil and South Africa. Carbonatites have a mean phosphate con-

Table 1.8 Important carbonatite deposits of the world.

Locality	*Important economic minerals*
Bayan Obo, China	Bastnasite, monazite, magnetite, pyrochlore
Jacupiranga, Brazil	Apatite, calcite
Palabora, Namibia	Apatite, copper, baddeleyite, vermiculite, uranothorite, magnetite
Mt. Pass, USA	Bastnasite
Kovdor (Russia)	Apatite, magnetite, baddeleyite, vermiculite
St. Honore, Canada	Pyrochlore
Lueshe, Zaire	Pyrochlore
Sulinjarvi, Finland	Apatite, phlogopite, calcite
Araxa and Catalao, Brazil	Pyrochlore, apatite
Ambadongar, India	Fluorite

tent of approximately 2.3% P_2O_5, nearly an order of magnitude greater than that of crustal igneous rocks. This represents just another example of the naturally occurring phenomena of minerals concentrating in different geological settings.

Immiscible liquid segregations result from the fact that silicate magmas at high temperatures can contain upto 10% of metallic sulfides in solution. During crystallisation, a sulfide rich melt separates from the predominantly silicate melt as immiscible droplets. These droplets segregate at the bottom of the magma chamber as a sulfide rich melt enriched in copper, nickel and iron, which on crystallisation gives rise to important sulfide deposits. The huge basin like nickel–copper bearing sulfide deposit at Sudbury, Canada, is one of the important examples of immiscible segregation. An account of ore deposits of magmatic origin will be incomplete without a mention of porphyry copper ores, which constitute the most important source of copper and molybdenum. The porphyry copper ores are associated with porphyritic rocks of granodiorite composition, originated from intermediate andesitic magmas generated at subduction zones of oceanic plates. These deposits are concentrated in the mountain arcs along the western margin of North and South America, and in the island arcs along the eastern margin of Asia. Besides copper and molybdenum, porphyry copper ores are important sources of metals like tin, tungsten, bismuth, tellurium, selenium, silver, gold, platinum and rhenium, obtained as by-products.

Contact metasomatic deposits have resulted from the effects of high temperature fluid emanations of magmatic origin escaping into and reacting with the surrounding rocks. As already mentioned, the magma is rich in several volatile components. During magmatic crystallisation, these volatiles get enriched in the residual fluids, which also carry with them those metals which are not accommodated in the already formed minerals. During and after the last stage of magmatic consolidation, these hot fluids may escape into the surrounding rocks, react with them and produce contact metasomatic deposits. Contact metasomatic zones are recognized by the presence of characteristic high temperature minerals like garnet, calcium bearing pyroxenes and amphiboles, scapolite, topaz, fluorite, etc. Important metals and minerals that occur in contact metasomatic deposits are tungsten, tin, molybdenum, lead, zinc, copper, iron, gold, silver, graphite, gemstones and fluorite.

Hydrothermal vein deposits result from hydrothermal solutions. Hydrothermal solutions are essentially the residual hot solutions remaining after magmatic crystallisation (juvenile

Table 1.9 Classification of hydrothermal vein deposits.

Type	*Temperature, pressure and geologic condition*	*Common ore metal association*
Hypothermal	High temperatures (> 400 °C), high pressures, located clse to the intrusive	Gold, tungsten, tin, bismuth, molybdenum
Mesothermal	Moderate temperatures (250–400 °C) and pressures, located away from the intrusive	Copper, molybdenum, lead, zinc, nickel, cobalt
Epithermal	Low temperatures (< 300 °C) and pressures, farthest from the intrusive, mixed with connate and meteroric waters	Gold, silver, mercury, antimony, arsenic, bismuth, selenium, lead, zinc
Xenothermal	High temperatures (600 °C) at low to very low pressures, close to the intrusive, near the surface	Tin, tungsten, molybdenum, silver
Telethermal	Essentially meteoric and connate waters with little addition of magmatic water, very low temperatures (< 100 °C) and pressures, near the surface	Lead, zinc, cadmium germanium

waters), which may be mixed with waters squeezed out of compacting rocks (connate waters) and downward migrating rain and surface waters (meteoric waters). The solutions carry with them a number of ore metals mainly in the form of complexes with volatiles like the halogens (fluorine and chlorine), hydrogen and sulfur. The solutions migrate into the surrounding rocks, away from the intrusive body, traversing along weak planes like fractures, joints, grain boundaries etc. With fall in temperatures and confining pressures, the metal constituents in the solutions precipitate in a sequence determined by the solubility and the stability of the complexes along these weak planes within the rocks traversed, forming the hydrothermal vein deposits. Typical alteration zones in the enclosing rocks adjacent to the veins are often observed, which help in locating the veins. Dolomitisation, silicification, argillisation, sericitisation, hematitisation and chloritisation are some of the important types of alteration associated with hydrothermal vein deposits.

For the formation of hydrothermal deposits the following are essential: (i) the availability of mineralising solutions capable of dissolving and transporting mineral matter, (ii) the availability of openings in rocks through which the solutions may be channelled, (iii) the availability of suitable sites for deposition and localisation of ore minerals, (iv) chemical reactions that result in deposition, and (v) sufficient concentration of mineral matter to constitute economic deposits.

Depending on temperature, pressure and geological conditions of deposition, the hydrothermal deposits may be classified into five types, the details of which are given in Table 1.9.

1.4.4.2 **Sedimentary Rocks and Sedimentary Processes of Ore Formation**

Sedimentary rocks have formed as a result of accumulation and compaction of mineral particles derived from pre-existing rocks, transported from their original places of occurrence and deposited in new environments. The essential ingredients for the formation of sedimentary rocks are: (i) source materials, (ii) mechanical and chemical disintegration of these source materials, (iii) transportation of the released materials either in a clastic form or in solution, to the site of new accumulation, (iv) deposition, mechanically or chemically, and (v) compaction and lithification.

The materials that accumulate to form sedimentary rocks are: (i) products of disintegration (weathering) of rocks, (ii) volcanic ejecta, (iii) insoluble decomposition products, (iv) precipitated substances from aqueous solutions, and (iv) bio-organically derived substances.

Material derived from the weathering of pre-existing rocks constitutes the bulk of the source materials, and this disintegration takes place by: (i) mechanical means which result in granular disintegration by abrasive forces into smaller fragments, (ii) chemical decomposition where the original constituents undergo changes as a result of chemical action, solution and reconstitution, and (iii) conversion of insoluble components into soluble ones by the action of organisms like bacteria, and fungi, etc.

The removal and transportation of the products of disintegration take place mainly by the agency of water, ice and air. In the case of water, material may be transported by drag or in suspension, or in solution.

The materials so transported are deposited in a new environment, on land (terrestrial deposition), rivers (fluvial deposition), along coastal areas (marginal deposition) or on the sea floor (marine deposition). Dissolved components are deposited either by precipitation, or by evaporation or by the action of biological agencies.

Deposition is followed by compaction and lithification, during which the particles adhere to one another, open space is reduced and the rock gains mechanical strength.

The sedimentary rocks are classified on the basis of their mineral, chemical and particulate characteristics. Some common sedimentary rocks are conglomerate, sandstone, shale and limestone.

As in the case of igneous processes, the sedimentary processes of rock formation lead to the formation economic mineral deposits. Many valuable mineral deposits of iron, manganese, copper, phosphorus, sulfur, zirconium, the rare Earths, uranium and vanadium owe their origin to sedimentary processes. Some of these constitute special types of sedimentary rocks, while others form important constituents of sedimentary rocks.

Depending on the mode of origin, four main types of sedimentary ore deposits are recognized. These are: (i) mechanical accumulations or placer deposits, (ii) residual deposits, (iii) syn-sedimentary chemical deposits, and (iv) volcano-sedimentary type deposits.

Placer deposits are formed by mechanical concentration where natural gravity separation of heavy minerals from light minerals and their concentration take place while moving through water and air. For concentration to take place, the three properties that are essential are high specific gravity, chemical resistance to weathering and durability. Sulfides never occur as placers, because they oxidize readily and are carried away in solution. Normally the source rocks are those which contain sparsely disseminated ore minerals, and which, by themselves, are not economical to exploit. The operation of placer concentration follows a few basic principles involving differences in specific gravity, size and shape of minerals, which affect the velocity of their movement in a moving fluid. Differential movement and the rate of settling of particles in a moving fluid medium are controlled by: (i) the specific gravity factor, which is given by the ratio of the difference of the specific gravities of the heavy mineral and the medium to the difference of the specific gravities of the light mineral and the medium; this ratio gets accentuated when the medium is water rather than air; (ii) the specific surface of particles – a particle with a smaller surface area sinks more rapidly in comparison with one with a higher surface area, both having same mass; (iii) the particle shape – a particle with a spherical shape settles faster than a particle with, say, a flat shape, both having same mass; and (iv) the velocity of the moving medium – the ability of a body of flowing water to transport a solid particle is proportional to the square of its velocity; thus any fall in the velocity sharply reduces the ability to transport. This ability is also affected by the specific gravity as well as the shape (and the size) of the particle. As a result of the synergistic effect of particle size and density and the velocity of the moving medium, lighter particles are kept in suspension and are more readily removed by a moving fluid compared to those which are at rest (heavier and coarser particles). The various factors described above operate in tandem and the result is a separation of light and fine mineral particles from heavy and coarse ones. With long and continued action, the heavy minerals eventually become sufficiently concentrated to form economically exploitable deposits. Essentially three types of placer deposits are recognized: eluvial, alluvial and beach deposits.

In eluvial deposits sorting takes place by both chemical and mechanical action. Elements such as sodium, potassium, calcium, magnesium, tin etc. are leached out preferentially over iron, manganese, aluminum, titanium, chromium, etc. by chemical action of percolating waters. Heavier resistant particles collect just below the outcrop, while the lighter products are swept downhill by rain wash or blown away by wind. Alternatively, as the weathered debris moves down the slope of a hill, by the action of gravity, heavier particles move downhill faster than the lighter ones. The overall effect is a differential concentration of heavy, chemically resistant mineral particles, either below the outcrop or down the hill slope. The latter are often called colluvial placers. Fairly rich concentrations of economic minerals in the provenance are necessary in order to yield workable deposits by this incomplete process of eluvial concentration. Gold, cassiterite and columbite–tantalite form the most important eluvial deposits. The Pitinga tin deposit in Rhondonia, Brazil, which is presently the largest tin producer in the world, is an eluvial–colluvial deposit.

Stream or alluvial placers develop during water transportation in rivers. The locales where a buildup of heavies occurs are the points where there is a drop in the velocity of moving waters. Favourable spots for the formation of alluvial placers are bends, sand and point bars, bed rock riffles, confluence of tributaries, points of discharge into lakes or sea etc. Gold, tin, precious stones and platinum group metals form important alluvial placers. The notable alluvial placer gold deposits are those occurring in California, Nevada, Idaho, Utah and Alaska in USA, Australia, Columbia, Siberia, Central Africa and New Guinea. Stream placers of Ural mountains, Russia, are important sources of platinum in the world. The well known Malaysian tin deposits also are alluvial placers.

Beach placers form along seashores by the concentrating effects of wave and shore current action. Sorting takes place while shore currents move materials along the shore, which is further accentuated by the action of waves operating at the same time. Pounding waves throw up sands on the beaches and the backwash and the undertow carry away the lighter and finer material, which in turn is moved along shore, while the larger and heavier materials are concentrated on the exposed beaches. Common minerals which form beach placers are gold, ilmenite, rutile, zircon, monazite, xenotime, garnet, cassiterite, columbite–tantalite, silliminate and kyanite. Beach placers of India, Australia, Brazil and Sri Lanka supply the bulk of the world's production of ilmenite, rutile, monazite, and zircon.

Palaeoplacers are placer concentrations that have occurred in the geological past and which are preserved till the present by a cover of later sedimentary rocks. The Witwatersrand gold–uranium deposits (South Africa) and the uranium deposits at Blind River (Ontario, Canada) and Jacobina (Brazil) are the most important examples of palaeoplacers.

Residual concentrations result from the accumulation of valuable minerals by the removal of lighter and soluble components during weathering. The basic requirements for the formation of residual concentrations are: (i) the availability of rocks containing valuable minerals in adequate concentrations, in which the major gangue constituents are soluble or easily disintegrable and the valuable minerals are stable and resistant under the prevailing surface conditions; (ii) climatic conditions favourable for the chemical decay of undesirable minerals; (iii) long lasting crustal stability in order that the residues may accumulate in quantity and the deposits are not destroyed by erosion; and (iv) favourable geomorphological features promoting the retention of residues without erosion and removal. The formation of lateritic crust over various rocks is one of the most common manifestations of residual concentration, where ferric and aluminum oxides constitute the insoluble residual components.

Valuable mineral deposits which form by residual concentration pertain to iron, manganese, aluminum, nickel, clays, tin and gold. Aluminum comes almost exclusively from residual concentrations of bauxite, which result from the lateritisation of alumina rich igneous rocks like syenites under tropical and subtropical climatic conditions. Laterites also contribute nearly 80% of the world's reserves of nickel at grades better than 1% Ni. They form by residual concentrations as a result of weathering of mafic and ultramafic igneous rocks, which are relatively enriched in nickel.

Enriched metal concentrations in the form of secondary enrichment often occur under zones of supergene oxidation and residual concentrations. Gossans, formed over copper and iron bearing sulfide deposits, often overlie zones of secondary enrichment in the form of secondary copper sulfides, and porphyry copper ore deposits very often contain such zones of secondary enrichment.

Syn-sedimentary chemical deposits form by chemical and biochemical precipitation of valuable metal components carried in solution, concomitant with the formation of the enclosing sedimentary rock. The manner of such deposition depends on the concentration of the metal in the solvent, the solubility of the precipitating product, the solution chemistry, and the deposition environment. Iron, manganese, phosphorus, lead, zinc, sulfur and uranium are some of the elements that have formed economically valuable deposits by chemical precipitation during sedimentation.

By far the most important ores of iron come from Precambrian banded iron formations (BIF), which are essentially chemical sediments of alternating siliceous and iron-rich bands. The most notable occurrences are those at Hamersley in Australia, Lake Superior in USA and Canada, Transvaal in South Africa, and Bihar and Karnataka in India. The important manganese deposits of the world are associated with sedimentary deposits; the manganese nodules on the ocean floor are also chemically precipitated from solutions. Phosphorites, the main source of phosphates, are special types of sedimentary deposits formed under marine conditions. Bedded iron sulfide deposits are formed by sulfate reducing bacteria in sedimentary environments. Similarly uranium–vanadium in sandstone-type uranium deposits and stratiform lead and zinc concentrations associated with carbonate rocks owe their origin to syngenetic chemical precipitation.

Volcano-sedimentary ore deposits are syngenetic deposits precipitated from sea water enriched in metals by submarine volcanic activity. Deposits of this type are also called submarine exhalative-sedimentary deposits. Stratabound lead–zinc–copper deposits associated with marine sedimentary volcanic sequences belong to this category. Important examples are Kuroko deposit in Japan, Mt. Isa in Australia, Sullivan deposit in British Columbia, Canada, Rammelsberg in Germany and Rampura-Agucha in Rajasthan, India.

1.4.4.3 **Metamorphic Rocks and Ore Processes**

Metamorphism is the term used to describe the changes in rocks brought about by physical and chemical changes in the environment, such changes essentially taking place in the solid state itself, without involving any melting. The changes brought about are predominantly recrystallisation and reconstitution of the minerals, the bulk chemical composition remaining essentially unchanged. The type of rock undergoing metamorphism, the relative predominance of one or more of the three agents of metamorphism, namely heat, pressure and chemical activity, and any addition or subtraction of chemical species are the factors that determine the direction of the chemical reconstitution and the mineralogical assemblage of the resulting metamorphic rocks.

Depending on the conditions of the main agents of metamorphism, four kinds of metamorphism are recognized. These are burial, contact, thermal and regional metamorphism.

The effect of metamorphism on ore mineralisation is essentially changing the form, the texture and the mineralogy of pre-existing mineral deposits, rather than forming new mineralisation per se. The changes are recrystallisation, recombination of materials to form new minerals, and introduction of new features like deformation, foliation, granularity etc. However, the most important change is in remobilization of ore metals, which may convert many a low grade syngenetic deposit into an economically minable epigenetic deposit by localizing the ore metals in certain structural features.

A number of nonmetallic mineral deposits are formed during metamorphism as a result of recrystallisation. Important among these are graphite, asbestos, talc, soapstone and pyrophyllite, kyanite, sillimanite, and semi precious stones like garnet and emery.

In summary, it is clear that the economic mineral deposits are also special types of rocks, and that the common rock forming processes result in the formation of ore deposits as well. Magmas constitute the ultimate source for all the ore forming metals; their solidification by crystallisation is the primary means of formation of ore forming minerals. Secondary processes like sedimentary and metamorphic processes only redistribute and reconstitute the metals into different forms. Thus the same metal may occur in totally different types of deposits, depending on the nature of the ore forming process in operation. However, the economics of ore exploitation are greatly influenced by the predominant process of ore formation, which determines the tenor, the lateral and the vertical extents, the uniformity of composition and above all, the total quantity available for exploitation. A classic example of deposits of a given metal formed by different processes is provided by iron deposits. One type may result from magmatic differentiation, a second type may form by the action of hot gases and vapours, a third type by hydrothermal solutions, and others by sedimentation and by weathering processes. Depending on the type, each of these deposits may have different economic importance. An iron deposit formed by magmatic processes may be limited in extent and its occurrence may be associated only with certain kinds of igneous rocks. The process of weathering can result in a deposit which carries many impurities, is restricted in areal extent and is of shallow depth. On the other hand, the sedimentary process may lead to the formation of a deposit which is large in areal extent and exhibits a general uniformity of thickness and quality. As other interesting features of deposition it may be noted that a single deposition process may give rise to similar deposits of many different metals and that a single deposit may form by the action of several processes. In the former category, the deposits of iron ore, gold, copper or fluorspar formed by the action of hydrothermal solutions, and deposits of sodium or potassium salts resulting from the evaporation of sea water may be cited as examples. A deposit of low grade iron ore, formed by sedimentation, may be enriched by weathering and further by metamorphism. This is typically illustrative of the latter category.

1.4.5
Other Resources

It is quite clear by now that actually it is the fortuitous concentration of one or more valuable minerals into an ore body by the mineralization processes that has ultimately enabled the production of materials economically from some regions of the lithosphere. Besides the terrestrial sources, there are some other sources of metals. For example, the oceans constitute a source. The relative abundance of metals in the oceans is shown in Table 1.10. In addition, there is another source on the ocean floors called the manganese nodules. Nodule deposits have been found in the north and south Atlantic and the Indian Ocean, as well as in the south Pacific. The chemical compositions of nodules from different locations vary widely. Pacific Ocean generally contains highest concentrations of valuable metals and are the most studied. The average composition of Pacific Ocean nodules, taken from over fifty locations, is shown in Table 1.11. Mineralogically, the nodules consist mainly of an intimate mixture of manganese and iron oxides. The grain size is extremely small, ranging from less than one micrometre to about five micrometres. Manganese may be present in upto three distinct mineral phases, whereas iron is present generally only as goethite. The main oxide minerals are listed in Table 1.11. The valuable metals in the nodules appear to be present as an integral part of the manganese and iron oxides, due either to lattice substitution, to ion exchange, or to adsorption.

The porosity and internal surface area of the nodules are very high. Due to high porosity, raw nodules generally contain 30–40% sea water, together with its contained salts. Several

Table 1.10 The abundances of the metals in the oceans.

Metal	*Abundance in sea water (tonnes)*
Magnesium	10^{15}–10^{16}
Silicon	10^{12}–10^{13}
Aluminum + iron + molybdenum + zinc	10^{10}–10^{11}
Tin + uranium + copper + nickel	10^{9} –10^{10}
Vanadium + titanium	10^{9} –10^{10}
Cobalt + silver + tungsten	10^{8} –10^{9}
Chromium + gold + zirconium + platinum	$< 10^{8}$

Table 1.11 Average composition of Pacific Ocean nodules and mineralogical composition of manganese nodules.

Average composition of Pacific Ocean nodules (concentrations in wt%)	*Mineralogical composition of manganese nodules*
Valuable metals: Mn – 24.2; Ni – 0.99; Cu – 0.53; Co – 0.35; V – 0.054; Mo – 0.052; Zn – 0.047	Mn Minerals: Todorokite (Ca, Na, Mn(II), K) (Mn(IV), Mn(II), Mg)$_6$O$_{12}$ · 3 H_2O
Impurities: Major: Fe – 14.0; Si – 9.4; Al – 2.9; Na – 2.6; Ca – 1.9; Mg – 1.7	Birnessite (Na_7Ca_3) $Mn_{70}O_{140}$ · 28 H_2O Delta manganese dioxide δ-MnO_2
Minor: K, Ti, Ba, P, S – 1.0 – 0.1; Pb, Sr, Zr, B, Y, La, C – 0.1 – 0.01; Yb, Cr, Ga, Sc, Ag, As, Sb – < 0.01	Fe minerals: Goethite α-FeOOH

industrial consortia have been engaged in research and development into the different areas of metal recovery from deep sea manganese nodules. The most technologically daunting tasks is mining or “harvesting” the nodules, which lie on the ocean floor at depths of 2000 to 3000 fathoms. Numerous mining systems have been proposed and some prototype dredges have been and are being tested, but full scale mining has not yet taken place. Apart from the technological problems associated with deep ocean mining, there are two another major problems which require to be resolved before commercial exploitation can come about. One is political. The political difficulties arise because there is no international law governing ownership of nodule deposits. Until the legal situation is clarified, the very large financial investments needed to make deep ocean mining a reality are not likely to be made. The second problem concerns with environmental issues. It stems from the fact the dredging operations may result in huge amounts of very fine silt from the ocean floor, together with cold, nutrient-rich, deep-ocean water being discharged into surface waters. Serious concerns has been voiced about the effects of these disturbances on the ecology of oceans. The potential effects are, of course, extremely difficult to forecast. It will get influenced to a great extent by the types of mining systems eventually put into operation for full-fledged production. This worry is likely to cease the first generation of ocean mining ship from embarking into their operation. However, if the ecological degradation caused by these is seen to be severe, then the long term prospect of deep sea mining may receive a serious setback. Lunar rocks and meteorites constitute yet another source of metals. Apollo and Luna-16, -17, and -20 space research projects have provided data concerning the chemical and mineral constituents of lunar rocks.

Finally, it may be added that it is the terrestrial resources which have served and will continue to serve as practically the sole suppliers of metals and materials. Among the other resources only the manganese nodules extracted from the ocean bed have drawn serious attention the world over for exploring economic methods of processing.

1.5
Mineral Properties

Like metals minerals also exhibit typical crystalline structures. As an example, the structure of molybdenite is shown in Figure 1.17. It is hexagonal with six-pole symmetry and contains two molecules per unit cell. Each sulfur atom is equidistant from three molybdenum atoms and each molybdenum atom is surrounded by six sulfur atoms located at the corners of a trigonal prism. There are two types of bonds that can be established between the atoms which constitute the molybdenite crystal structure. They are the covalent bonds between sulfur and molybdenum atoms and the Van der Waals bonds between sulfur–sulfur atoms. The Van der Waals bond is considerably weaker than the covalent sulfur–molybdenum bond. This causes the bonds of sulfur–sulfur to cleave easily, imparting to molybdenite the property of being a dry lubricant. Molybdenite adheres to metallic surfaces with the development of a molecular bond and the friction between metallic surfaces is replaced by easy friction between two layers of sulfur atoms.

Some minerals have the same kind of crystals, but differ in one or more of the atoms that make it up. For example, olivine has a basic crystal made of oxygen and silicon atoms. Either iron or magnesium can fit into this crystal. As a result, there are two kinds of olivines–forsterite, which contains magnesium atoms, and fayalite, which contains iron atoms. Mineralogists use the term isomorphic for minerals that have same structure but different compositions. To cite some other examples, mention may be made of huebnerite ($MnWO_4$) and ferberite ($FeWO_4$) which are the extreme members of the isomorphic series of wolframite

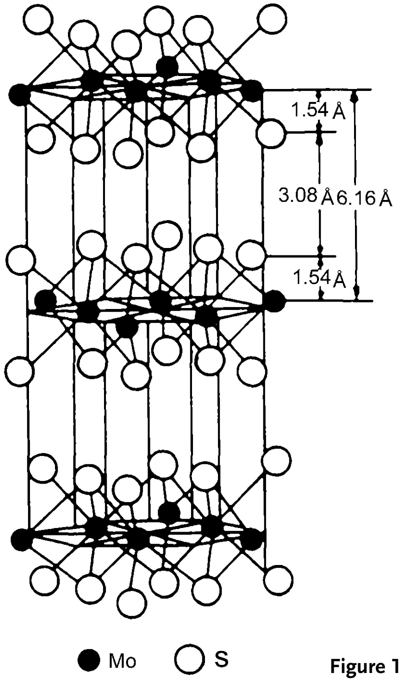


Figure 1.17 Molybdenite structure in globular models.

$(Mn,Fe)WO_4$, and of columbite $(Fe,Mn)Nb_2O_6$ and tantalite $(Fe,Mn)Ta_2O_6$ which are the extreme members of the isomorphic series of columbite–tantalite $(Fe,Mn,Nb,Ta)_2O_6$. Some mineral crystals are made of same kinds of atoms, but different in the ways the atoms are arranged. Mineralogists use the term polymorphic to describe the minerals that have the same composition but different structures. The term implies "many forms". Each form has its own set of physical properties and its own distinct crystal structure. The phenomenon of polymorphism indicates that the chemical composition does not control the crystal structure. It further indicates that there is more than one geometrical arrangement in which the same atoms or ions may be placed in proper proportions, depending upon the conditions of formation. The two minerals graphite and diamond typically represent the phenomenon of polymorphism. The two are chemically alike in being entirely constituted of carbon atoms. They have, however, vastly different properties on account of the difference in the manner in which the carbon atoms are arranged in the crystal lattice (graphite has a hexagonal while diamond has a cubic crystal structure). Some other common examples of polymorphism can be mentioned here: silicon dioxide (SiO_2) forms quartz (hexagonal), tridymite (monoclinic) and also cristobolite (tetragonal); titanium dioxide forms rutile (tetragonal), brookite (orthorhombic), and anatase (tetragonal).

In the previous paragraph, it has been stated that minerals have the same structure but different compositions (phenomenon of isomorphism of minerals) while some minerals have the same composition but different structures (phenomenon of polymorphism of minerals). Mineral composition and structure are both important in studying and classifying minerals. The major class of minerals – based on composition and structure – include elements, sulfides, halides, carbonates, sulfates, oxides, phosphates, and silicates. The silicate class is especially important, because silicon makes up 95% of the minerals, by volume, in the Earth's crust. Mineral classes are divided into families on the basis of the chemicals in each mineral. Families, in turn, are made of groups of minerals that have a similar structure. Groups are further divided into species.

The density of minerals (measured in units of mass per unit of volume, g/cm^3 or kg/m^3) fluctuates within wide limits and reaches upto 23.0 g/cm^3 (platiniridium). On the basis of their densities minerals can be divided into the light (upto 3.0 g/cm^3), the medium (from 3.0 to 4.0 g/cm^3) and the heavy (more than 4.0 g/cm^3) mineral groups. All the minerals bearing the elements belonging to the upper part of the periodic table are light minerals. Minerals containing heavy metals have, as a rule, greater density. The density differences of various minerals cause them to respond differently to identical accelerating forces and provide the means for their separation.

The mechanical properties of minerals are revealed when they are subjected to external forces during which compression, stretching or shock takes place. Analogous to the case of metals, the main types of deformation that are relevant to minerals are elastic, brittle, and plastic. Hardness is also an important parameter for minerals. In a mineralogical context, hardness is an indicator of the resistance to abrasion. Following Friedrich Mohs, a German mineralogist, it is measured by the use of a series of successively harder minerals arranged on a scale ranging from 1 (softest) to 10 (hardest). In this scheme, each mineral will scratch any mineral lower in the scale (lower in number) and can be scratched by any mineral higher in the scale. The hardness of all other minerals are compared to these ten in Mohs scale. For example, a mineral that scratches apatite (No. 5) but is scratched by orthoclase

(No. 6) has a hardness somewhere between 5 and 6; this may be designated as 5.5. The relative character of Mohs scale must be borne in mind. If the hardness of apatite is 5 and that of talc is 1, it does not mean that apatite is 5 times as hard as talc. Other measures of hardness, particularly resistance to indentation, are employed by metallurgists. This involves microhardness determination carried out with sclerometers. The technique is quite precise. The procedure involves indentation on an even surface of a mineral by a diamond pyramid of a square section under a certain load, F (in kg). The diameter, d (in mm), of the imprint is measured. The microhardness, H, of the mineral is calculated from the formula $H = 0.7\ F/d^2$ kg/mm^2. The minerals listed according to the degree of hardness to serve as standards in Mohs scale of hardness have been indicated in Table 1.12 which also shows the corresponding microhardness values. The mechanical properties of minerals are of considerable relevance in the mineral comminution processes. The hardness tends to correlate with the weakest of the bonds in the crystal structure, ranging from the Van der Waals bonds in talc, the soft mineral, to the covalent bonds in diamond, the octahedral surfaces of which exhibit the greatest hardness among all minerals. Hardness is of particular importance in mineral dressing because of the wear of the screens, the jaws and the plates of crushers and grinders.

In general, minerals which accumulate under placer conditions must be hard and abrasion-resistant to survive. The same properties are important if minerals are to be concentrated by gravity methods of separation, based on the difference in their densities. Although heavy, soft minerals can be concentrated in gravity plants, losses are high. Gold is an exception; it is not a hard mineral, but it is cohesive and although battered out of shape, does not slime to a fine mud.

The colour is the most obvious and conspicuous external property of a large number of minerals. Minerals are distinguished by an extraordinary variety of colours and shades of varying richness and intensity. Some mineral species are characterised by a constant colour, which enables one to detect them almost unerroneously. Just as an example, mention may be made of a sulphidic mineral of copper, bornite (Cu_5FeS_4). The best identifying feature of this mineral is its purplish-blue tarnish over a bronze colour ("peacock" ore).

Some minerals, on being irradiated or acted upon by other external factors, can radiate light; the ability to do so is called luminescence. In the case of minerals the natural colour

Table 1.12 Hardness of Minerals.

Moh's scale	*Minerals name*	*Mircohardness*
1	Talc $Mg_3[Si_4O_{10}](OH)_2$	2.4
2	Gypsum $Ca[SO_4] \cdot 2\ H_2O$	36
3	Calcite $Ca[CO_3]$	109
4	Fluorite CaF_2	189
5	Apatite $Ca_5[PO_4]_3(FCl)$	536
6	Feldspar (orthoclase) $K[Si_3AlO_8]$	795
7	Quartz SiO_2	1130
8	Topaz $Al_2[SiO_4](F \cdot OH)_2$	1427
9	Corundum Al_2O_3	2060
10	Diamond C	10060

bears no relation to the luminescent color. Depending on the method of excitation, there are several terms that are relevant in the context of luminescence. These are cathodoluminescence, thermoluminescence and triboluminescence. The first refers to excitation by accelerated electrons and is routinely deployed to identify some rock-forming minerals and to map variations of composition in minerals. The second term pertains to light emission from excited energy levels, the excitation being brought about by heating below incandescence. The third refers to light emission induced by mechanical deformation.

The light incident on a mineral surface divides itself in a number of ways. It is partly reflected, partly transmitted, and partly absorbed. Minerals exhibiting metallic bonding have a high reflectivity. Those characterized by ionic or covalent bonding have a high transmissivity. The optical properties are anisotropic; they are different in different directions and depend on the arrangement of atoms in the crystals.

The reflected light from polished surfaces permits ready distinction between many opaque minerals on the basis of brightness, colour, and anisotropy. This feature is very important in the study of ore minerals and host rocks. Transparent minerals (especially in rocks) are commonly studied by transmitted light. In this case, polarized light is passed through thin sections or through fragments mounted in oil.

Electrical conductivity, measured in terms of the specific electrical resistance, ρ, or the specific electrical conductivity, $\sigma = 1/\rho$, represents one of the fundamental physical characteristics of minerals. In the scale of conductivity, the range is from electrical conductors (such as metals) through semiconductors to insulators (such as mica). Minerals endowed with good conductivity have metallic lustre. Most of the transparent minerals have low conductivities. Natural and synthetic mica have found widespread use as insulators. Nonconducting mineral crystals with polar directions may become electrically charged under compression (piezoelectricity) or upon heating (pyroelectricity). These properties of minerals are utilized in technical applications. The uses of quartz piezoelectric oscillators in ultrasonic wave generators, exploited in the navy for the detection of submarines, and of tourmaline pyroelectric crystals in pressure gauges are among the examples that can be cited in this context.

All minerals in some way or the other are influenced by an external magnetic field although the degree of this response varies widely. Based on different response of different minerals in external magnetic field minerals have been classified into different groups that have essentially to development of an important physical separation method called magnetic separation which has been described quite in detail in the next chapter on mineral processing. Present topic is, therefore, not pursued any further.

Radioactivity and radioactive properties are important aspects of some minerals. The term radioactivity in simple terms means the nuclear phenomenon of spontaneous disintegration (accompanied by the emission of alpha, beta, gamma rays) exhibited by certain types of atomic nuclei (usually heavy). Alpha rays consisted of alpha particles. An alpha particle carries two units of positive charge and has a mass of four units; it is nothing but a nucleus of a helium atom. Beta rays consist of beta particles. A beta particle can be negatively (β^-) or positively (β^+) charged and the magnitude of this charge is the same as that of an electron. The same is true of the mass. Gamma rays consist of high energy electromagnetic radiations which are emitted due to nuclear transitions. They are distinct from high energy X-rays which are also electromagnetic radiations in that they originate from electronic transitions outside the nucleus. The alpha and beta emission processes have been summed up in the form of a law called the group displacement law which may be stated thus: the emission of an alpha particle results in the formation of an element which lies two groups to the left while the expulsion of a beta particle results in the formation of an element which lies one group to the right of the parent element in the periodic table. The phenomenon of radioactive decay is closely linked with a ratio of the number of neutrons (n) to the number of protons (p) in the nucleus of any atom. This ratio, n/p has an important bearing on nuclear stability. If the number of neutrons is plotted against the number of protons then a region or zone of stability is obtained. All stable nuclei lie within this zone. A nucleus that lies outside this zone of stability is unstable. A nucleus lying above this zone has an excess of neutrons while one laying below this zone has an excess of protons. Such nuclei tend to achieve stability by adjusting the n/p ratio in such a manner that they are shifted to the stability zone. It follows that where neutrons are in excess the tendency would be to reduce their number and or increase the number of protons and an analogous situation would be obtained in the case of an excess of protons. The resulting radioactive decay is termed natural or spontaneous when naturally occurring nuclei are involved. If the instability is brought about by artificial means in an otherwise stable nucleus then the consequent radioactive decay is termed artificial radioactivity. The law of radioactive decay may be stated in the following manner: if N nuclei of a radioactive element are present in an assembly at time t then the rate at which N decreases, i.e., radioactive decay occurs is proportional to N itself; in other words $-\mathrm{d}N/\mathrm{d}t \propto N$ or $-\mathrm{d}N/\mathrm{d}t = \lambda N$, where the constant of proportionality λ is called the disintegration constant or the decay constant. The half life of a radioactive element whose decay constant is λ is given by $0.693/\lambda$. Natural radioactivity is shared by minerals whose constituents include unstable, radioactive isotopes of uranium, thorium, radium, radon, potassium, strontium etc. Strong natural radioactivity serves as a diagnostic feature of uranium and thorium minerals, for example, uraninite (UO_2), and thorite ($Th(SiO_4)$). Moderate and weak radioactivity is caused by the presence of small amounts of impurities in the form of uranium or thorium isotopes as well as other radioactive isotopes contained, for instance, in minerals such as pyrochlore, samarskite, and monazite. The weak radioactivity of sylvite, microcline, muscovite and other potassium minerals is due to the presence of the radioactive isotope of potassium (K^{40}).

It can be pointed out when a radioactive element decays to yield a new element, this product element may again decay and this process of disintegration and formation of new elements continues until a stable nonradioactive end product is reached. The whole chain of such elements starting from the parent and ending with the final stable product is called a radioactive disintegration series. All the known heavy radioactive elements have been classed into four series, depending upon their mass numbers. These four radioactive series have been named after the member of the series. They are thorium series, neptunium series, uranium series, and actinium series. The elements of the neptunium series are all transuranic elements with very small half life periods (with the exception of neptunium). No member of this series is now found in nature. The end products of each of the other three series is an isotope of lead. This explains the observed fact of lead being present in most of the naturally occurring radioactive minerals. It may finally be added that a radioactive decay reaction differs on several counts from a chemical reaction. The former has its origin in the nucleus, involves large energy changes, does not require any activation, and is unaffected by factors such as pressure and temperature. By contrast, a chemical reaction is extranuclear in origin, involves relatively small energy changes, requires activation for its occurrence, and is, affected by factors such as pressure, temperature etc.

Thermal properties such as thermal capacity, thermal expansion, melting temperature, thermal decomposition and sublimation are all important in considering processes to which minerals may be directly subjected in a pyro way. As for example, roasting or calcination or any pyro pre-treatment of a mineral concentrate is greatly influenced by its thermal properties. The chapter on pyrometallurgy deals with these aspects.

Physicochemical properties and stability of minerals decide many vital processes relevant to their treatment. The solubility of minerals in various media and oxidation–reduction reactions involving minerals and various reagents are all very significant in the technology of mineral raw material processing.

Surface properties such as the absorptional ability and the wettability of minerals are again of significant technical importance. On the wettability scale, as for example, minerals are classified as hydrophilic minerals (which are easily wetted by water) and hydrophobic minerals (which are not wetted by water). Hydrophobicity is very helpful in obtaining enrichment of ores by flotation.

1.6
Mining

Mining essentially comprises extracting valuable rock material (mineral) out of the ground and marketing it at a profit. An economically minable mineral as may be recounted is referred to as ore and the measure used to distinguish ore from waste is the cut-off grade, commonly expressed in terms of metal content (e.g., gold in grams per ton or copper in percent by weight). In most cases, ore is not sold directly by the mine to its customers. To save on transport costs it is usually processed (the processing involves crushing and milling, followed by separation of ore minerals from waste minerals) to remove as much waste material as possible.

Mining methods are grouped into two: surface mining and underground mining. From economical and mine design points of view the controlling factors that influence the choice between the two mining methods are mining cost and ore recovery and dilution. In surface mining, mining cost includes the cost of removing the waste overburden and waste side rock in the slopes of the pit. The ratio of the number of tons of waste that must be moved per ton of ore mined is termed the Stripping Ratio (SR).

$$\mathrm{SR} = \frac{\text{Tons of waste removed}}{\text{Tons of ore mined}}$$

The Break Even Stripping Ratio (BESR) or the economic limit for surface operations in comparison with underground mining is therefore determined as:

$$\mathrm{BESR} = \frac{\text{Underground mining/cost tonne ore-surface mining cost/ton ore}}{\text{Waste removal cost/tonne of waste in surface mining}}$$

The above expression is a simple determination of the viability of surface mining operations. Actually, the calculation involves a number of other factors such as the ore grade; mineral types; direct operating expenses incurred with mining, processing and smelting; initial and replacement capital costs of plant; taxes and royalties; market and capital constraints; and environmental considerations. It may so happen that the viability of the surface mining operation is determined not by the BESR, but by the ore grade. Large, shallow ore bodies with a low SR are generally more economical when mining is carried out by surface methods. Deep ore bodies with high values of the SR, on the other hand, are usually subjected to underground methods.

1.6.1
Surface Mining

Ease of large scale mechanisation for large volume production with enhanced safety and economy has been instrumental to the wide acceptable of surface mining throughout the world wherever the geological, geotechnical, mining, economical and environmental conditions have been suitable. Surface mining has generally been considered to be more advantageous than underground mining with regard to recovery, grade control, flexibility of operation, safety and working environment. There occur, however, many deposits that are small, irregular, steeply dipping, and deeply buried. They cannot be extracted by surface methods. Furthermore, even where mineralisation extends to a greater depth in surface mines, the rapidly increasing volume of overburden required to be removed imposes economic limits beyond which mining must be abandoned or converted from surface to underground mining.

A number of factors control the type, the shape and the size of a surface mine. The principal factors that affect the pit design and the shape of the mine are: geology, grade and localisation of the mineralisation, extent of the deposit, topography, production rates, bench height, pit slopes, stripping ratio, and cut-off grade. The surface mining operations can broadly be classified as: (i) ground preparation, (ii) drilling and blasting, (iii) excavation and loading, (iv) transportation, and (v) storage and reclamation. It is clear by now that surface mining methods are used when deposits occur at or near the surface of the Earth. The different methods of surface mining are placer mining, dredging, open pit mining, strip mining and quarrying. It is only appropriate to refer to mining literature for a detailed knowledge on them. The scope and orientation of the present text do not warrant such inclusion.

1.6.2
Underground Mining

A carefully planned network of shafts, drifts, and raises are the requisites of a producing underground mine. The word development stands for the preparation of this network. In normal development one can recognize four different kinds of rock excavation and they are shafts, drifts, raises and inclines. The main aim of provision of a shaft is to provide access to or a connection with underground. This access may be utilized for a variety of purposes: hoisting rock and ore, personnel and material transport, ventilation, etc. Most modern shafts are circular. The circular shafts are the most popular as they are more stable and easy to line as compared with other shapes such as rectangular or elliptical. The horizontal drifts are used for various purposes: development tunnelling, exploration, haulage etc. A raise serves as connections between different levels with the functions of ore pass, manway, ventilation passage and for stope development. Inclined transport drifts are mainly utilized for: communications and transport of personnel and material between horizontal levels, transport of different equipment between mine areas and workshops underground.

The factors that influence the selection and design of underground mining layouts are: rock mechanics; geological features, engineering design factors, geology, rock structure and geometry. The various mining operations include surveying, drilling, the use of explosives, loading and haulage, hoisting and ventilation and lighting. In underground mining, careful selection must be made of the intervals between different levels and the support systems employed. Mining methods include open stoping, room and pillar mining, sublevel stoping, shrinkage stoping, cut-and-fill mining, sublevel caving, block caving and longwall mining. These mining methods like those of surface mining methods have been extensively described in mining literature and the present text, therefore, does not advance to deal further with them.

1.7
Availability

Sources of metals or the mineral resources are distributed quite non-uniformly over the Earth's surface. No country can claim that it has domestic supplies of all the minerals it needs. The situation and outlook as to the availability of minerals thus varies from country to country and commodity to commodity.

World production of the majority of mineral commodities is steadily increasing. In keeping with technological advancements, the emphasis placed on special metals and materials is much more now than ever before. Concurrently, new developments have opened up new avenues of processing resources to meet the demands. Exploration, improved recovery technology, more efficient use, conservation involving curtailment of unnecessary use and avoidance of waste, recycling and substitution – any or all of these can extend supplies. The limits of these processes cannot be considered to have been reached for any mineral resource. For instance, let the case of fluorine be considered. According to an estimation, the ratio of the identified resources to the cumulative demand globally, in the year 2000 A. D., would be only 0.8. Some relief in respect of this estimation is, however, already in sight. The estimation has not taken into account the fluorine occurring in the identified resources of phosphate rocks, in which it is present in amounts of 3 to 4% and from which its recovery as a by-product is a reality now.

The present indications do not project a progressive scarcity of many minerals on a world wide scale. There are, however, some signs of regional and countrywise depletion. This is particularly true for the industrialised countries. There are examples of such countries which have shifted from being a net exporter to a net importer of many minerals. This situation is not necessarily due to the exhaustion of all exploitable deposits of the pertinent minerals. Rather, it is a consequence of the facts that some of the remaining deposits have not proved to be economically competitive with foreign sources or that these are not sufficient to meet the enhanced demands. Productive deposits of many minerals are becoming more difficult to find. Gold production, as for instance, has fallen inspite of the spiralling rise in its price. New discoveries of gold deposits are still being made. Ultimately workable resources should not to be taken to be limited to those already identified.

There is concern over the possible inadequacy of mineral resources to meet future world needs. There are, however, schools of thought which see no signs of an impending scarcity of minerals. Without debating on these issues, it may be pointed out here that in examining the future availability of minerals, due emphasis must be laid on the rate of consumption as well as on the magnitude of untapped and unmined mineral resources. In the present context it is also relevant to take into account the fact that there is an in-built tendency for the rate of increase in resource consumption to decline or slacken, once recycling starts after the initial uses.

Mineral resources are broadly divided into discovered and the undiscovered categories. Features such as size, quality, characteristics and exact location of individual resources are matters of almost pure speculation for the latter. Undiscovered resources are unlikely to contribute much to the total supply in the immediate future. In the case of discovered resources estimates can be made, with an indication of the degree of reliability, of the timing and the future rates of production on a deposit-by-deposit basis. Using such estimation the occurrence and the likely rate of future availability can be combined in plots such as those shown in Figure 1.18 for discovered resources. Three situations are depicted. The first corresponds to future supply from sources that are reliable, the second to likely sources

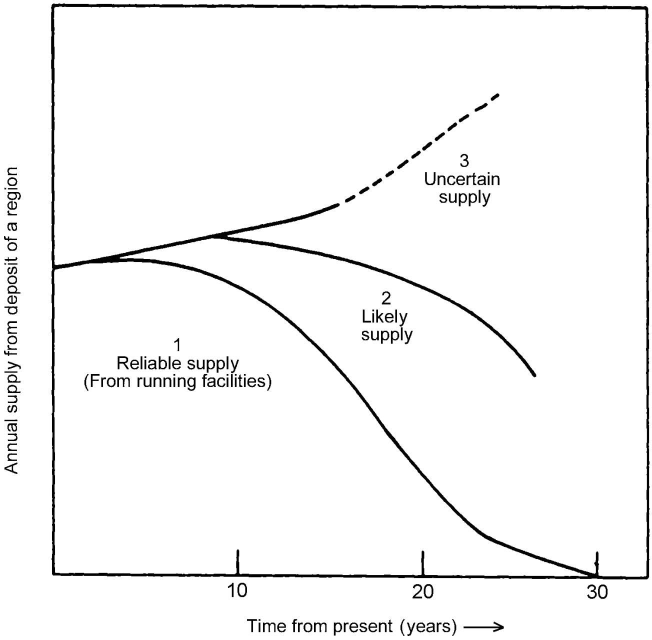


Figure 1.18 Mine supply of a mineral commodity.

that can be reasonably counted upon, and the third to additional sources for which the timing and the supply rate cannot be estimated at present.

1.8
Resource Classification

For obvious reasons it is desirable to obtain estimates of the magnitudes of specific mineral resources – at a specific mine site, in a region, in a country and in the world at large. Diverse terms and classifications have been introduced in the accomplishment of this task. None has so far emerged as to become universally acceptable. The terms, proved, possible and probable, are often used. The equivalent terms measured, indicated, and inferred (corresponding to the designations, proved, possible and probable) have also been used by several government organizations. All these terms are illustrative of attempts to indicate degrees of certainty in resource estimates and have been used with reference to known deposits believed to be recoverable at a profit. Interest has, however, now grown in the quantitative assessment of deposits that are as yet undiscovered or that are not profitably exploitable at present but may turn out to be economic in the future. This has come about as advancing technology has lowered the cut-off grade (the lowest grade of ore that can be mined economically) and has demonstrated the power of exploration in discovering new deposits, and as mineral shortages/depletions have appeared or threatened to appear.

1.9
Minerals Description

A system of minerals classification is presented in Table 1.13. The various classes of minerals are derived and named according to the large anions (simple or complex) that make up the main framework of their structures. There is one exception to this scheme. The class

Table 1.13 Classification of minerals.

Serial No.	*Class*	*Typical examples*
1.	Native elements, metals, semimetals, nonmetals	Gold, silver, copper, arsenic, antimony, bismuth, copper, sulfur
2.	Sulfides	Galena, sphalerite, cinnabar, pyrrhotite
3.	Halides	Halite, sylvite, fluorite, iodoargyrite
4.	Oxides and hydroxides	Cuprite, uraninite, baddeleyite, corundum, haematite, rutile, cassiterite, brucite, diaspore, goethite, limonite
5.	Silicates	Zircon, beryl, thorite, topaz, sillimanite
6.	Borates	Colemanite, borax
7.	Carbonates	Siderite, magnesite, dolomite, smithsonite
8.	Nitrates	Soda–niter
9.	Phosphates	Monazite, xenotime
10.	Sulfates	Barite, anglesite, jarosite, gypsum
11.	Molybdates and tungstates	Scheelite, powellite, wulfenite, ferrimolybdite

known as native elements consists of minerals whose structural framework is constituted not of cations or anions but of electrically neutral atoms. The remaining classes of minerals are named on the basis of the large anion that appears to the right in the formulas. The sections hereunder briefly account for mineralogical aspects of some metals. The account also serves to illustrate the diversity of the mineral sources of metals which chemical metallurgists confront and deal with.

1.9.1
Molybdenum

Molybdenum is not found naturally in its elemental form. It is obtained primarily from the mineral molybdenite (MoS_2), which contains an average 59.9% of molybdenum. It is the only source of molybdenum which accounts for most of the world's molybdenum supply. Processing flowsheet of molybdenum from this commercial source into principal commercial forms is illustrative of the wide and diverse applications of molybdenum and its chemicals (Figure 1.19).

World molybdenum reserves are generally located along the western mountain regions of north and south America, from ranges in Alaska down to the Andes Mountains in Chile.

Major portion of US reserves occur in Alaska, Colorado, Idaho, Nevada, New Mexico, and Utah. In Canada, British Columbia holds the richest reserves of molybdenum. Central and south American molybdenum reserves are found mainly in copper porphyry deposits. Chile's Chuquicamata and El Teniente deposits are two of the largest deposits in the world, and account for 85% of the country's molybdenum reserves.

The five types of molybdenum deposits include: (i) molybdenum and copper porphyry deposits; (ii) Quartz vein and pipes; (iii) Pegmatites and apatites dikes; (iv) Contact-metamorphic rocks and tactite bodies of silica bearing limestone; and (v) Sedimentary rocks containing bedded deposits.

The average crustal abundance of molybdenum is 1 to 2 parts per million. It occurs most readily in conjunction with silica – as the silica content in the igneous rocks goes up, so does the quantity of molybdenum. It is sometimes also found associated with uranium, as well as with coals and petroleum residues. In its host rock, molybdenum tends to occur in thin, tabular, and hexagonal plate forms, or simply as fine specks.

Molybdenum is mined chiefly from molybdenite deposits but is also recovered as a by-product during copper and tungsten mining. Copper deposits generally register grades between 0.02 and 0.08% molybdenite. Molybdenum ore is mined using both underground and open pit mining methods. The USA, China, Chile, Iran, and Canada are the world's leading producers of molybdenum.

As a specific illustration reference may be drawn to molybdenum reserve scenario in the United States. The reserves are mainly grouped under five categories: (i) primary, (ii) by-product of copper ores, (iii) co-product of copper–molybdenum ores, (iv) by-product of tungsten ores, and (v) by-product of uranium ores. These have been presented and briefly elaborated in Table 1.14. It may finally be recorded by way of summary that the present day molybdenum sources in the world today seem to be principally of two main kinds: first, the large-tonnage, low-grade, disseminated type of deposit in which molybdenite is the principal economic mineral; second, the deposits in which molybdenite occurs as a by-product in

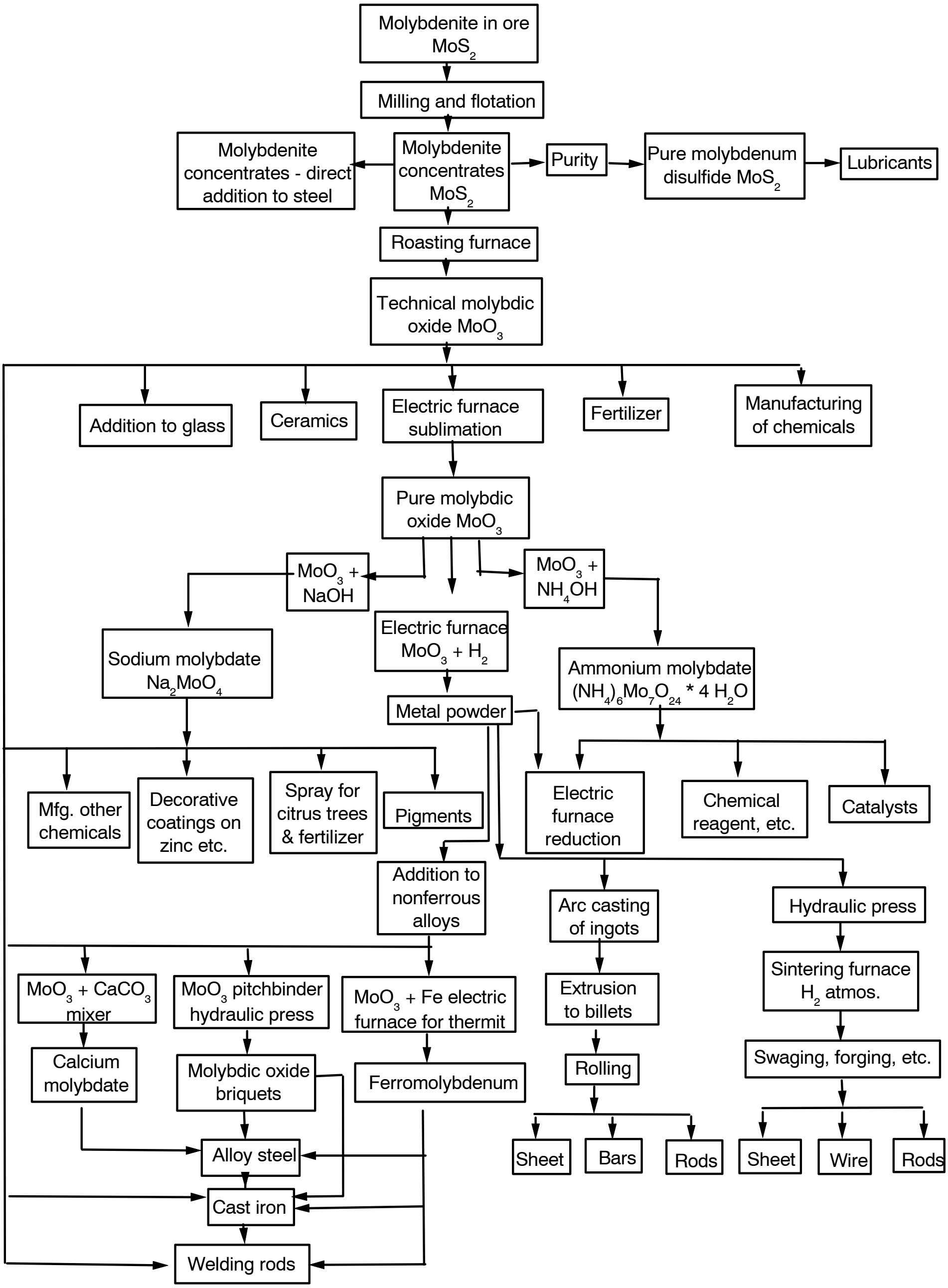


Figure 1.19 Processing flowsheet of molybdenum into principal commercial forms.

Table 1.14 Molybdenum reserves in the United States.

Type of reserve	*Description*
Primary	Mined particularly for the molybdenum contained in the ores. In some instances, molybdenum could be the only valuable metal recovered from the ore. The Questa deposit in New Mexico is mined exclusively for molybdenum content. In other deposits molybdenum may be the main product recovered together with one or more products. In these deposits the molybdenum content alone would allow for a profitable operation. The ore at the Climax mine in Colorado is of this type. Currently, monazite, pyrite, tin, and tungsten are recovered from the ore; none of these by-products exists singly nor together in sufficient quantity so that the ore could be mined profitably merely for the extraction of one or all of these by-products.
By-product of copper ores	By-product reserves of copper ores are those contained in ores that are or would be mined mainly for the copper content. Molybdenum recovery occurs as a by-product or secondary product during processing of the ore for the recovery of copper.
Co-product of copper molybdenum ores	In these ores neither copper nor molybdenum occurs in large enough quantity for the ore to be mined profitably for the extraction of just one. Operation would be profitable when both are recovered.
By-product of tungsten ores	The Pine Creek mine in California is the only operation that is having such reserves.
By-product of uranium ores	The reserves belonging to this category consist mostly of the uraniferous lignites in North and South Dakota.

disseminated porphyry copper ores and also, to a certain extent, in some tungsten and uranium ores. The molybdenum sulfide (MoS_2) content of the disseminated molybdenum deposits is generally in the range of 0.10 to 0.50% MoS_2, in the by-product ores, it is as low as 0.005%.

A section earlier in the present text has made a brief reference to some aspects on mining. It will be of interest to describe as an example the way by which molybdenum mining operation is carried out. Cyprus Amax of Colorado is the world's largest primary molybdenum producer. The company conducts primary molybdenum mining at its Henderson and Climax mines in Colorado, and by-product extraction at the Sierrita and Bagdad copper mines in Arizona. In 1994, half of the production of the company was primary production from the Henderson mine. The Henderson deposit, which was discovered in 1963 beneath the depleted Urad molybdenum mine, is understood to continue to produce primary molybdenum. Primary molybdenite ore is mined at Henderson from a 300 million tonnes Precambrian granite porphyry deposit 3,542 feet below the peak of Red Mountain near Empire, Colorado. It yields roughly 0.4% molybdenite (or between 5 and 8 pounds of molybdenum per ton of mined ore). The ore body consists of an igneous granitic intrusion in which molybdenum has been enriched by several episodes of magmatic differentiation. Both Henderson and Climax are examples of hydrothermal molybdenum stock work deposits, which are characterised by the presence of molybdenum-bearing minerals in the cavities, cracks, or interstices of matrix rock. The panel caving method of mining is utilised at the Henderson mine. Panel caving involves drilling holes into the ore body, loading the holes with ANFO (ammonium nitrate fuel oil) explosives, and blasting away the ore to form extraction tunnels. “Long hole” drilling takes place inside these tunnels. Long holes are drilled in a ring pattern into the walls of the extraction tunnels, and loaded with ANFO. The blasts cause the ore to cave in and fall to the floors of the tunnels. From there, caved ore is packed up and hauled by front end loaders to ore bins that lead down to the railcar receiving level. Henderson’s onsite mill is the world’s largest producer of molybdenum disulfide. Ore is hauled by automated underground railcars that pass through the mountain tunnel at some intervals, crossing the Continental Divide to arrive at the mill site on the surface. The ore is unloaded into a gyratory crusher, in which it is pulverised to rocks to an acceptable size, then delivered to one of four semi-autogenous grinding (SAG) mills. The SAG mills grind the rocks into small particles, which are then sent to a flotation machine to produce molysulfide concentrate.

1.9.2
Nickel

Nickel is a malleable, ductile, tenacious, slightly magnetic, silvery white metal, which conducts heat and electricity fairly well. It is ferromagnetic at ordinary temperatures but becomes paramagnetic at elevated temperatures. Nickel is closely related in chemical properties to iron and cobalt. While sulphidic sources of nickel account for the world’s major nickel supplies, it may be pointed out that lateritic nickel deposits (which essentially constitute an oxidic source of the metal) are more extensive than the sulphidic sources.

Mineralogy on nickel like a good many of others finely illustrate some among the processes that lead to formation of minerals and ores described earlier. Lateritic nickel deposits are essentially heterogeneous mixtures of hydrated iron oxides and hydrous magnesium silicates, each holding low concentrations of nickel and cobalt. These deposits are formed as a consequence of weathering of ultrabasic rocks such as peridotite or serpentine. They are usually found in tropical or subtropical regions, which get a good rainfall. A major constituent of peridotite rock is olivine, a silicate of magnesium and iron, ($(Fe,Mg)_2SiO_4$). This often carries small amounts of nickel because of the fact that the ionic radii of Fe^{2+}, Mg^{2+} and Ni^{2+} are quite similar so that nickel can substitute into the olivine structure in place of either iron or magnesium. So called nickeliferous peridotite typically has about 0.2% nickel, 0.02% copper, 0.2% chromium and 10% iron. Serpentine is altered product of olivine, from which weathering has removed iron, leaving a hydrous magnesium silicate structure.

Nickeliferous peridotites are leached by surface waters that have been rendered acidic by dissolved carbon dioxide and organic acids derived from decomposing vegetable matter. The ground water, containing dissolved iron, nickel, magnesium and silica, moves downwards. Iron quickly oxidises and precipitates from solution near the surface as a hydrated iron oxide, goethite. Much of the cobalt and part of the dissolved nickel coprecipitate with the iron in solid solution in the goethite lattice, giving rise to an iron-rich, nickeliferous mineralization which is usually described as limonitic ore. The remaining dissolved nickel, along with the magnesium and the silica, carry on down through the underlying basic rock. As it runs down, the pH of ground water goes up because of reactions with the bed rock and this results in the precipitation of hydrous nickel–magnesium silicates. These formations are known as garnierites. Since nickel is less basic than magnesium, it shows propensity to precipitate preferentially as the pH goes up and thus precipitated garnierites get enriched with nickel as compared with the source peridotite rock from which the solutions emanated.

A typical lateritic nickel deposit can therefore usually be divided into three distinct zones, which are encountered as one goes down to the depths from the surface. The first distinct zone is nickeliferous limonite zone. This zone resides very close to the surface and consists mainly of goethite α-FeOOH. The nickel-rich, hydrous magnesium silicates (garnierite zone) are found at lower depths just above the bed rock. A transition zone is usually found occurring between limonitic and the garnierite zones. The zone consists of various magnesium silicates. Again, this tends to be very heterogeneous material like the silicates constituting the garnierite zone. Looking at a profile of the variations in composition of a typical lateritic deposit it may be observed that the average concentration of iron steadily comes down with increasing depth, while those of magnesia and silica go up with depth. Cobalt shows tendency to follow iron, with the peak concentrations taking place in the limontic zone. The story of nickel, on the other hand, is that it follows magnesium and silica and is found at peak concentrations in the granieritic zone. A common feature of all the three laterites is that they contain a good amount of water which keeps an important bearing on process selection for nickel since, should a process need a dry feed, considerable amounts of energy must be spent in drying the associated water. As regards the compositional variations in the various zones, it may be seen that with increasing depth the concentration of iron steadily comes down, whereas those of magnesium and silica increase. Cobalt tends to follow iron, with its highest concentration occurring in the near surface limonitic zone. Nickel, on the other hand, follows magnesium and silica and is found at highest concentrations in the garnieritic zone.

1.9.3
Niobium-Tantalum

The mineralogy of niobium and tantalum is complex. Tantalite and microlite are the most common of the tantalum minerals and these are present, to a greater or lesser extent, in most tantalum-bearing ores. Tantalite constitutes the tantalum-rich end of the columbite–tantalite isomorphous series, (Fe,Mn) $(Nb,Ta)_2O_6$. Iron and manganese may substitute completely for each other; likewise, tantalum and niobium. In a similar manner, microlite is the end member of the microlite-pyrochlore isomorphous series, (Na,Ca,Ce) $(Nb,Ti,Ta)_2$ $(O,OH,F)_7$, with mutual free substitution of the three elements within the three components in the parentheses. Niobium occupies the thirty-third place in the order of natural abundance, being present in the Earth's crust at an average concentration of about 20 g t^{-1}. It is more abundant than cobalt, molybdenum or tantalum. The most important niobium mineral is pyrochlore, a compound with the general formula $(Ca,Na)_{2-m}Nb_2O_6(O,OH,F)_{1-n} \cdot x\,H_2O$. The lattice positions of sodium and calcium can also be occupied by barium, strontium, the rare Earths, thorium, and uranium. The latter two elements account for the radioactivity of some pyrochlores. The second important niobium mineral is columbite, $(Fe,Mn)(Nb,Ta)_2O_6$, in which niobium is always present with tantalum. These ores are referred to as columbites if the Nb_2O_5 content is greater than the Ta_2O_5 content; otherwise they are called tantalites. Table 1.15 lists the chemical compositions of various niobium and tantalum minerals. It may be pointed out that carbonatites account for more than 90% of

Table 1.15 Chemical composition of the principal niobium–tantalum-bearing minerals.

Mineral	*Nb_2O_5*	*Ta_2O_5*	*TiO_2*	*Fe*	*MnO*	*SnO_2*
Pyrochlore $NaCaNb_2O_6F$	40 – 65	2	1 – 6	2		
Columbite $(Fe,Mn)(Nb,Ta)_2O_6$	40 – 75	1 – 40	0.5 – 3	10 – 20	2.6	2
Tantalo-columbite $(Fe,Mn)(Ta,Nb)_2O_6$	20 – 60	20 – 50	0.5 – 3	10 – 20	2.6	2
Tantalite $(Fe,Mn)(Nb,Ta)_2O_6$	2 – 40	42 – 84	0.5 – 3	10 – 20	2.6	2
Microlite $Ca_2(Ta,Nb)_2O_6(OH,F)$	2 – 40	42 – 84	0.5 – 3	10 – 20	2.6	2

Table 1.16 Niobium and tantalum pentoxide contents in tin slags from various countries.

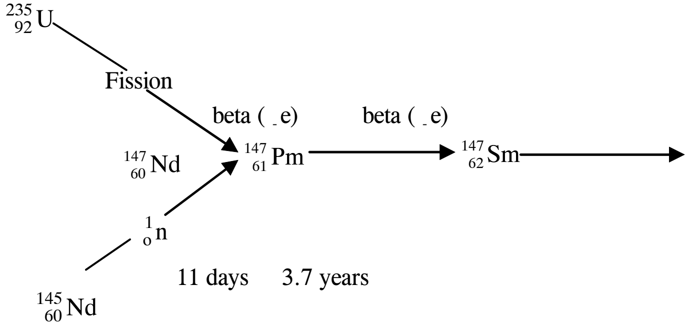
Country	*Nb_2O_5*	*Ta_2O_5*
Malaysia	4	4
Nigeria	14	4
Portugal	7	7
Singapore	3	2
Thailand	8	12
Zaire	5	9

the commercial production of niobium, the pyrochlore group having replaced columbite as the most important source of niobium. Pyrochlore is the only mineral mined for niobium in carbonatites. Niobium may also occur as iron substitution in rock-forming minerals (e.g., perovskite) and as a major element in accessory minerals (e.g., ferrocolumbite, fersmite, niocalite, and wohlerite). A further source of niobium and tantalum is provided by tantalum–niobium slags from tin production, since columbites and tantalites are often associated with cassiterite. The niobium and tantalum oxide contents of various tin slags originating from some leading tin producing countries in the world are given in Table 1.16.

1.9.4
Rare Earths

As pointed out earlier and indicated in Figure 1.1, lanthanum, the lanthanides, yttrium and scandium have been grouped together under the name of the rare Earths. Although not lanthanides, yttrium and scandium, atomic numbers 39 and 21, respectively are included in the family of rare Earths because they invariably occur with them in nature, having similar chemical properties and similar ionic radii. Based on property differences due largely to varying ionic radii, the rare Earths have been broadly classified into two groups: the cerium subgroup comprising lanthanum and the first six members of the lanthanide series (atomic numbers from 58 to 63) and of first seven numbers (atomic numbers from 57 to 63); and the yttrium subgroup comprising the remaining lanthanide elements (atomic numbers from 64 to 71) together with yttrium and scandium. The term light rare Earths is also used to denote the former; likewise, the yttrium subgroup is referred to as heavy rare Earths. The name rare Earths is a misnomer, because these elements are neither rare nor

Earths. The early Greeks believed that everything in the world was made up of four elements: air, Earth, fire, and water. The Earths were substances which could not be changed by heating to the highest temperatures then available to the scientists, and in the early part of the 19th century, when the first rare Earths were discovered, they resembled the common Earths, which were really oxides of magnesium, calcium, and aluminum. Rare Earths are not rare: cerium, the most plentiful, is nearly three times more abundant than lead in the Earth's crust; thulium, the least plentiful, is more abundant than cadmium, silver, gold, or platinum (Figure 1.20). All the members of the rare Earth family, except promethium ($z = 61$), occur in nature. Although this "missing" element in the rare Earth family does not occur in nature, it has been produced artificially from the stable neodymium isotope ${}_{60}\mathrm{Nd}^{146}$ by bombardment with neutrons. The process produces the ${}_{60}\mathrm{Nd}^{147}$ isotope which decays by beta emission to yield (${}_{61}\mathrm{Pm}^{147}$) which is radioactive and has a half-life of 3.7 years. This radioactive isotope decays, again by beta emission, to yield a stable isotope of samarium (${}_{62}\mathrm{Sm}^{147}$). Promethium also results from the beta decay of ${}_{60}\mathrm{Nd}^{147}$ which occurs among the fission products in ${}_{92}\mathrm{U}^{235}$ fission:



Rare Earths are produced primarily from three ores, monazite, xenotime, and bastnasite. Monazite is a phosphate mineral of essentially the cerium subgroup metals and thorium – (light rare Earths, Th)$\mathrm{PO_4}$. The composition of monazite is reasonably constant throughout the world, with almost 50% of its rare Earth content as cerium and most of the remaining 50% as the other members of the cerium subgroup. Xenotime, like monazite, is a rare Earth orthophosphate but contains up to 63% yttrium oxide and also a markedly higher propor-

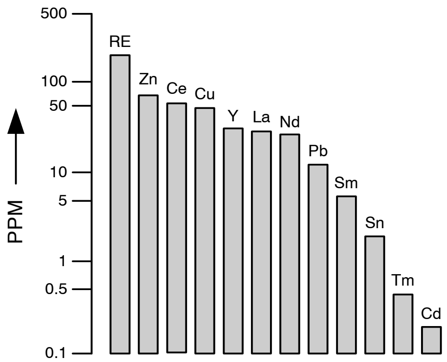


Figure 1.20 Abundance of rare earths and some common metals in earth's curst.

Table 1.17 Analysis of bastnasite, monazite, and xenotime from different locations[a] (Percent of total rare Earth oxide).

Rare Earth	*Bastnasite ($REFCO_3$*		*Monazite ($RE,Y,ThPO_4$)*					*Xenotime ($YREPO_4$)*
	California	*China*	*Eastern Australia*	*Western Australia*	*Florida*	*India*	*China*	*Malaysia*
La	32.00	27.00	20.20	23.90	17.47	23.00	23.95	0.50
Ce	49.00	50.00	45.30	46.03	43.73	46.00	45.68	5.00
Pr	4.40	5.00	5.40	5.05	4.98	5.50	4.16	0.70
Nd	13.50	15.00	18.30	17.38	17.47	20.00	15.74	2.20
Sm	0.50	1.10	4.60	2.53	4.87	4.00	3.05	1.90
Eu	0.10	0.20	0.10	0.05	0.16		0.10	0.20
Gd	0.30	0.40	2.00	1.49	6.56		2.03	4.00
Tb	0.01		0.20	0.04	0.26		0.10	1.00
Dy	0.03		1.15	0.69	0.90		1.01	8.70
Ho	0.01		0.05	0.05	0.11	1.50	0.10	2.10
Er	0.01	1.00	0.40	0.21	0.04		0.51	5.40
Tm	0.02		trace	0.01	0.03		0.51	0.90
Yb	0.01		0.20	0.12	0.21		0.51	6.20
Lu	0.01		trace	0.04	0.03		0.10	0.40
Y	0.10	0.30	2.10	2.41	3.18		3.05	60.80
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

[a] Bastnasite, the world's principal source of rare Earths, is mined as a primary product in the United States (the most notable commercial deposit is at Mountain Pass, Calif.), and as a by-product of iron-ore mining in China. Significant quantities of rare Earths are also recovered from monazite, primarily a by-product of heavy-mineral sands mined for titanium, and zirconium minerals or tin in Australia, Brazil, China, India, Malaysia, and several other countries. Small quantities of rare Earths, especially yttrium, are obtained from the yttrium-rich mineral xenotime, recovered primarily as a by-product of processing tin ore in Malaysia, Thailand, and China.

tion of the heavy rare Earths. Bastnasite is a rare Earth fluorocarbonate, generally represented as $REFCO_3$. The mineral resembles monazite physically and may contain a variety of other elements. Unlike monazite, however, its composition varies from locality to locality and it seldom contains appreciable quantities of thorium. Table 1.17 shows the distribution of the various rare Earth metals in these three resources, along with their major occurrences.

1.9.5
Uranium

Uranium is not a very rare element. It is widely disseminated in nature with estimates of its average abundance in the Earth's crust varying from 2 to 4 ppm, close to that of molybdenum, tungsten, arsenic, and beryllium, but richer than such metals as bismuth, cadmium, mercury, and silver; its crustal abundance is 2.7 ppm. The economically usable tenor of uranium ore deposits is about 0.2%, and hence the concentration factor needed to form economic ore deposits is about 750. In contrast, the enrichment factors needed to form usable ore deposits of common metals such as lead and chromium are as high as 3125 and 1750, respectively.

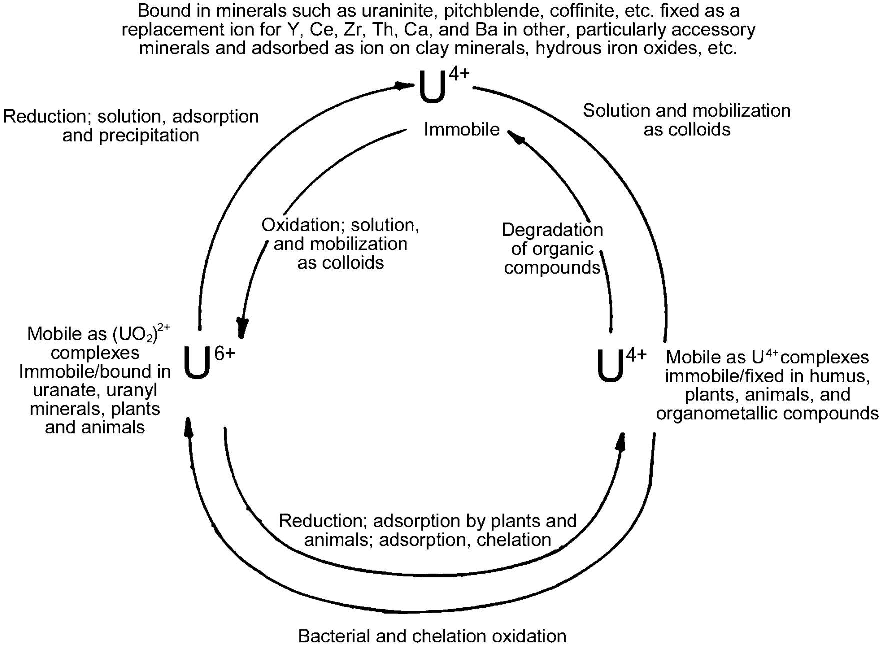


Figure 1.21 Interconversion cycle of tetravalent (U^{4+}) and hexavalent (U^{6+}) uranium in nature.

Uranium is a strong lithophile element and always occurs in nature in combination with oxygen. Though 2, 3, 4, 5, and 6 valence states of uranium are known, geochemically only the reduced form U^{4+} and the oxidized form U^{6+} are important. U^{4+} is stable under reducing conditions and with increase in oxidation potential, it readily transforms into U^{6+}. While U^{4+} is insoluble in water, U^{6+} is readily soluble, forming the uranyl complex ion $(U^{6+}O_2)^{2+}$. This immobile–mobile nature of the two valence states of uranium under reducing-oxidizing conditions is a most important geochemical feature of uranium, unlike its neighbor thorium in the periodic table, and is in fact responsible for the formation of several types of uranium deposits as well as a large number of uranium minerals. The interconversion cycle of U^{4+} and U^{6+} in nature is illustrated in Figure 1.21.

The geochemical cycle of uranium follows the cyclic character of the petrogenetic evolution of the crust of the Earth. The uranium ore concentrations occur in all the three principal environments of geochemical cycle, namely, igneous, sedimentary, and metamorphic, by interconversion from one type to the other as depicted in Figure 1.22. Accordingly, three stages of formation of uranium deposits are identified. These are: (i) primary stage by endogenous magmatic processes; (ii) secondary stage by exogenous sedimentary processes; and (iii) tertiary stage by metamorphic processes.

The geological term, uranium occurrence, implies a naturally occurring anomalous concentration of uranium. The term, uranium deposit, implies a mass of naturally occurring mineral material from which uranium could be exploited at present or in the future. An often-encountered term in uranium mineralogy is uranium ore mineral. It is a mineral having such physical and chemical properties and occurring in a deposit in such concentra-

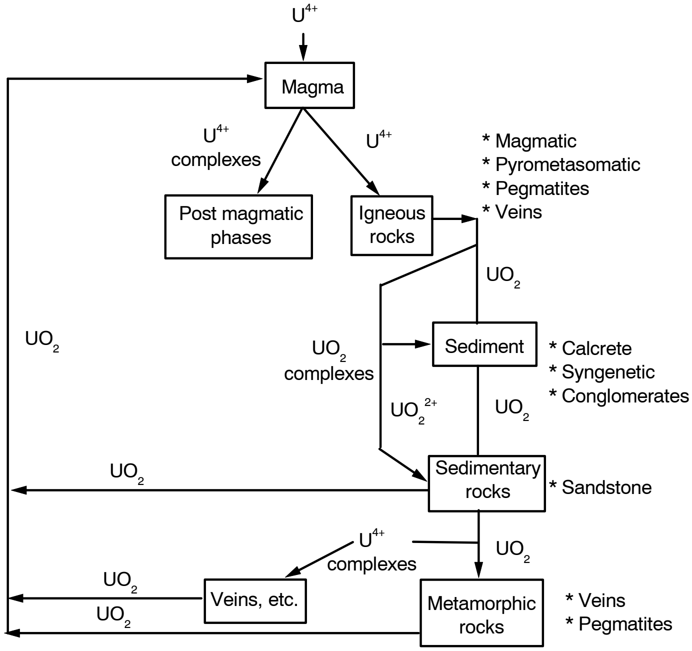


Figure 1.22 Geochemical cycle of uranium showing relationships of ore deposits and most important form of uranium in various parts of the cycle.

tions that it may be used for profitable extraction of uranium, either alone or together with one or more metals.

There are only a few of the many uranium minerals which meet these qualifications, and still fewer in which uranium is the major constituent. It must be appreciated that the uranium content does not of itself, however, speak for its being uranium ore mineral. If the uranium is present in a mineral in such complex combinations with other constituents that it is too uneconomic to extract, or if the mineral does not occur sufficiently to implement extraction worthwhile, that mineral is not to be called a uranium ore mineral. In this manner, the definition for an ore mineral, like that of an ore deposit, depends upon economics and time and upon the values of uranium and the results of future exploration and metallurgical progress. A uranium mineral deposit that is not an uranium ore mineral deposit today may be one in the future. It may, however, be stated that although all uranium ore mineral deposits are uranium mineral deposits, the reverse is not true. This is in fact follows from the general statement that all ore deposits are mineral deposits but the reverse is not true, which stems very obviously from the text on ores and minerals provided in the earlier section. Most of the uranium minerals in pegmatites and placers are refractory. This means that uranium is present in such combinations that they are extremely difficult to break down chemically in order to recover the uranium. The minerals belonging to the refractory group occur scattered sparsely throughout the deposit so that recovery is difficult and expensive. Therefore, even though some of the individual minerals may contain upto 50% uranium, they are not to be addressed as uranium ore minerals.

Table 1.18 Major uranium resources of the world numbered in sequence on the basis of their geological setting and arranged according to their approximate economic significance.

Major uranium resources
(1) Unconformity-related: The ore bodies at Cluff Lake, Key Lake, and Rabbit Lake in northern Saskatchewan, Canada, and those in the Alligator rivers area in northern Australia
(2) Sandstone: The tertiary, Jurassic and Triassic sandstones of the western Cordillera of the United States account for most of the uranium production in that country. Cretaceous and Permian sandstones are important host rocks in Argentina. Other important deposits are found in carboniferous deltaic sandstones in Niger; in Permian Lacustrine siltstones in France; and in Permian sandstones of the Alpine region. The deposits in Precambrian marginal marine sandstones in Gabon have also been classified as sandstone deposits.
(3) Quartz–pebble conglomerate: Commercial deposits are available in Canada and South Africa, and subeconomic occurrences are reported in Brazil and India.
(4) Vein: The dimensions of the openings have a wide range, from the massive veins of pitchblende at Jachymov, Shinkolobwe, and Port Radium to the narrow pitchblende filled cracks, faults, and fissures in some of the ore bodies in Europe, Canada, and Australia.
(5) Breccia complex: The main representative of this type is Olympic Dam deposit in South Australia. Deposits in Zambia, Zaire, and Aillik group in Labrador, Canada, may also belong to this group.
(6) Intrusive: Rossing deposit in Nambia, uranium occurrences in porphyry copper deposits as Bingham Canyon and Twin Buttle in USA, the Palabora in South Africa, deposits in the Bancroft area, Canada.
(7) Phosphorite: Deposits in Florida, USA, and the large deposits in North African and Middle-eastern countries. Uranium is recovered as a by-product from Florida deposits.
(8) Collapse breccia pipe: Deposits in the Arizona strip in Arizona, USA.
(9) Volcanic: Deposits Michelin in Canada, Nopal I in Chichuahua, Mexico, Macusani in Peru and many deposits in China and the CIS.
(10) Superficial: Deposits associated with calcrete occurring in Australia, Namibia, and Somalia.
(11) Metasomatic: Deposits Esphinharas in Brazil, Ros Adams in Alaska, USA, as well as the Zheltye Vody deposit in Krivoy Rog area, Ukraine.
(12) Metamorphic: Deposits at Frostau, Australia.
(13) Lignite: Uraniferous deposits in the Serres Basin, Greece, North, and South Dakota, USA and Melovoe, in the CIS.
(14) Black shale: Uraniferous alum shale in Sweden, the Chatanooga shale in the USA, the deposit of Gera-Ronneburg in the eastern part of Germany.
Others: Deposits in Jurrasic Todilto limestone in the Grants district, New Mexico, USA.

Depending upon lithologic and structural relationship with host rocks, mineralogy, attendant alteration, paragenesis and spatial and temporal constraints, the uranium resources of the world can be assigned to the 15 main categories of uranium ore deposits. They have been shown numerically numbered in sequence in the order of their approximate economic significance in Table 1.18. At present, only 7 can be said to be economically important (see Table 1.19) and these account for more than 95% of the world resources of ura-

Table 1.19 Important types of uranium deposits.

1	***Unconformity related-type (both contact and subconformity-type)***
2	Sandstone-type (tabular, roll front and tectonic lithologic)
3	Quartz-pebble conglomerate-type
4	Breccia complex (U-Au-Cu-REE)
5	Vein-type (disseminated hydrothermal)
6	Intrusive-type (carbonatite, pegmatite, quartz-monazite, etc.)
7	Superficial-type (calcrete etc.)

nium (Figure 1.23). Countrywise (other than Russia and China), distribution of uranium resources of the world is illustrated in Figure 1.24.

A characteristic feature of uranium deposits is their clear time-bound character, showing preponderant concentration during certain periods of the Earth's history. Essentially, five periods of major concentrations are observed; these are 2800–2200 M years, 2000–1500 M years, 1300–1100 M years, 500–400 M years, and 300 M years to recent. Corresponding with these periods, one also sees the concentration of a particular genetic type of uranium ore deposit. Concentration during the period 2800–2200 M years comes from quartz–pebble conglomerate-type deposits, which are detrital concentrations that have taken place during a period when an oxygenated atmosphere was lacking. That in the period 2000–1500 M years is accounted for by paleo-surface and unconformity related vein deposits – these often have spectacular grades, as in the Cigar and Key lake areas of Canada. The concentration during the 1300–1100 M years period comes mainly from the recently categorized breccia-complex type, the main example being the Olympic Dam deposit in Australia, containing an estimated 2 billion tonnes of ore of tenor 0.06% U_3O_8 (1.2 million tonnes of

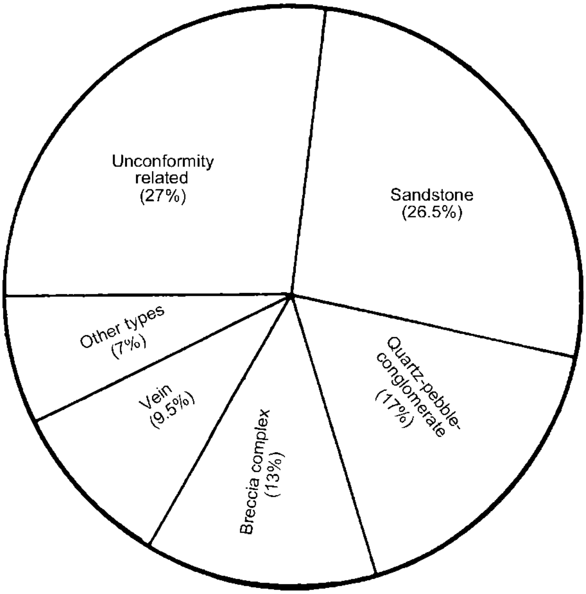


Figure 1.23 Uranium resources – Distribution in major types of deposits.

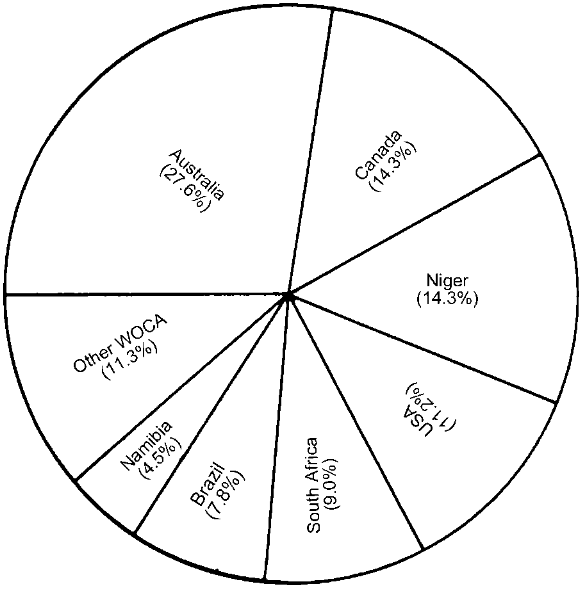


Figure 1.24 Uranium resources – Country-wide distribution (WOCA Countries).

U_3O_8). The concentration during the period 400–300 M years occurs in marine black shales, while that in the 300 M years to recent period is accounted for by sedimentary-type deposits, an important example being the Colorado Plateau deposits of USA.

The polyvalence of uranium and the relatively high solubility of the hexavalent form leads to a large number of minerals containing this element as an essential ingredient. The uranium minerals may be grouped into chemical categories as simple silicates, multiple oxides, hydrated oxides, and hydrated uranyl salts. This mineralogical classification is strictly chemical. From the point of view of metallurgical processing, uranium ores may be grouped into yet another number of general mineralogical classification based on chemical nature of the uranium minerals and their response to leaching or on physico-chemical associations of the uranium and their influence on treatment procedures. These categories are: (i) ores having tetravalent uranium; (ii) ores having hexavalent uranium; (iii) refractory uranium minerals; (iv) associations of uranium and carbon; and (v) phosphates and miscellaneous.

Besides the chemical and metallurgical categories, uranium minerals are usually divided into two main groups – the so-called "primary" and "secondary" minerals. This classification is based on the valence state of the uranium. The term "primary" is assigned to the family of uranium minerals in which tetravalent uranium is the dominant valence state, and "secondary" to that in which hexavalent uranium is the dominant valence state. The primary uranium minerals are generally black or dark brown, noticeably heavy, and often have a shiny or pitch-like luster. Alteration of the oxides by hydration and by chemical reaction leads to a great variety of the secondary uranium minerals, nearly all of which are hydrated. The secondary uranium minerals provide a spectacle of colors. Instead of the physical colors as stated for the primary minerals, they present a collection of brilliant yellow, orange, green, and all of the combinations and in-between shades of those colors. As a group, they are probably more beautiful than the minerals of any other element, and this facilitates their identification in the field. However, prospectors who are inexperienced may frequently mistake them with other colorful minerals, such as malachite (copper carbonate), a copper mineral, to name just one. Some representative examples of primary and secondary uranium ore minerals have been shown in Table 1.20. Most of the world's important uranium deposits contain a significant portion of their uranium in the tetravalent form. The most common mineral containing tetravalent uranium which according to the laid down norms of classification based on valency state of uranium, belong to the category of primary ore minerals of uranium are uraninite and pitchblende (preferably defined as an amorphous, noncrystalline variety of uraninite) as shown in Table 1.20. They are mixtures of UO_2 and UO_3, the ratio depending upon the conditions of formations and changes thereof. The two names are often found as used synonymously in literature. The response of primary uranium ore minerals which, as mentioned, are characterized by predominance of presence of tetravalent uranium which is an important consideration in leaching of an uranium source. Uranium in tetravalent form is virtually insoluble in dilute and in sodium carbonate solutions without an oxidant being present. The uranium source containing uranium, or pitchblende, to leaching is variable. An oxidant is needed, and fine grinding may be necessary to ensure exposure of uraninite to the leaching solution. This is particularly important with carbonate leaching, because alkalis do not attack the gangue minerals enclosing the uraninite. The acid, on the other hand, attacks the carbonates that are commonly intimately associated with uraninite, and this condition facilitates exposing uraninite to the leaching solution. An advantage of fine grinding is that high leaching rates are obtainable during carbonate leaching. The leaching of uraninite in carbonate solution is kinetically slower than leaching in sulfuric acid medium. The secondary minerals have not contributed to any significant extent to the total uranium production todate. However, these deposits are more voluminous and wide ranging than those in the category of primary ore minerals and, as a consequence of all-out prospecting activity their significance is steadily gaining. The most important of secondary uranium ore minerals is carnotite and according to a source it provided at a point of time possibly a sizeable portion amounting to about 90% of the uranium production from secondary deposits. The Colorado Plateau area of the United States was a peer example of deposits of carnotite. There it was identified in 1898 and it has since provided the major domestic uranium production. The chemical composi-

Table 1.20 Some types of uranium ore minerals deposits.

Uranium ore mineral type	***Chemical composition***
Primary (predominantly tetravalent uranium)	
Uraninite	Ideally UO_2
Pitchblende (a variety of uranium)	$UO_{2.2}$–$UO_{2.67}$
Uranothorite	$Th_{(1-x)}U_xSiO_4$
Coffenite	$U(SiO_4)_{1-x}(OH)_{4x}$
Secondary (predominantly hexavalent uranium)	
Carnotite	$K_2O \cdot 2\ UO_3 \cdot V_2O_3 \cdot n\ H_2O$
Torbernite and meta-torbernite	$CuO \cdot 2\ UO_3 \cdot P_2O_5 \cdot n\ H_2O$
Autunite and meta-autunite	$CaO \cdot 2\ UO_3 \cdot P_2O_5 \cdot n\ H_2O$
Uranophane	$CaO \cdot 2\ UO_3 \cdot 2\ SiO_2 \cdot 6\ H_2O$

tion of the source immediately identifies it also as a source for another element, vanadium. This actually proved to be also a source of vanadium and vanadium emerged as a shadow of uranium. So went the history. Carnotite had this legacy as an additional feather in its cap apart from being the principal supplier of uranium from the category of secondary uranium ore minerals. Unlike primary ores, the secondary minerals like carnotites and others belonging to the category contain uranium predominantly in its hexavalent form, this being readily soluble in acids and alkalies without any oxidant being present. An interesting point may be added that, unlike uranium, the number of thorium minerals is small, mainly because thorium does not form secondary minerals.

1.10
Extraction Flowsheets

1.10.1
Features

A general process flowsheet shown in Figure 1.25. It is found to be an assemblage of several unit operations placed in sequence as needed. Though many of the extraction and processing steps are similar for the common and the rare or the less-common metals, there are certain characteristic differences. First, resources of rare metals are usually lean and complex in composition. Some of the rare metals occur only as very minor constituents in ores and in wastes of ferrous and common nonferrous metals processing. Second, while the rare metals resources have complex compositions, the metals themselves must be obtained in a very pure condition. These metals generally show a great sensitivity to the presence of impurities. For example, the mechanical properties of refractory rare metals belonging to groups 4 to 6 of the periodic table are markedly impaired by the presence of interstitial impurities such as carbon, nitrogen, oxygen, and hydrogen. Pure niobium, which is cold-ductile, becomes brittle like pumice stone if its oxygen content exceeds even by some small specified amounts. In the case of rare metals, the maximum permissible concentrations of impurities in the finished product are often of the order of a few thousandths of one percent. Third, the task of meeting the purity specifications of finished metals becomes really difficult, if not impossible, and this factor generally plays against the economics of production. As an example, mention may be made of the separation of chemically similar elements – separation of niobium from tantalum, of rare Earth elements from one another, and of hafnium from zirconium. The elimination of impurities and the production of high-purity metals and compounds are of crucial importance in the technological processing of the rare metals and the relevant raw materials.

Finally, it may be pointed out that none of the rare metals can be smelted directly from the ore. The concentrate must first be converted to a pure chemical compound which is utilized as the raw material for the production of the metal. The refractory rare metals are often obtained in the form of a powder or sponge. They are consolidated and refined by powder metallurgy techniques or by arc melting or by electron beam melting. In fact, the current refractory rare metals technology has been crucially dependent on the development of vacuum metallurgical techniques and processes.

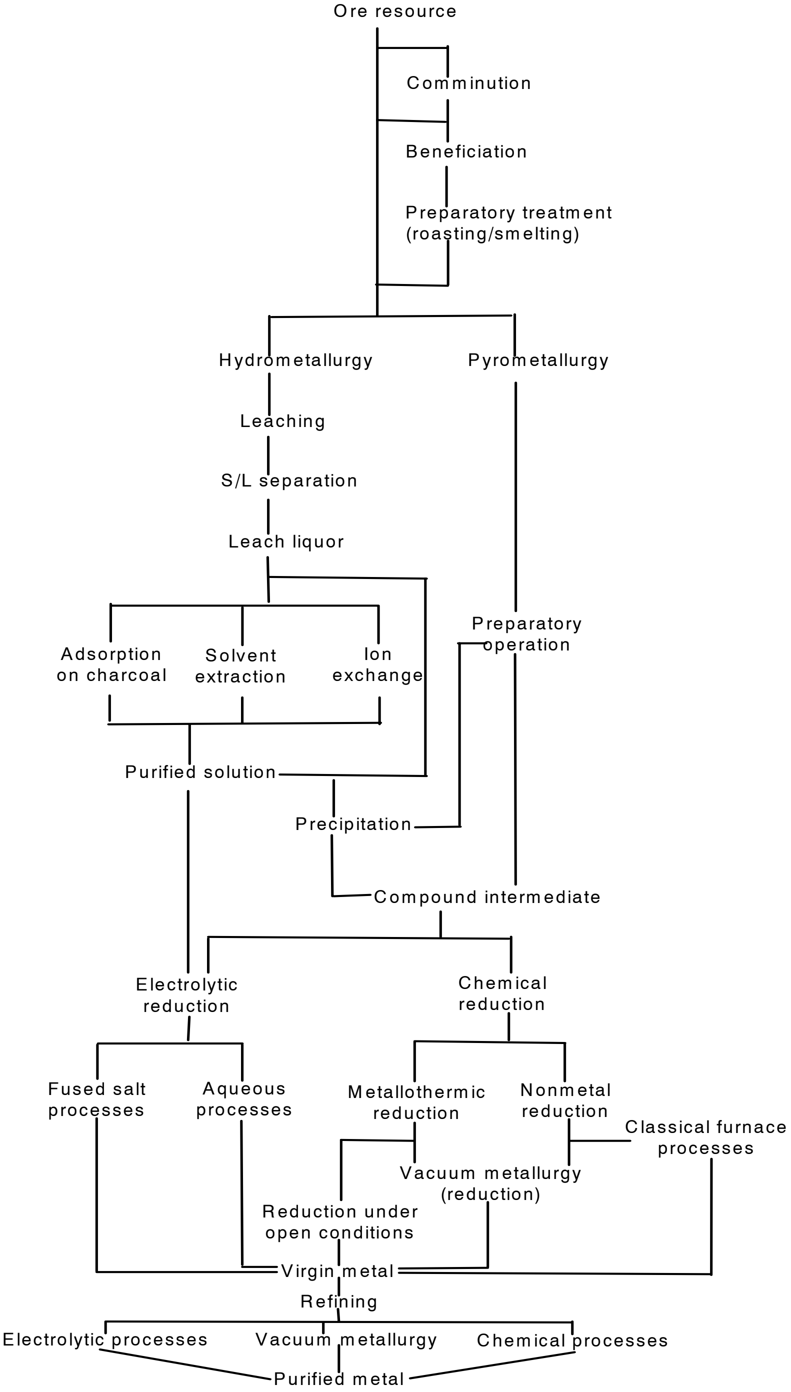


Figure 1.25 General flowsheet outline for extraction of metals.

1.10.2
Process Routes

The process objectives defined earlier must relate to the process routes. A process route essentially consists of several sequential steps with the ultimate aim of achieving the process objective. There are one or more of basic objectives, namely, separation, production of a compound intermediate, metal reduction, and metal refining. With a given starting source material the four basic objectives can be pursued singly or in combination to arrive at the ultimate aim. For example, if the ultimate aim is to prepare a concentrate for the market then it is only the separation that is required for reaching to the product. If, on the other hand, purified metal production is the ultimate aim then possibly all the four objectives have to be fulfilled.

The first step in establishing a process route is concerned with the identification of the source material and its characteristics. With a given source material there can be a number of processed products. It is necessary that these are identified and the market, the product specifications and the value of such products determined. The products of the operation may be concentrates, metal compounds, impure metals or high-purity metals. Following the selection of a particular product, the second step pertains to defining the objectives of the relevant processes. The third step involves the choice of the main processes for achieving these objectives. The fourth step is devoted to choosing the link process steps such that any process in the series has an input and output of materials which are compatible with the preceding and the following processes. In the fifth and final step the process route is further developed and the process characteristics are defined, becoming more detailed in each step. When a process route has been established in detail for a preliminary analysis to be carried out, the exercise is repeated in order that a number of alternative routes can be formulated. When the possible routes for one product have been defined or identified, the various routes for producing the second product, if any, are determined in the same way. After all the possible routes have been considered, a preliminary economic analysis may be carried out.

As an example of the analysis of the existing process routes, reference is drawn to Figure 1.26, which essentially represents a leading commercially important process route for the treatment of a low-grade oxidic copper ore. It is one of the prime examples wherein hydrometallurgy is seen to have played an important role in the field of chemical metallurgy. The first step in this illustration shows that the ore is an oxidic copper ore. The ore grade of the deposit assays 0.5% copper. The final product of the process is to be high-purity copper. The second step, which is concerned with the process objectives, therefore, includes: (i) separation; and (ii) metal production. From a glance at the flowsheet it is apparent that the intention is to achieve the process objectives and the final specifications. It is not intended to implement steps leading to compound formation and metal purification. In the third step, as could be seen from the figure, the key process that has been selected for separation is leaching and that for metal production, electrowinning. The fourth step depicts dump leaching, involving the use of sulfuric acid as the leachant, as the key separation process. The leach liquor so obtained is lean in copper and is impure. It is not suitable in that good grade copper cannot be electrowon from it. The introduction of two link processes, involving desliming the liquor and solvent extraction, produces the correct quality feed for electrowinning. The solvent extraction process not only upgrades the copper con-

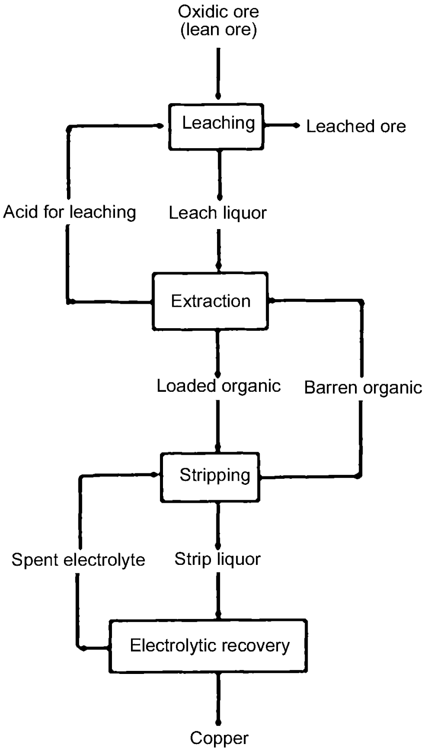


Figure 1.26 Process route for treatment of low-grade oxidic copper ore.

centration of the solution but also extracts copper selectively from the leach solution, discarding the unwanted impurities. It is also found that the process regenerates and recycles the leaching agent used in the key separation process.

As an additional example, the present, the description may be compared to germanium. In the period between 1986 and 1990, the Apex copper mine in southwestern Utah produced germanium as a primary product; gallium was produced as a by-product and small amounts of copper were also produced. This operation was not profitable because it involved high processing costs. A shrinking germanium market caused further injury. Since then, germanium production the USA has remained principally tied to zinc smelting. When zinc concentrates are subjected to roasting and sintering, germanium volatilizes and concentrates in sinter fumes. To recover the germanium, the sinter fumes are leached and the contained germanium is selectively precipitated in sulfide form by fractional naturalization, using hydrogen sulfide or tannic acid. Sodium dichlorate or permanganate is then used to oxidize the germanium sulfide prior to its dissolution in concentrated hydrochloric acid. Finally, germanium tetrachloride ($GeCl_4$) is recovered by fractional distillation. Electrolytic plants in USA are also becoming an important source of germanium. As the presence of germanium has an adverse influence on electrolysis, it is required to be removed from the zinc sulfate electrolyte. Several solvent extraction and ion-exchange processes have come into being to separate the germanium impurity from the electrolyte, which often contains concentrations of germanium adequate for commercial extraction. In Russia and

China, germanium is recovered primarily from coal. When coal is burnt in power plants, germanium gathers in the fly ash produced. In copper–lead concentrates of Tsumes, Namibia, germanium sulfide is sublimed and separated. In Katanga, Zaire, copper–zinc ores having with them germanium are roasted with sulfuric acid and leached; the germanium is then precipitated using magnesium oxide. Regardless of the source of germanium concentrate, further processing of germanium into usable products follows a similar path. Once separated from other metals by fractional distillation, germanium tetrachloride is hydrolyzed into oxide form, and then reduced with hydrogen to produce germanium metal. The different processing stages for the production of several germanium compounds and metal are depicted in Figure 1.27. After germanium concentrates are chlorinated to produce germanium tetrachloride, an oxidizing agent is usually added during primary distillation to suppress the volatility of arsenic. The distillation process is carried out in a glass or quartz receptacle in order to minimize the absorption of metallic impurities, the levels of which must be maintained at less than a few parts per million for most germanium tetrachloride applications. Next, the purified tetrachloride is hydrolyzed using deionized water to produce germanium dioxide, which is filtered and dried. To produce germanium metal powder, germanium dioxide is reduced with hydrogen at a temperature of 760 °C. "First reduction" or "as-reduced" germanium bars are formed by subsequent melting and casting. "Intrinsic" or electronic-grade germanium is produced by zone refining. This particular technique of purification involves melting one zone at one extremity of the germanium bar and progressing the melting process through to the other extremity of the bar. Impurities accumulate in the moving melted zones and become concentrated in the last portion of the bar to melt and solidify; this portion is subsequently removed and reprocessed. However, any contained boron and silicon impurities must be removed from the melt prior to zone refining since this method proves ineffective in removing these metals.

1.10.3
Process Reactors

A reactor is principally meant to bring the reacting species together under conditions in which chemical reactions are favorable, to supply the requisite energy, and ultimately to allow a separation of the reacted product phases. More often than not, the chemical treatment step that occurs in a reactor is the heart of the process. This step can be crucially important to make or break the process, on the basis of considerations of economic viability.

Reactors of various designs abound. Most of them, however, may be classified as belong to certain types, each characterized by some essential features that are common. For example, reactors may be classified as being continuous or discontinuous. A classification can also be made on a functional basis; for instance, there are reactors which are used exclusively for pyrometallurgical operations. Similarly there are reactors for carrying out only hydrometallurgical or electrometallurgical operations. It may, in general, be added in the context of process reactors that they may consist of several smaller units which work either in a series or in a parallel mode and, with the whole set of units functioning together, implement the desired process. As examples mention may be made of flotation cells in mineral processing, of mixer settlers in hydrometallurgy and of electrolytic "winning" and "refining" cells in electrometallurgy.

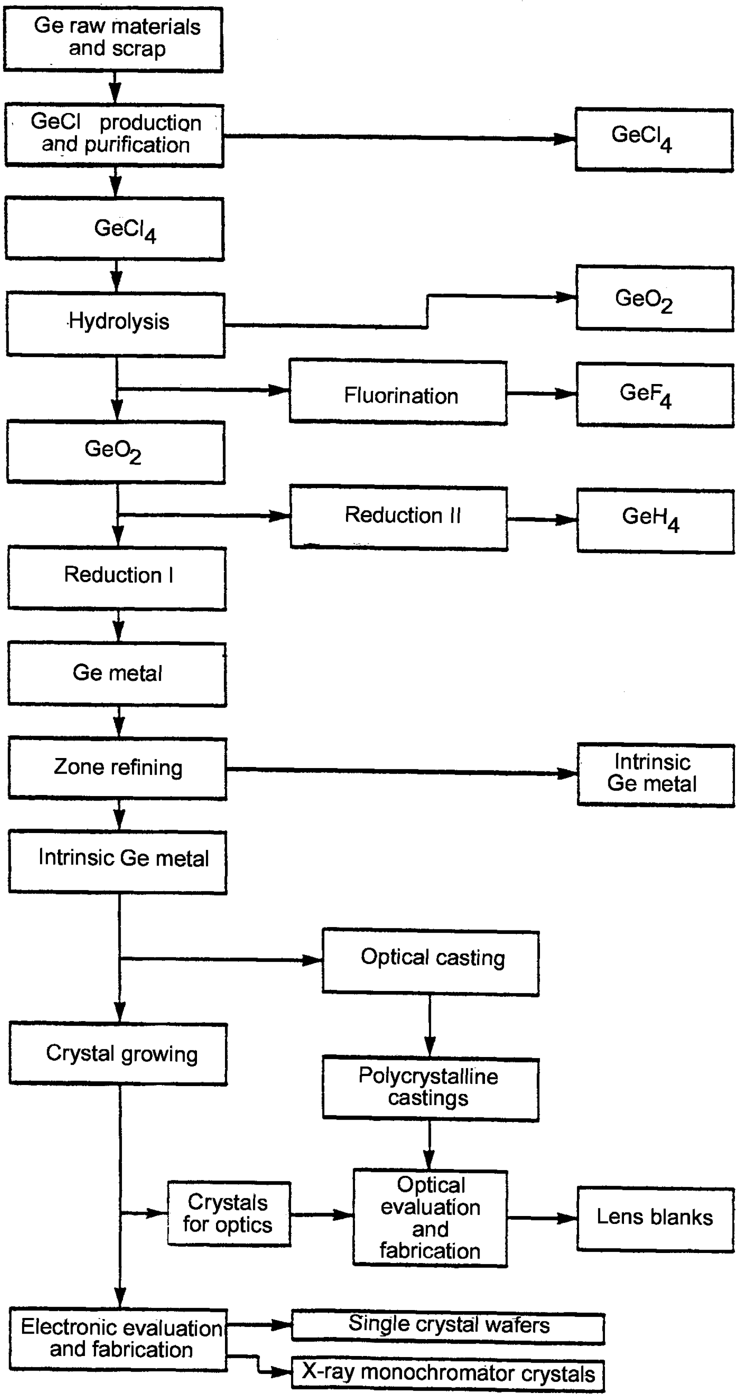


Figure 1.27 Germanium processing flowsheet.

From another view point it can be said that equipment in which homogeneous reactions are effected can be of one of three general types: the batch, the steady-state flow, and the unsteady-state flow or semi batch reactors. The third category includes all reactors that do not fall in the first two categories. The various forms of the semi batch reactor include those in which the volume and the composition change, those in which the volume changes but the composition remains unchanged, and those in which the volume is invariant but the composition changes. The batch reactor is characterised by its simplicity. It needs little supporting equipment and thus has the advantage of flexibility of operation (may be shut down easily and readily). It, however, has the disadvantages of high labour and handling costs, often of high shut down time to empty, clean out, and refill, and of inferior quality control of the product. Taking all these factors into account a generalised statement can be made that the batch reactor is well suited to treat small amounts of material and to produce correspondingly small amounts of the product or to produce many different products from one piece of equipment. The steady-state flow reactor is ideal in those situations where large quantities of material are to be processed and where the rate of reaction is extremely rapid. For these reactor the requirements of supporting equipment are considerable. However, an extremely good product quality control can be obtained. There are essentially two types of the ideal steady-state flow reactors. The first one is variously known as the plug flow, the slug flow, the ideal tubular, and the unmixed flow reactor. These are characterised by the feature that the flow of fluid through the reactor is orderly with no element of fluid overtaking or mixing with any other element behind or ahead. Actually, there may be some lateral mixing of fluid in a plug flow reactor; however there must be no mixing or diffusion along the flow path. The necessary and sufficient condition for plug flow is that the residence time in the reactor should be the same for all elements of fluid. The second type of the two ideal steady state flow reactor types is called the mixed reactor. It is also known by various other terms, the backmix reactor, the ideal stirred tank reactor, or the CFSTR (constant flow stirred tank reactor). As the name suggests, it is a reactor in which the contents are well stirred and uniform throughout. Thus, the exit stream from this reactor has the same composition as the fluid within the reactor. The ore industry avidly uses steady-state flow reactors. The semi-batch reactor is a flexible system, but it is more difficult to analyze than the other reactor types. It offers a good control of the reaction rate because the reaction progresses on the reactants are added. Such reactors are used in a variety of applications extending from laboratory reactors to industrial open-hearth furnaces for the production of steel.

At this stage of presentation a familiarization is provided for the reader with some representative types of reactors which are used for carrying out chemical metallurgical operations. It is also very much in order to indicate at this stage that later chapters contain accounts of different reactors in different fundamental positions.

By way of an example, one may consider the case of hydrometallurgical reactors. Leaching is the most important of the different unit operations, and is prominently placed and assigned due emphasis in a typical hydrometallurgical process flowsheet. A representative list of the various types of reactors used for agitation leaching is given in Table 1.21.

Pyrometallurgy, the dominant process in chemical metallurgy, uses reactor of different types and designs. In terms of the physical states of the reactants, one generally finds that the different reactions carried out in pyrometallurgy include principally, gas/liquid, liquid/

Table 1.21 Reactors for agitation leaching.

Reactor name	*Description*
Pachuca tank	The simplest and most inexpensive device for agitating the pulp. Agitation is achieved by the injection of air under pressure into the bottom of a tall tank. The rising gas draws the surrounding liquid with it to the surface
Low-speed agitators	These are suitable for systems not needing high turbulence. Large-diameter paddles or rakes may be used to mix slurries containing fine material
High-speed agitators	These are suitable for leaching reactions that are limited by diffusion in the leach liquor. An agitator of this type requires a propeller or a turbine to provide high-speed agitation
Agitated autoclaves	These systems are used for leaching under conditions of elevated temperatures and pressures

liquid, gas/solid, and solid/solid reactions. These reactions are implemented in different types of reactors. The classification of reactors or furnaces may be: batch type, continuous type, direct heating type, and indirect heating type. Some of the furnaces used in the main metallurgical operations are: crucible furnace; hearth furnace-open hearth; shaft furnace-blast furnace; converters–Bessemer, side-blown or top-blown (LD); muffle furnace; soaking pits; reheating furnaces; and annealing furnace. Among the other types of furnaces mention may be made of rotary kiln-cement kiln; tunnel kiln; boiler furnace; electric furnaces (three-phase or single-phase, heating done by metallic resistors, or by induction). A broad classification of furnaces based on various factors is provided in Figure 1.28. It may, however, be pointed out that the classification of furnaces does not serve such a useful purpose as classification of the processes that occur in the furnace. Two furnaces may be alike as far as one process is concerned, but entirely dissimilar from the viewpoint of another process.

It is clear that many of the chemical metallurgy processes must be carried out at high temperatures. In this respect, it is necessary to be acquainted not only with the process reactors but also with the methods of heat generation and with the refractories that are needed in the reactors to cope up with the high temperatures attained.

1.10.3.1 **Heat Sources**

Thermal energy for use in the industrial sector is usually generated by the combustion of carbonaceous fuels by air or oxygen or by the conversion of electrical energy. Temperatures up to a maximum of about 1500 °C, which corresponds to the maximum energy available due to the breaking of the chemical bonds in the fuel, can be attained during combustion. When a carbonaceous fuel burns in a process reactor (furnace), heat transfer to the charge occurs by conduction, convection and radiation. One of these modes is predominant, depending on the design of the reactor. Flue gases constitute one of the products of combustion; they are usually at high temperatures, and it is necessary that their heat is recovered before release to the atmosphere. This particular aspect is covered in Chapter 7. However, at this stage it may be pointed out that the amount of air for the combustion of the carbonaceous fuel has to be determined with great care. If an exactly stoichiometric amount

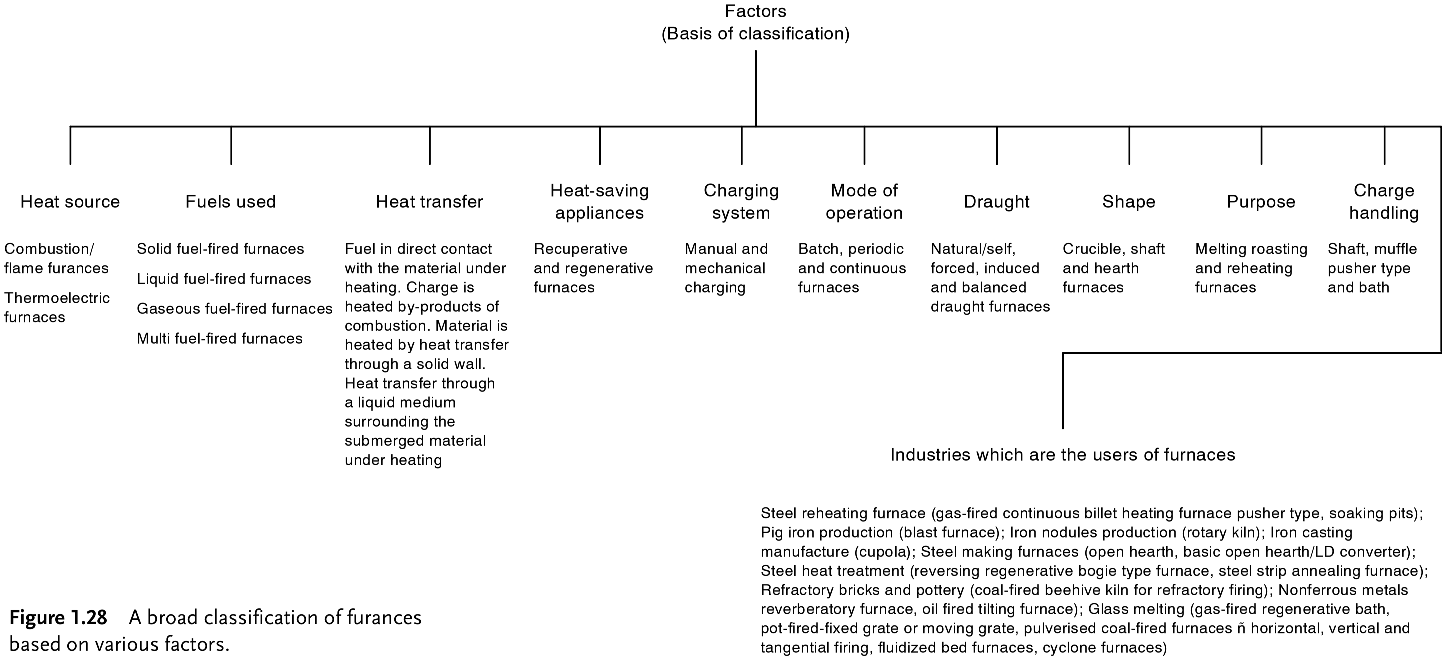


Figure 1.28 A broad classification of furances based on various factors.

of air is used, a fraction of the fuel intended to be burnt inevitably escapes combustion because of the very nature of the reactor and/or the combustion kinetics. The failure to utilize this fraction amounts to some heat loss, and a remedial measure that is usually adopted is to implement the reaction with an excess supply of air. However, the quantity of excess air must be carefully regulated because the introduction of excess air entails some heat loss due to the nitrogen contained in it. There must be compromise between the amount of unutilized fuel saved and the heat lost due to excess air.

Any source of heat energy is termed as fuel. This term embraces all combustible substances available in bulk which may be subjected to combustion or burning by atmospheric air in such a way as to render the heat evolved capable of being economically used for domestic and industrial purposes. The modern concept of fuel is of any chemical or reactant which produces energy in a form that is utilized for producing power is called fuel. The principal factors taken into account in the selection of a particular type of fuel are: (i) suitability to process, (ii) supply position, and (iii) cost. The economical importance of a fuel depends upon: (i) its geographical distribution (whether it is distributed in easily accessible area or not); (ii) the cost involved in its tapping and transport; (iii) calorific value of fuel; and (iv) its combustion or burning quality in air (whether it burns efficiently and without smoke). It will be useful to record as some important characteristics of a fuel as to be called a good fuel the following: high calorific value, moderate ignition temperature, low moisture content, low noncombustible matter content, moderate rate of combustion, combustion products as not to be harmful, available at low cost, associated with ease of handling, storing and transportation cost, should have easily controllable combustion characteristics, should not contain spontaneous combustion features on a account of possibility of fire hazards, storage cost in bulk should be low, should burn in air with efficiency, without much smoke, the size of solid fuel should be uniform to provide an uniform combustion.

Fuels are of three types: solid, liquid, and gaseous. Each category has been further classified into natural, manufactured, or by-product. Natural fuels are called primary fuels, while artificially produced fuels for a purpose or market, together with the products which are unavoidable by-product of some regular manufacturing process, are called secondary fuels. The main raw materials for secondary fuel are generally primary fuels. A list of the important fuels is shown in Table 1.22.

Some general comments may be made of some of the different types of fuels. The use of coal has been on the decline, and there has been an increase in petroleum and natural gas

Table 1.22 Classification of fuels.

General grouping	*Primary fuels*	*Secondary fuels*
	Natural	*Manufactured/by-product*
Solid	Anthracite coal; bituminous coal; lignite; peat; wood	Coke; charcoal; petroleum; coke breeze; semi-coke (low-temperature coal distillate); pulverized coal
Liquid	Petroleum	Tar; kerosene; diesel petrol; fuel oil; synthetic; LPG; gasoline; naphtha; pitch
Gaseous	Natural gas	Producer gas; coal gas; water gas; oil gas; blast furnace gas; coke oven gas; oil refinery gas

consumption. However, they are unlikely to surpass coal as an industrial fuel. Coal is still by far the major fuel for power generation, and it is essential to the iron and steel industries for coke manufacture. It has been supplanted to a great measure by liquid fuels for the generation of motive power by rail roads. It is a major raw material in many chemical plants as a source of carbon, hydrogen, and their compounds.

The growth of petroleum consumption has been quite substantial as a result of increasing demand for its distillation products. As examples, mention may be made of use of gasoline as a motor fuel, of light oil for diesel engines, of distillate and residual oils for industrial and domestic heating.

Natural gas has replaced coal to a great extent for domestic and industrial heating. This is a consequence of installation of very large pipelines from producing to consuming places, the rise in solid fuel price, convenience, cleanliness, controllability and versatility as a fuel. The by-product gaseous fuels, coke oven gas and blast furnace gas are well-known important fuel for the ferrous industry, and require no further elaboration.

An important addition to this list of fuels is electric energy which, when viewed as a source of heat is also identified as fuel. It bears the reputation of the cleanest source of energy. The advantages and disadvantages of the three types of fuels, solid, liquid, and gaseous fuels are presented in Tables 1.23 to 1.25, respectively. The main factors that come under consideration when a fuel or type of fuel is chosen for a particular purpose are presented in Table 1.26. These serve as useful guidelines.

Large-scale generation of electrical energy is achieved primarily by utilizing the kinetic energy of falling water (hydroelectric power plants), by burning carbonaceous fuels (thermal power plants) or by fissioning nuclear fuels (nuclear power plants). Each method of electricity generation has its own merits and demerits. Each, however, supplements or complements the other. There is no competition between the different forms of energy; individually and collectively they serve for the common cause for the supply of energy to fulfill human needs for years to come. The largest share of the electricity produced in most countries comes from thermal power plants. However, the electricity generated by the burning of carbonaceous fuels in these plants is rendered expensive because only about 40% of the total energy available is used, the remainder being lost mainly in the cooling water and the

Table 1.23 Advantages and disadvantages of solid fuels.

Advantages	***Disadvantages***
(1) Easily transportable; (2) Storage convenience, having no risk of spontaneous explosion; (3) Production cost is low; (4) Moderate ignition temperatures; (5) Comparatively less sulfur content and as a consequence leads to reduced atmospheric pollution and corrosion to equipment; (6) Pulverised with associated flexibility of liquid fuels.	(1) High ash content; (2) Low thermal efficiency; (3) Burns with clinker formation; (4) Combustion operation not controllable easily; (5) Handling cost high; (6) Calorific value lower than liquid fuels; (7) A large excess of air needed for complete combustion; (8) Enough storage space needed; (9) Liable to spontaneous combustion and catch fire during storage; (10) Deteriorates on storage causing disintegration and lowering of calorific value.

Table 1.24 Advantages and disadvantages of liquid fuels.

Advantages	***Disadvantages***
(1) Possess higher calorific value per unit mass than solid fuels; (2) Combustion without formation of dust, ash, and clinkers; (3) Firing easier and also fire easily extinguishable by stopping the fuel supply; (4) Easy transportation through pipes; (5) Stored indefinitely, not liable to spontaneous combustion and deterioration on storage like coal; (6) Less excess furnace space; (7) No wear and tear on furnace parts such as those for solid fuels; (8) Stored more compactly than solid fuels; (9) For equal heat output, much less space occupancy and much less weight than solid fuels, (10) Low sulfur oils are next to gaseous fuels in terms of cleanliness and controllability; (11) Usable as internal combustion of fuel.	(1) Costlier than solid fuels; (2) Requirement of costly special storage tanks; (3) Associated with a greater risk of fire hazards, particularly true of highly inflammable and volatile liquid fuels; (4) Requirement of efficient burning, specially designed burners and spraying systems for efficient burning.

Table 1.25 Advantages and disadvantages of gaseous fuels.

Advantages	***Disadvantages***
(1) Carried easily through pipelines; (2) Easy to light; (3) Preheated by the heat of hot waste gases and thereby affording heat economy; (4) Combustion controllable respond to changes in demand like oxidising or reducing atmosphere, flame length, and temperature; (5) Ashless burning without any soot (or smoke); (6) Need no special burners; (7) Being free from solid and liquid impurities they do not adversely influence the quality of metal produced, when used as a metallurgical fuel; (8) Uniformity of air and fuel mixing results in complete combustion without pollution.	(1) Very large storage vessels requirement; (2) Highly inflammability, high fire hazards; (3) More costly as compared to solid and liquid fuels; (4) Explosive and poisonous nature of some fuel gases (e.g., blast furnace gas, converter gas etc.), requirement of careful handling and utilisation

stack gas and also in the electrical transmission systems. There is a major incentive for enhancing the efficiency of electricity generation from the combustion of carbonaceous fuels. Concerted efforts are being made to convert such fuels directly into electrical energy by using devices such as: (i) fuel cells, where the fuel is oxidized in an electrolytic cell to produce electric current directly; (ii) gas turbines, where the hot gas produced due to combustion is used directly to generate electric current in a generator, obviating the necessity of using a boiler; and (iii) magnetohydrodynamic units, in which gases moving at elevated temperatures in a magnetic field generate electric current. In the list of energy sources, solar energy figures strongly. The protagonists maintain that solar energy is clean, safe, free and virtually inexhaustible, and that everyday the sun showers the Earth with several

Table 1.26 Main factors in the choice of type of fuel (takes solid, liquid and gaseous fuels into account in the presentation).

1. The type of heating with respect to size or whether continuous or intermittent operation is involved. In the case of intermittent operation, coal, coke, producer and water gas are obviously unsuited
2. The availability and reliability of supply of fuels in question
3. The price of the fuel delivered to the place where it is needed as some fuels require storage and feeding equipment, as for example, steam-heated lines are necessary in the cases of some heavy fuel oil and some coal tar fuels
4. The efficiency of the heating operation with the chosen fuel. A costly fuel with a high efficiency ultimately is cheaper than a cheap fuel at a poor efficiency
5. The ratio of cost of heating to the cost of finished product. A high-grade, costly fuel needs to be considered in case the ratio is low
6. The undesirable effect factor of fuel of the finished product quality
7. The availability of adequate storage facility for the fuels should be present
8. The chosen fuel should give rise to smokeless combustions
9. The cleanliness and good hygienic working conditions

thousand times as much energy as is used. Even the small amount of energy that falls on the roof is many times that which comes in through the electric wires. In less than three days, the solar energy reaching the Earth more than matches the estimated total output from all fossil fuels. Solar energy, it is asserted, can be used productively to unravel all energy problems. A contrasting view is that, although abundant, solar energy is time-varying and transient. Apart from being available only for about 50% of day, it is also limited by masks of clouds, air pollutants, geographical spots and seasonal changes, and all these call for storage systems. Solar energy is an extremely diffuse source of energy, and the main bottleneck in tapping it lies in converting an erratic, fluctuating energy source into a reliable power supply. Large-scale use of solar power at the present time bears the tag of an expensive proposition and technology must advance in order to solve some of the problems cited here.

In chemical metallurgy, the methods of electric heating in common use are resistance heating, induction heating and plasma heating. Resistance heating is used most extensively and is generally implemented by passing an electric current through the charge with the help of graphite electrodes which may be arranged in different configurations. In the first arrangement electrodes are placed above the charge which may be a metal in the hEarth of a furnace. When an arc is struck sufficient heat can be generated to melt the charge. This arrangement is generally employed for scrap melting and metal refining. An alternative arrangement of the electrodes can be that they are immersed in the layer of slag located above the molten bath. The resistance of this slag layer generates the heat required. This electrode configuration is commonly used during the smelting of ores and concentrates. In yet a third arrangement the electrodes are placed in contact with a solid charge and the necessary heat is produced due to the resistivity of the charge. This arrangement is also used for smelting. In all these arrangements deterioration of the electrodes occurs during operation so that they have a limited life and need periodic replacement. When an electric conductor is subjected to a changing magnetic field an eddy current flows in it and generates heat; this is the principle of induction heating. The magnetic field is produced by passing an alternating current of a suitable frequency through a coil. A plasma which is often referred to as the forth state of matter is essentially comprised of a partially ionized gas which contains molecules, atoms, ions, electrons and free radicals. A plasma is formed at very high temperatures. Plasma can be stated as the source of the steady and the highest continuously controllable temperatures available. In the arc plasma a current (AC or DC) of several thousands of amperes is passed through a gas space located between two electrodes. The lower electrode of the arc has a hole drilled in it, and a gas is forced around the upper electrode and through this hole. During the passage of gas through the arc, the gas is heated up to the arc temperature and forms a high temperature plasma. A plasma can also be generated by induction heating; here, heating is accomplished with a radiofrequency induction coil. A starter carbon rod is first positioned in the center of the coil and heated by induction. After the main discharge is established the rod can be withdrawn. The gas stream transports the ionized gas away from the induction coil in the form of a plasma flame. An advantage of such a system is that there is no requirement for electrodes. Plasma heating has some advantages vis-à-vis heating by more conventional devices. One of these is that very high temperatures can be attained. The plasma is produced in the form of a jet with an extremely hot core and very much cooler peripheral regions. Because of this there is no contact between the hot gases and the container. This is a very advantageous situation in that the need to use a refractory is eliminated and many problems pertaining to contamination are avoided. Since more information about plasma as applied to metal extraction appears in Chapter 4, further elaboration of the subject will not be made at this stage.

Although heating by the combustion of carbonaceous fuels is generally less expensive than electric heating, the latter offers some advantages. These pertain mainly to cleaner operation, smaller volumes of gases handled and feasibility of attaining higher temperatures. There are no combustion gases in an electrically heated reactor. The only gases that may be present are the air that may leak in and the gases that evolve from the charge. It was mentioned earlier that the maximum temperature attainable by the combustion of carbonaceous fuels is around 1500 °C. In contrast, temperatures as high as 2000 °C can be readily obtained in an electric arc furnace. The use of higher temperatures enhances reaction kinetics. It can also promote the volatilization and the consequent separation of some unwanted constituents of the ore which may, at the same time, be valuable by-products. Higher temperatures can also lead to an enhancement in the fluidity of slags. A good example is the partial reduction of ilmenite to produce pig iron and titanium slag. Since no fluxes can be added to this slag in order that it has a high titanium content, its viscosity is unacceptably high at temperatures below 1500 °C. This problem of high slag viscosity is circumvented by using an electric furnace wherein sufficiently high temperatures can be achieved.

1.10.3.1.1 **Solid Fuels**

The most widely used form of the carbonaceous fuels is perhaps the solid fuel, coal. Though occurring basically in the solid form, coal can be converted to both liquid and gaseous forms. In the solid form, coal is basically of two types: charcoal (prepared by carbonization of wood) and mineral coal (obtained from coal mines). Coal is found on every continent, with deposits occurring as far north as the Arctic circle and as far south as Antarctica. Some coal deposits occur off ocean coastlines, but deep underwater deposits have little value at this point of time because they are difficult to mine. Those coal deposits that can be mined profitably are called coal reserves. In most cases, a coal seam must have a minimum specified thickness for mining engineers to classify it as a reserve.

Wood is a domestic fuel used in tropical countries where forests are abundant and other fuels are not easily and cheaply available. The main combustible components of wood are cellulose and lignin, which are compounds of carbon, hydrogen and oxygen. Other minor combustibles are resin and waxes. Wood charcoal which is called simply **charcoal** and was used previously for metallurgical purposes; nowadays it is used almost exclusively for household purposes. It is the carbonization (destructive distillation, i.e., heating in absence of air) process of wood at 600 °C by which charcoal is made. In the process, charcoal is the solid product left after the carbonization of wood, while the hot gases are cooled to separate wood gas and liquid into two layers. The upper layer of the liquid is pyroligneous acid, and the lower layer is wood tar. The former is an aqueous solution of acetone, methyl alcohol, acetone and wood spirit principally. The latter can be subjected to fractionation to extract many chemicals. The carbonization process is carried out in open pits (old method, now out of date), kilns or metal retorts. Pits and kilns are installed in forests, and retorts in factories. Open-pit carbonization involves the burning of wood in large heaps with a restricted supply of air. An inferior quality charcoal with a yield figure of 20% results. The by-products, gases and liquid, are lost to the atmosphere and cannot be recovered. In the kiln process, charcoal (of better yield and quality) is the only product as gases and liquid by-products are not recovered. Carbonization in metal retorts is carried out at a low temperature of 350 °C and also at a high temperature of 1000–1200 °C. The high-temperature operation is mainly carried out for the production of town gas and chemicals besides, of course, for charcoal. A very high specific surface area compared to coal, low ash content and high calorific value may be mentioned as merits of charcoal as a fuel. As demerits, it may be mentioned that charcoal's mechanical strength is very poor. Hence, it is very easily crushed in operation to a powder which is easily swept away in currents of gases, and also it may disturb or prevent the correct flow of gases in the furnace.

Peat is the first stage in the coal formation from wood, and not strictly called a coal. It can at best be termed as the most immature coal. It has come into being as a result of gradual decaying of vegetable matter in moist places. A freshly mined peat has rather a high moisture content, and it needs to be air-dried to reduce the moisture content of $\leq 30\%$ before it can be used. Sun-dried peat having 20% moisture is carbonized (heated in absence of air) to yield tar, gas and peat charcoal. Producer gas is produced by gasification of peat in the presence of steam. The requirement for steam is very low in comparison with coal; this is simply because peat itself has enough moisture content.

The formation of mineral coal is not an instantaneous process, but is an extremely lengthy one, spread over an extended period. Millions of years ago, when the temperature was moderate and rainfall was heavy, vegetation was quite thick, especially in the low-lying areas of the Earth. Coal-forming plants probably grew in swamps, and as the plants died, their debris gradually formed a thick layer of matter on the swamp floor. Over a prolonged period, this matter hardened into a substance called peat. The peat deposits became buried under sand or other mineral matter. As the mineral matter accumulated, some of it turned into such rocks as sandstone and shale. The increasing weight of the rock layers and of the other overlying materials began to transform peat into coal. The various types of coal commonly recognized on the basis of the rank or the degree of alternation or caolification are: (i) peat; (ii) lignite; (iii) bituminous coal; and (iv) anthracite. In this series from peat to anthracite each member is more mature (higher "rank") than the preceding one in the series. Thus, antracites are of higher rank than bituminous and bituminous are of higher rank than lignite, and so on. Anthracites are the oldest coals in most cases, and lignites the youngest. The progressive transformation of peat, which was the first stage in the coalification process of the original vegetative matter, to anthracite resulted in: (i) a decrease in the moisture content, and also in the contents of hydrogen, oxygen and nitrogen, with a corresponding increase in the carbon content; and (ii) an increase in hardness. The highest ranking anthracites contain about 98% carbon while the lowest-ranking lignites have a carbon content of only about 30%. Bituminous coals are by far the most plentiful and the most widely used among the major grades of coals. Anthracites are the least plentiful of the four grades of coal. The selection of the types of coal for various applications depends on several factors, and these have been shown representatively in Table 1.27.

The composition of coal is conveyed by representing its proximate and ultimate analysis. The former implies determination of contents of moisture, volatile matter, fixed carbon, and ash, while the latter implies total carbon, hydrogen, oxygen, nitrogen, sulfur and ash. Here, an account will be provided of the constituents of coal, moisture, volatile matter, ash, fixed carbon, and some miscellaneous components.

A high moisture content of coal is not desirable because: (i) it lowers the calorific value of the fuel; (ii) it enhances the consumption of coal for heating purposes; (iii) it prolongs the time of heating; and (iv) it increases the costs of buying and transporting the coal. There are, however, certain specific cases where moisture is desirable to some extent. Dust remains controlled while handling coal in a wet condition. The moisture decomposes endothermically, and this causes a reduction in the temperature of the hot coal bed (either at the time of its burning on the grate or during the production of producer gas). This helps to reduce fusion and clinker formation, which otherwise would have choked the air passage. Coal dust charged in the coke oven is sometimes sprayed with water. Apart from limiting the dust problems during coal charging, this helps to protect methane and other hydrocarbons present in the coke oven gas from cracking in presence of hot coke and hot coke oven walls. The endothermic decomposition of moisture leads to a reduction in the temperature of coke oven gas as well as that of the coke mass, and thereby its fusion (called graphitization) is eliminated. Moisture always remains in combination with coal, and this is due to its nature, origin and occurrence. On exposure to the atmosphere, the external moisture (also called accidental or free moisture) is expelled from wet coal. The apparently dry coal still holds some moisture which is expelled only on heating above 100 °C. The inherent moisture in coal is called equilibrium or air-dried or hygroscopic moisture and the quantity present depends on the mode of occurrence and handling of coal. The air-dried moisture content of coal lessens with raising rank, from 25% for lignites to a marginal amount of 0.5% for low volatile (15% volatile matter) bituminous varieties. Beyond the marginal amount, however, the value rises to about 3% for anthracites. For coals having a moisture content > 3%, it serves as a useful yardstick of the rank and hence of other qualities indicated by the rank.

Table 1.27 Factors on selection of coal for different applications.

Factors	*General description*
Calorific value	This should be high so that a high heat is obtained from a small quality of coal. This results in reduction of the cost of storage and also handling.
Moisture content	This should be low. It reduces the heating value. In monetary terms moisture is incurring a loss, since it is paid for at the same rate (by weight) as the coal itself.
Ash content	This should be low. It is a noncombustible matter and reduces the heating value of the coal. The presence of ash (like moisture) increases transporting, handling and storage costs. It also involves additional cost in ash disposal. The composition of ash is an important factor since it influences the metal and slag compositions and dictates the selection of the correct flux in metallurgical operations. Besides this, coal fusion temperature is important; this is especially so when coal is meant to be used in boilers. If the constituents of ash are such that there is fusion at the working temperature then lumps of ash (called clinker) begin to form on the fire-grates, and this restricts the primary air supply to the fuel. The coal particles of ash may stick to the boiler tubes, and this may adversely influence heat transfer. Low-melting ash forms low-melting slag, which penetrates the pores of the refractory lining of the boiler. Since the coefficients of expansion and contraction of penetrated ash are quite different from those of refractory lining material, such low-melting slag absorption may cause considerable problems. From there viewpoints it is desirable that the fusion temperature of the ash should be 1430 °C.
Size	This should be uniform or it facilitates both handling and regulation of the combustion process.
Coking quality	This is an important factor for coal selection in the production of metallurgical coke. The coals which upon heating in the absence of air, become soft, plastic and fuse together as large coherent masses, are called caking coals. Consequently, such coals are difficult to be oxidized. If the residue (coke) obtained after heating is porous, hard, strong and usable for metallurgical purpose, the original coal is known as coking coal. Thus, all caking coals are caking, but all caking coals are not essentially coking coals.
Sulfur and phosphorus content	Coals should assay low in these harmful impurities as they have adverse effects on the properties of the metal. Moreover, gases produced from sulfur- and phosphorus-bearing coals are corrosive to equipment and pollute the atmosphere.

Certain gases such as CO, CO_2, CH_4, H_2, N_2, O_2, and hydrocarbons exist in the coal and are expelled during its heating period. These are the volatile matter of the coal, and the coal with higher volatile matter content ignites easily (it has low ignition temperature), burns with a long smoky yellowish flame, has a lower calorific value, will provide a greater quantity of coke oven gas when subjected to heating in the absence of air, requires a larger furnace volume for combustion, and possesses a higher tendency to catching fire when stored in open space. It may be pointed out that the moisture in coal is not included in the volatile matter. However coal does contain water that is produced from its the hydrogen and oxygen content during the decomposition.

Ash is the product of combustion of mineral matters associated with coal. It consists principally of silica, alumina, and ferric oxide with variable amounts of other oxides such as CaO, MgO, and Na_2O. A high ash content is in general not desirable. A coal with high ash is harder and stronger, has a lower calorific value, and generates a more slag in the blast furnace when coke prepared from it is used. Coal holds inorganic mineral matters which are transformed into ash by chemical reactions occurring in the combustion of coal. The ash and mineral matter of coal are therefore not to be construed as being the same. The ash content of the coal is reduced by washing. The coal ash may be the source of minor elements such as germanium. Fly ash produced from coal-based thermal power stations is useful in many ways, including, in the production of cement, concrete bricks, filling material, and light-weight aggregates.

The pure carbon that occurs in coal is fixed carbon, and the higher the content, the greater the calorific value of the coal. Total carbon implies the fixed carbon plus the carbon present in the volatile matters (in CO, CO_2, CH_4, and hydrocarbons). The total carbon content is thus always higher than the fixed carbon in any coal. A high total carbon-bearing coal will be characterized by a high calorific value.

Apart from carbon, it is of interest to refer to other elements present in the coal and their consequences or significances. For example, hydrogen, which is associated with the volatile matter of the coal, increases its calorific value. In addition, a higher hydrogen-bearing coal produces a coke oven gas with more NH_3; this NH_3 is recovered as ammonium sulfate that can be used as a fertilizer. The nitrogen in coal is present up to 1–3%, and stems from the proteinaceous matter present. The presence of inert nitrogen reduces the calorific value of the coal. However, upon heating the coal in absence of air, its N_2 and H_2 combine to yield NH_3 which is in turn recovered as ammonium sulfate. Sulfur, through its presence (mainly as sulfides) causes an increase in the calorific value of the coal, but confers several undesirable effects. The oxidation products of sulfur, SO_2 and SO_3 (especially in presence of moisture) cause corrosion of equipment and atmospheric pollution. The presence of sulfur is not at all desirable in metallurgical coal used in iron and steel making as it adversely influences the properties of the iron and steel produced. It is responsible for cracking of the steel surface during hot rolling (hot shortness of steel). As regards oxygen, the less said the better as it reduces the calorific value of coal. While the mineral matter or ash, hydrogen, nitrogen, sulfur contents bear no relation to the rank of coal, oxygen and carbon contents have a close relation to the rank. While the carbon content of coal increases with the increase in rank, the oxygen content decreases. Like sulfur, another element, phosphorus, is undesirable in metallurgical coal as it causes cracking of the steel surface during cold rolling (cold shortness).

Coals are classified based on various parameters such as proximate analysis, calorific value, maturity (rank), ultimate analysis, and caking properties. Coal is a heterogeneous mixture of organic mass, mineral matters and moisture in uncertain proportions. The organic mass, being heterogeneous, comprises many microcomponents, and this implies that coals of the same ultimate analysis do not necessarily have the same properties, while coals of different compositions may in some respects behave similarly. The amount and composition of mineral matters in coal varies widely, and this greatly affects the properties of the entire coal. The quality and quantity of the microcomponents vary from coal to coal. For these reasons, it has not been possible to evolve universal classification system of coal, and many coal systems exist. The rank of coal (which is the most important variable in the nature of coal) is decided by its volatile matter, calorific value and carbon content, singly or in combination. This classifies the coal broadly into groups such as lignite, bituminous and anthracite, and these are regarded as satisfactory for most practical purposes.

Table 1.28 Some salient features of low-temperature carbonization (LTC)and high-temperature carbonization (HTC).

Low-temperature carbonization	***High-temperature carbonization***
The process is conducted at 700 °C. It yields semi-coke, which is popular as a smokeless domestic fuel. It can at times be used in boiler also to avoid smoke. Yield of coke oven gas is less, of tar high, and of ammonia less. Calorific value of coke oven gas generated is more. The process produces aliphatic natured tar. Following carbonization the coke discharging process is difficult as it swells extensively but does not shrink much upon carbonization. Free carbon in tar (produced from the cracking of hydrocarbons) is less; Coke produced is weaker. Volatile matter in the coke produced is more. Hydrogen content in the coke oven gas is less.	The process is implemented at 1000 °C. It yields metallurgical grade coke which is used widely in blast furnaces and cupolas. Yield of coke oven gas is more, of tar less, and of ammonia more. Calorific value of coke oven gas generated is less. The process produces the tar which has more aromatic ring compounds. Following carbonization, discharging is far more easy as the final stage of the process is associated with shrinkage. Free carbon in tar is more; this stems from more intense cracking of hydrocarbons. Coke produced is stronger. Volatile matter in the coke produced is less. Hydrogen content in coke oven gas is more.

The production of coke involves the heating of coal in the absence of air, called the carbonization or destructive distillation of coal. Carbonization, besides its main purpose of production of coke, also results in a coproduct called coke oven gas from which various liquid products such as tar, benzol, naphthalene, phenol, and anthracene are separated. There are two main types of carbonization based on the temperature to which the coal is heated in the absence of air. One type is low-temperature carbonization (LTC); the other is high-temperature carbonisation (HTC). Some features of LTC and HTC are listed in Table 1.28. The LTC Process is mainly carried out to manufacture domestic smokeless fuel. This presentation, however, concentrates on the HTC process by which metallurgical coke is produced.

The production of coke from coal is an important activity in the ferrous metallurgical industries. While coal serves as the principal source for coke, a second source, namely, heavy petroleum fractions, is especially important for countries which have large petroleum resources and lack coal deposits. The properties of metallurgical coke are listed in Table 1.29.

Not all types of coal can be utilized to produce coke. The coal which first softens and then solidifies into a strong coke, when heated to a temperature close to its decomposition temperature of about 1000 °C in the absence of air, is coking coal. A coal which is non-coking yields a powdery char when carbonized in the manner described. Coking coals that contain not more than 1.25% sulfur and 80% ash, as mined or following coal-washing, are known for metallurgical uses. Depending upon their volatile matter contents, metallurgical-grade coking coals are further classified into high-volatile coals (the most common type contains about 35% volatile matter) and low-volatile coals (contains about 17% volatile matter). A single type of coal, even if it is of metallurgical grade, is seldom used alone for coke production. Low-volatile coals swell and tend to damage the walls of the reaction chamber, while the high-volatile ones yield cokes of inferior physical properties. Therefore, coals are normally used in blends of composition (e.g., 80% high-volatile coals and 20% medium or low-volatile coals).

Table 1.29 Properties of metallurgical coke.

Purity	It should have moisture, ash, sulfur and phosphorus contents as low as possible.
Porosity	It should be porous as this facilitates oxygen contact with the carbon of coke. A factor most important for accomplishing complete combustion at a high rate.
Strength	It should be compact, hard and strong to withstand abrasion as well as overburden pressure in the furnaces.
Size	It should neither be too big nor too small. Uniform heating is not obtained with large size.
Cost	It should be cheap and easily available near the plant site so that transportation cost is low.
Reactivity	It should not be too reactive. Reactive cokes do not produce intense heat.
Combustibility	It should burn easily.
Reactivity to steam	It must be reactive to steam, a requisite if used for water–gas production.

There are two methods for manufacturing metallurgical coke by HTC, and these are known as the beehive process, and the by-product or the retort process. The **beehive process** involves the use of beehive ovens. The earliest metallurgical cokes were produced in the now obsolete beehive oven, is shown in Figure 1.29 (A). Coal was charged into the hot oven through a hole in the roof, and formed a layer. The volatile matter was burnt inside the chamber by air admitted through the partially bricked-up door, and provided the heat for carbonization of the coal. When carbonization was complete, the coke was quenched with water and raked out, leaving the furnace hot enough to start the carbonisation of the next charge. The merits and demerits of the beehive oven practice is given in Table 1.30.

The **by-product process** involves essentially by-product coke ovens which can be the waste heat ovens or regeneration ovens. They are designed to produce coke as well as to recover the products of carbonisation. The ovens are narrow rectangular refractory chamber. The ovens are heated from both sides through vertical flues. The necessary heat is produced by burning gases inside the narrow flue chambers. The ovens are the coking chambers and

Table 1.30 Merits and demerits of beehive oven practice.

Merits	***Demerits***
Produces strong, blocky coke having good reactivity. Involves low capital and running costs. Production process delinks with availability of markets for byproducts. Allows shut down without any detrimental effects to refractory. Produces hard coke for foundry. The process is characterized by simplicity. There involves no requirements of extra fuel for heating as in by-product oven practice.	There is no by-products recovery. Yield of coke is lower as a result of partial combustion of coal. The process cannot be used to produce good coke from blends of inferior coals. The process lacks in flexibility in operation. The process needs a large coking time of about 2–3 days.

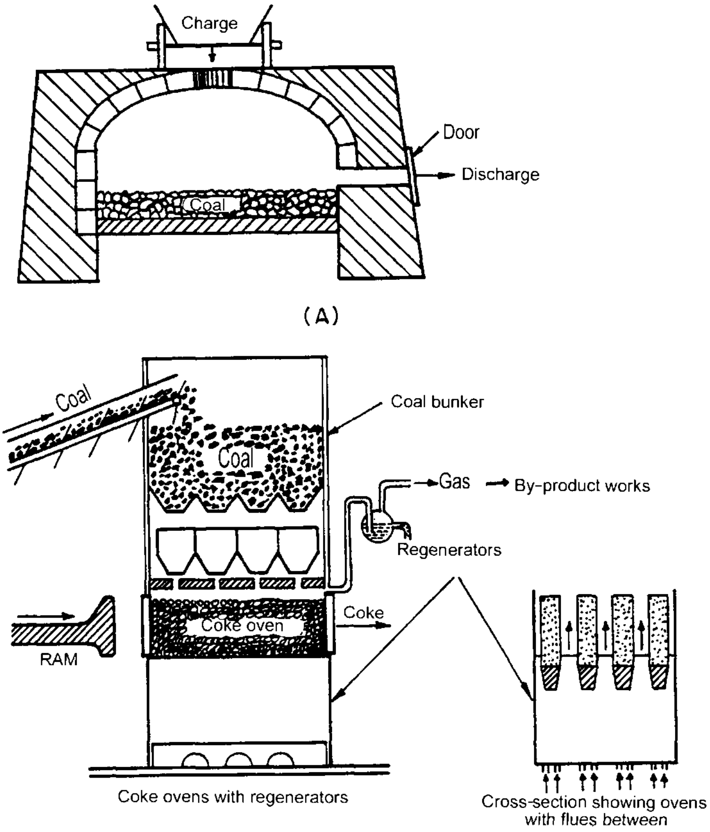


Figure 1.29 Coke production processes. (A) Beehive oven; (B) by-product coke oven.

the flue chambers are the heating chambers. A number of ovens (up to 100) constitute what is termed a "battery" of ovens in which coking chambers alternate with heating chambers so that, in effect, there is a heating chamber on each side of every coking chamber. The regenerators for heat exchange between the hot flue gases and combustion air are placed below the heating and coking chambers. Thus, the three main parts which carry out the by-product process of coke production are the coking chambers, heating chambers and regenerators. The coking coal blend is introduced into the coke oven chambers from the top by the charging car and continuously leveled. Following completion of the charging operation, the charging holes are closed. Each pair of ovens, which is separated by a system of vertical flues, can be heated by producer gas, coke oven gas, or blast furnace gas. Air needed for combustion is preheated in regenerators. Blast furnace or producer gas, provided for heating, can also be preheated, but coke oven gas is not preheated as hydrocarbons (mainly methane) present in it crack, giving rise to deposition of carbon soots on regenerator walls and adversely influencing heat transfer capacity. Carbon soot may also choke the small-diameter burners in the heating chambers. Coke oven gas is, therefore, not preheated but burnt in preheated air. Each heating chamber is provided with two regenerators. While the waste gas (flue gas) passes through the one set (thereby heating its bricks), the flue gas (blast furnace gas, producer gas, etc.) and air is heated in the other set before allowing them to perform their functions in coke production. Flue temperature in the heating chamber is maintained at about 1200–1300 °C. The carbonization time for a 22-ton coal charge varies from 16 to 28 h, depending on the width of the oven. The oven walls are made of silica bricks, the high temperature strength of which ensures a long life and enables the walls to be constructed thin for a high heat transfer rate through them. At the end of coking, the doors on both sides of coke ovens are opened and the pushing ram pushes the red-hot coke into the quenching car. The coke oven wall is tapered from the pusher's side. The side of the coke oven where the pusher machine works is known as ram side or pusher side, and the other side is known as coke side. The ovens are narrower on the ram side, and the taper is provided to suit the expansion or shrinkage properties of the coal to be coked. During carbonization the coal swells at first but shrinks as the temperature rises. This exerts some pressure on the walls and the oven should not be pushed until the coke has shrunk clear of walls. Hence blending of coal charge is done in order to limit its swelling. The ram pushes a more or less solid wall of coke from the coking chamber into a larger quencher car and thence to a central quenching wherein water is sprayed liberally to cool the coke rapidly. Quenching is carried out so that sufficient heat remains at the center of the coke lumps to dry excess surface water, such that not more than about 2.5% moisture is contained in the final product. It is then made ready to use after sizing in crushers and screening. The wet quenching operation, on account of its being a source of air pollution, has largely been replaced by a dry method in which cooling is accomplished by recycling an inert gas such as nitrogen. The dry process also allows the recovery of sensible heat which can be used for steam generation. The coke obtained by dry quenching is free from moisture, and the generation of fines which is popularly known as coke breeze is greatly reduced in comparison with the wet process. A simplified sketch of the Otto Hoffmann by-product oven is shown in Figure 1.29 (B).

In the context of coke manufacturing processes the recovery aspects of coal chemicals constitute an important consideration. During carbonization about 20–30% (by weight) of the initial charge of coal is evolved as mixed gases and vapours which come out of the ovens and pass into the collecting mains; these are processes to produce coal chemicals. The coke oven gas contains the fixed gases. These are hydrogen (H_2), methane (CH_4), ethane (C_2H_6), carbon monoxide (CO), carbon dioxide (CO_2) and illuminants which are essentially unsaturated hydrocarbons such as ethylene (C_2H_4), propylene (C_3H_6), butylene (C_4H_8), and acetylene (C_2H_2). Also present are hydrogen sulfide (H_2S), ammonia (NH_3), oxygen (O_2), and nitrogen (N_2). Some other substances in the raw gases and vapours leaving the ovens, which are liquids at ordinary temperatures, include ammonia liquor, tar and light oil.

The coke oven is treated in the by-product plant to recover some important chemicals from it, after which the coke oven gas is used as gaseous fuel in the furnaces of steel plant. Coke oven gas is emitted at about 700 °C and is cooled to 80 °C with ammoniacal liquor (NH_4OH) by spraying its goose neck. Here, the tar from the coke oven gas is condensed and separated in the separator. A further cooling of the gas to about 30 °C is accomplished in the primary cooler by water, and a further quantity of tar is condensed. The last traces of tar vapour present in the gas are removed in the next operation, which involves bringing the cooled gas to the electrostatic tar precipitator. This sends the tar-stripped gas to the exhauster, which is essentially a turbo-blower sucking gas from the coke oven and discharging a high pressure. The gas discharged by the exhauster is reheated at 60 °C and bubbled through sulfuric acid in the saturator in which the ammonia associated with the coke oven gas reacts with sulfuric acid and forms ammonium sulfate. The gas from the saturator passes to final cooler and is cooled to 25 °C by water. The cooled gas is treated with wash oil in the naphthalene scrubber where naphthalene associated with the coke oven gas is removed along with benzol. The coke oven gas is then separated into three streams. One stream is passed through a bed made up of mixture of iron dust and saw dust which removes the sulfur compounds of the coke oven gas. The desulfurized gas is used for hot scarfing of slab in the slabbing mill to remove oxidized surface steel slabs. The second stream is further treated in another set of electrostatic precipitator called Return Electrostatic Tar Precipitation (RETP). This gas is used for heating the oven battery. The third stream is used as an admixture to the blast furnace gas for use as a fuel gas in some of the steel plant furnaces such as reheating furnace soaking pits, thermal power plant boilers, blast furnaces stoves, foundry ovens, and ladle dries.

To continue with the by-product recovery process, particular reference may be drawn to the coal tar fuels recovered. Coal tar is a black to brown oily and viscous fluid of characteristic odour. The fact that tar is a store house of chemicals leads to it being discouraged directly as a fuel. In order to recover some of the chemicals associated with coal tar it is subjected to distillation. Typical tar composition: pitch, 64.8%; creosote oil, 28.3%; naphthalene, 4.3%; phenol, 0.3%; anthracene, 0.3%; benzol,1%; other light oil, 0.7%. A flow diagram of recovery of various chemicals, fractions, yields and boiling ranges from coal tar distillation is shown in Figure 1.30. It is clear from the figure that the main constituents of

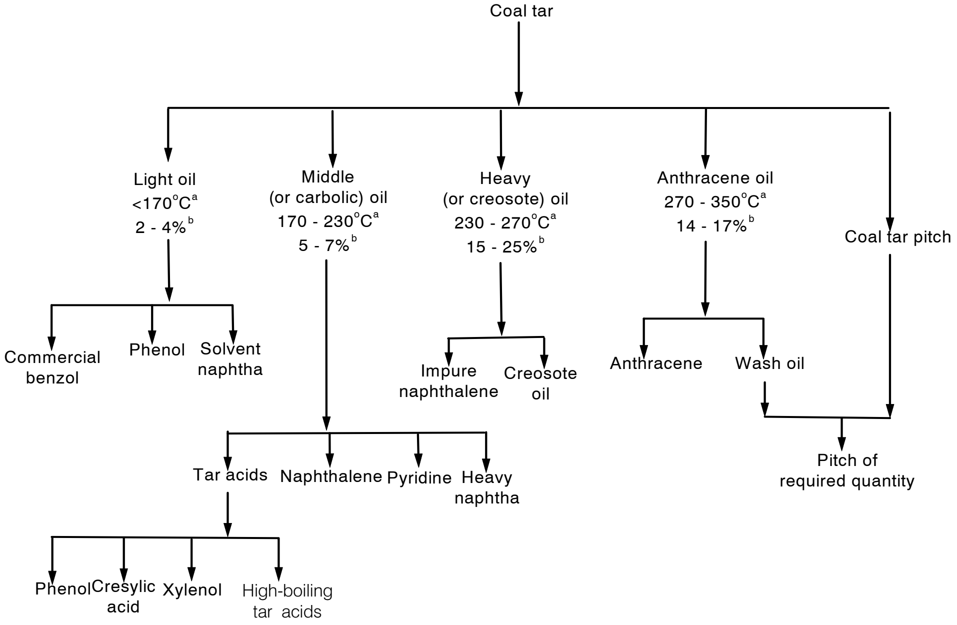


Figure 1.30 Chemical products from coal tar distillation.

the light oil fraction are benzol, phenol and naphtha, of the middle (or carbolic oil) fraction are tar acids, naphthalene, pyridine and heavy naphtha, of heavy (or creosote) oil are impure naphthalene and creosote oil, of anthracene oil are anthracene and wash oil, and of pitch which is a residue. A sketch of tar distillation plant is shown in Figure 1.31. The crude tar, before being subjected to distillation, is separated from the ammoniacal liquid fraction; this prevents corrosion problems in tar stills. In order to reduce corrosion to about 8%, soda solution is added to the tar, before feeding it to a pipe still. Tar from storage tank is heated up to 120–140 °C in the first stage of the pipe still. After dehydrating this tar in an evaporator (first stage) it is brought back to second stage pipe still for heating/dehydrating up to 380–410 °C (depending upon the quantity of pitch to be produced). From the second stage of pipe still heater, dehydrated tar is fed to another evaporator, thereby generating a vapour mixture of various fractions. Superheated steam is fed to the bottom of the second stage evaporator. Hot pitch is obtained from the bottom of the second stage evaporator, and anthracene II is drawn from the side. The top temperature is maintained by means of anthracene I reflux. The vapours of the fractions from the top of the second stage evaporator are fed to the fractionating column. A supply of saturated steam is provided at the bottom of the column, and anthracene is withdrawn from the bottom of the column. The other fractions (wash oil, phenol and naphthalene) are taken out through side tappings. The fractions are taken out from the fractionating column flow to 60–80 °C. Except for anthracene I, remaining all the fractions are taken to their storage tanks. Coal tar fuels are the liquid fuels obtained by mixing the different tar distillation products. Although the different products of tar distillation contain valuable chemicals, the demand for them is limited and therefore, large amounts of tar are prepared into a series of coal tar fuels (CTF). There are as many of six types of CTF, such as CTF50 and CTF100, which are mixtures of carbolic oil, creosote oil and anthracene oil fractions of tar.

Continuing further with the recovery aspects from coke oven gas reference may be drawn to the recovery of light oil (crude benzol). In a typical process used, the coke oven gas (from which benzol is to be recovered) after removal of tar, ammonia etc. is passed through the benzol scrubber where the benzol vapours are scrubbed by wash oil flowing countercurrent to the gas. Benzolised wash oil is then pumped to the recovery section where the crude benzol, absorbed in the wash oil is stripped off by steam. The steam vapour mixture, com-

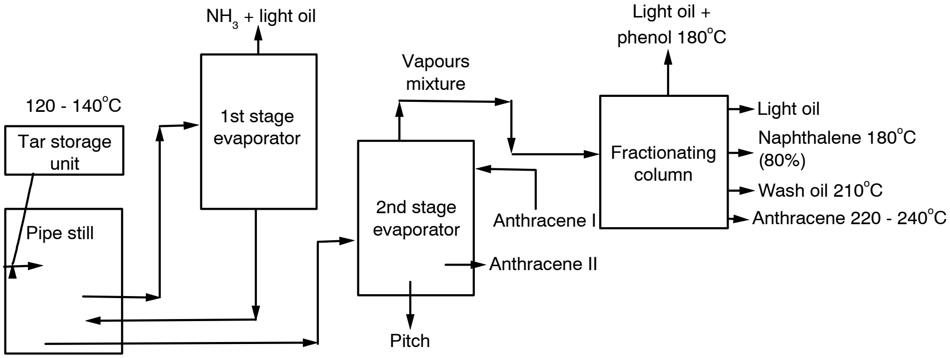


Figure 1.31 Tar distillation plant.

ing from the stripping column is then condensed and liquified. Benzol and water are separated in tw layers. Water is drained off and the crude benzol stored for further distillation. The debenzolized oil coming out from the bottom is cooled and stored for supply to benzol scrubber. Benzol thus recovered contains the following chemicals: benzene 60–70%, toluene 15–20%, xylene 5–10%, solvent naphtha, phenol, naphthalene etc. 1–5%. A benzol distillation plant is subsequently operated in order to recover the chemicals present in benzol.

1.10.3.1.2 **Liquid Fuels**

Most of the liquid fuels in use today are obtained from crude oil, also called petroleum, a brownish-green to black colored viscous oil found under the crust of the Earth either on shore or off shore. This oil either flows out by itself due to underground gas or hydrostatic pressure, or it is mechanically pumped out. Petroleum almost always occurs along with gas called natural gas. When the oil well contains both oil and gas it is called a wet well, and when it contains only gas it is called a dry well.

The principal constituents of petroleum are paraffins (C_nH_{2n+2}), naphthenes (C_nH_{2n}), aromatic series of hydrocarbons, and asphaltic compounds. Depending on the nature of hydrocarbons present, petroleum is classified as: (i) paraffin-base crudes: these have low asphaltic contents and only traces of sulfur and nitrogen; (ii) mixed-base crudes: these have a lower content of paraffins and a higher content of naphthenes than the paraffin-base crudes while the content of asphaltic compounds is higher. The sulfur content is usually $< 0.4\%$ and the paraffin wax content is generally high; (iii) naphthene-base crudes: these contain a high percentage of naphthenes, very little paraffin wax, and have a relatively high specific gravity; and (iv) aromatic crudes: these generally have a high content of asphaltic compounds; the sulfur content varies from 0.1 to 4.13%, and the nitrogen content is relatively high. The petroleum or crude oil is never used as such. The refining of petroleum is accomplished by three processes: (i) fractional distillation, (ii) cracking, and (iii) treating.

The fractional distillation process is carried out in a fractionating still (its modern version is also called a topping still). The three most important liquid fuels derived from petroleum are gasoline or petrol, kerosene, and diesel oil.

The fractionation process yields 20–25% gasoline or petrol, 30–35% intermediate oils (kerosene, naphtha, diesel and tube oil), and 25–50% residual fuel oils. Of all these fractions, gasoline has the largest demand and the yield figure falls very much short of the demand. Thus, there arises a necessity to conduct cracking process to produce the gasoline. There are two methods of cracking: (i) thermal cracking; and (ii) catalytic cracking.

In the **thermal cracking** methods, the higher-boiling petroleum fractions like heavy oils are subjected to high temperature and pressure by which the bigger hydrocarbon molecules break down to yield lower-boiling lighter fractions:

$$\begin{array}{cccc} C_{10}H_{22} & \xrightarrow{\text{Cracking}} & C_5H_2 & + \; C_5H_{10} \\ \text{(Decane)} & & \text{(Paraffin)} & \text{(Olefine)} \\ \text{(B. pt. } 174\,^\circ\text{C)} & & \multicolumn{2}{c}{\leftarrow \text{B. pt. } 36\,^\circ\text{C} \rightarrow} \end{array}$$

In the **catalytic cracking** method, a suitable catalyst such as aluminum silicate or alumina is used. This provision produces an improved quality and yield of gasoline. This method has several advantages over the thermal cracking method. Among these, special mention may be made of: (i) petrol is obtained in higher yields and is of a better quality; (ii) there is no need for any external fuel for cracking; (iii) the pressure needed for cracking is much lower; (iv) the product contains a higher amount of aromatic compounds and hence has better anti-knock characteristics; (v) the presence of the catalyst leads to the cracking of more of naphthenic materials than of paraffinic, and this implies that the products resulting from catalytic cracking are more paraffinic; and (vi) the catalytically cracked product contains a very little of the undesirable impurity sulfur, this being due to the fact that a major part of the sulfur present escapes as hydrogen sulfide gas during cracking. Depending upon the physical condition of the catalyst bed there are three main processes for catalytic cracking. They are the fixed bed, the moving bed, and the fluidized bed catalytic cracking process. The fixed bed process was first used, but this has now been replaced by the moving bed and fluidized bed processes.

The coverage on liquid fuels must include an account of the processes for synthesis of gasoline. The synthesis process is carried out by any one of the following: (i) polymerization, (ii) Fischer–Tropsch method; and (iii) Bergius process. The following description relates only to the first of these methods.

The gases obtained as by-products from the cracking of petroleum or other heavier oils are: (i) olefinic such as ethylene, propene and butanes, and (ii) saturated hydrocarbons or alkanic such as methane, ethane, propane and butanes. When the gaseous mixture of these is subjected to high temperature and high pressure, with or without the presence of a catalyst, it polymerizes to form higher hydrocarbons, having semblance of gasoline which goes by the name, polymer gasoline. The polymerisation can be of two types:

- Thermal polymerization, in which polymerization of cracked gases is implemented at specified temperature and pressure; the product is a mixture of gasoline and gas oil. A subsequent fractionation process accomplishes separation between the two.
- Catalytic polymerization, which is implemented in presence of a catalyst such as phosphoric acid; in this case, lower temperatures are used and the products are gasoline and unpolymerized gases. The unpolymerized portion is separated and recycled for polymerization.

All in all, gasoline is an important product of the synthetic processes briefly described here. Some idealities of gasoline may be mentioned as: (i) cheapness and ready availability; (ii) burns cleanly and no corrosive products on combustion; (iii) knock-resistant; (iv) no easy pre-ignition production of pre-ignite; and (v) have a high calorific value. The straight-run gasoline (obtained either from distillation of crude petroleum or by synthesis) contains some unwelcoming unsaturated straight-chain hydrocarbons and sulfur compounds. It is refined by a process called “treating”, which encompasses a number of processes each designed to remove specific impurity associated with the petroleum products. The processes may be divided under four categories: (i) removal of sulfur (the sweetening process); (ii) removal of colour; (iii) removal of gum; and (iv) stabilization and gas concentration of gasoline.

Sweetening of petroleum products implies the removal of dissolved free sulfur and its compounds like hydrogen sulfide, and mercaptans in order that the product has no bad odour and does not tend to cause corrosion. The removal of these is accomplished by oxidation processes, solvent processes or catalytic desulfurization processes.

There are generally four oxidation processes:

- Sulfuric acid treatment. In this treatment, oxidation of mercaptans occurs. If alkyl radical in mercaptans is denoted by R, the reaction can be described as shown below:
  $RHS + H_2SO_4 \rightarrow RS \cdot SO_3 \cdot H + H_2O$; $RHS + RSSO_3H \rightarrow (RS)_2SO_2 + H_2O$; $(RS)_2SO_2 \rightarrow R_2S_2 + SO_2$;
  $2\ RHS + H_2SO_4 \rightarrow R_2S_2 + 2\ H_2O + SO_2$
  Thus, mercaptans are converted into disulfides. A large quantity of acid is used in this type of oxidation.

- The process wherein sodium plumbite is used to remove mercaptans; this is also known as the Doctor's treatment:
  $2\ RHS + Na_2PbO_2 \rightarrow (RS)_2Pb + 2\ NaOH$; $(RS)_2Pb + S \rightarrow R_2S_2 + PbS$
  Free sulfur is added in the oil if it is not in sufficient quantity.

- Catalytic removal. In this process, lead sulfide serves as the catalyst for the following reaction when the oil is treated with sodium hydroxide:
  $2\ RSH + S + 2\ NaOH \rightarrow R_2S_2 + Na_2S + 2\ H_2O$
  The overall reaction is like that in the Doctor's treatment.

- Copper sweetening. In this process, cupric chloride is used. The reaction is shown as:
  $2\ RHS + 2\ CuCl_2 \rightarrow R_2S_2 + 2\ CuCl + 2\ HCl$
  The cuprous chloride formed is again converted into cupric chloride by exposing to air.

In the oxidation processes described it is clear that sulfur is converted into disulfides. This does not serve the purpose as the sulfur is still in the oil, though its form has changed. The octane number is lowered by the presence of sulfur, and the combustion of disulfides leads to the presence of sulfur dioxide emission via the exhaust pipe. Hence, other methods of sulfur removal have found preference.

The list of solvent processes for sulfur removal consists of the following:

- Caustic washing. Here, caustic solution 5–15% strength is reacted with liquid gasoline or gaseous hydrocarbons. This interacts with H_2S and lower molecular-weight mercaptans and they are thus removed.
- Solutizer process. In this process, caustic alkali of 25% strength containing a small amount of solutizer agent such as potassium isobutyrate is used. This makes the mercaptans more soluble in caustic solution and easily removable. Solutizer solution is boiled for regeneration.
- Tannin solutizer process. In this process, alkyl phenols or isobutyric acid is used in combination with tannic acid and caustic solution. The spent tannin solution is again regenerated by air blown into the solution.
- Unisol process. In this process, mixture of caustic soda and methanol removes mercaptans from gasoline.

The catalytic desulfurization method removes all types of sulfur, except for heterocyclic sulfur compounds. The sulfur compounds are decomposed at high temperature, yielding H_2S and are removed by fractionization. The processes that belong to this category are:

(i) perco catalytic process – gasoline vapour at 370–400 °C goes through a bed of bauxite catalyst, whereupon sulfur compounds are converted into H_2S. Its further removal occurs by fractionization; (ii) gray desulfurization process – this process is like the previous process, but Fuller's Earth is used as a catalyst.

Sulfur compounds, high-boiling molecules, nitrogen or gum impart colour to gasoline. Simply passing gasoline vapours through a bed of Fuller's Earth, or by subjecting them to cold sulfuric acid treatment can effectively remove the gasoline colour.

Gum is a dark coloured polymer which is formed by oxidation or polymerization of diolefines. The gums precipitate on carburettors and also choke intake valves and deposit on to the cylinder walls of engines. Natural gasoline contains no diolefines, and accordingly gum formation does not occur with its use. However, gasoline obtained from thermal cracking contains diolefines in large amounts, especially when thermal cracking of the vapour phase is carried out. In the manufacture of gasoline by catalytic cracking and reforming processes, diolefines are cracked and are present in the gasoline only in very small amounts. Therefore, inhibitors which do not permit the polymerization of diolefines to occur are added to control gum formation. Newly formed gasoline contains very little gum, but on standing and keeping gasoline diolefines react together to form more and more gum. "Potential gum" is the name given to the quantity of gum that will be formed upon long exposure to air or light. Sulfuric acid treatment removes preformed gum. Potential gum-forming molecules are not removed, but inhibitors are introduced to retard formation of gum for several months. These inhibitors are subjected to preferential oxidation and thereby delay the oxidation process for gum-forming diolefines (those used generally include butyl amino phenols, benzyl amino phenols, phenylene diamenes, cresols and cresote). The quantities added, though small, are sufficient to delay gum formation for several months.

Finally, our attention is focused on stabilization and gas concentration. The gasoline ensuing from fractionating column or from its various cracking processes, or from polymerization, etc. contains dissolved gases. The stabilization of gasoline is accomplished by removing methane, ethane, propane and some of the butanes to obtain a gasoline of the correct boiling ranging and vapour pressure. The stabilizer used for this purpose consists of a fractionating column having 40 plates. The introduction of feed is carried out at 27, 24, 21 and 18 plates. The feed contains mostly low-boiling paraffin and hydrocarbons, as well as small quantities of hydrocarbons up to nonane. The stable gasoline is removed from the bottom of the fractionating column. The material removed from the top of the column contains very little isopentane.

In the context of liquid fuels it is important to become familiar with the two terms, "reforming" and "knocking".

The reforming process brings structural modifications in the components of straight-run gasoline (produced by the fractional distillation of crude oil); the primary objective is to improve upon its anti-knock characteristics. The process can be either thermal reforming or catalytic reforming. These are usually carried out in a reactor maintained at 500–600 °C and at a pressure of 85 atmospheres. The feed stock is straight-run gasoline containing low-molecular-weight and shorter-chain hydrocarbons, which require drastic conditions. In order to avoid gas formation (at the expense of gasoline), the conditions are controlled by quenching the products with cold oil spray. The reformed products are subsequently fractionated for removal of residual gas (stabilizer).

Catalytic reforming (Pt, 0.75% supported on alumina) is implemented by either a fixed bed or fluidized bed at 400–530 °C and 35–40 atmospheric pressure to obtain a better grade and yield of gasolines. The hydrogenation, dehydrocyclization, hydrocracking, and isomerization are the principal reactions during catalytic reforming process. The hydrogen produced in catalytic reforming is used to hydrogenate alkenes, promote cracking of large alkane molecules (hydrocracking), and eliminate sulfur in the feed stock as H_2S gas.

The fuel in **internal combustion engines** is a mixture of gasoline vapour and air. The combustion reaction is initiated by a spark in the cylinder; the flame produced thereby should spread rapidly and smoothly through the gaseous mixture, causing the expanding gas to drive the piston down the cylinder. The ratio of the gaseous volume in the cylinder at the conclusion of the suction stroke to the volume at the conclusion of the compression stoke of the piston is called the compression ratio. The efficiency of an internal combustion engine increases with the compression ratio. However, the success in attaining a high compression ratio is dependent on the nature of the constituents present in the gasoline used. In certain cases, due to the presence of some constituents in the gasoline used, the oxidation rate becomes so powerful that the last portion of the fuel–air mixture becomes ignited instantaneously, producing an explosive violence, and this is known as "knocking". The consequence of knocking is a loss of efficiency, since it ultimately brings the compression ratio down. This abnormal behaviour causes the cylinder head temperature to rise and may sometimes damage the cylinder head and the pistons structurally. The causes of knocking can be ascribed to the characteristics of the fuel and also of the engine (such as design, mechanical conditions and manner of operation). The knocking tendency of fuels decreases in following order: straight-chain paraffins > branched-chain paraffins > olefins > cycloparaffins > aromatics. Thus, olefins of the same carbon chain length possess better antiknock properties in comparison with the corresponding paraffins. A fuel which yields minimum knocking is decidedly a good quality fuel. The quality of a fuel is determined by its octane number. An arbitrary scale of octane number has been introduced, with *n*-heptane and *iso*-octane as reference compounds. Iso-octane is considered an ideal fuel and is given an octane number 100. Heptane causes very bad knocking, and so was given an octane number zero. The two are mixed in proportions to produce a series of fuels having varying octane numbers starting from 0 to 100 and such mixtures are treated as standards to compare gasolines with respect to their anti-knock property. A given sample of gasoline is assigned an octane number 70, if on compressing it in a standard engine, it starts to knock at the same compression ratio which causes a mixture of 70 parts of iso-octane and 30 parts of heptane to generate a knock with the same engine under the same conditions. Nowadays, gasolines with very high octane ratings are produced and these are used for aviation purposes. The octane number of many poor fuels can be improved by adding such poisonous substances as tetraethyl lead, $(C_2H_5)_4Pb$ (TEL), and diethyl telluride, $(C_2H_5)_4Te$. The amounts added are about 0.5 mL^{-1} of motor spirit (or motor fuel) and about 1.0–1.5 mL^{-1} of aviation fuels. The mode of action of TEL is that it transforms into a cloud of finely divided lead oxide particles in the cylinder, and these react with any hydrocarbon peroxide molecule formed, thereby slowing down the chain oxidation reaction and thus reducing the chances of any early detonation. The engine life can be adversely influenced due to lead oxide deposition, and in order to avoid this a small amount of ethylene dibromide is usually added to the petrol. The addition leads to the removal of lead oxide as volatile lead bromide along with the exhaust gases.

In a **diesel engine**, the fuel is exploded by heat and pressure, and not by a spark. Diesel engine fuels consist of longer-chain hydrocarbons and should easily ignite below the compression temperature, with the induction lag being as short as possible. It is essential that the hydrocarbon molecules in a diesel fuel should be (as far as possible) straight chain ones, with a minimum admixture of aromatic and side-chain hydrocarbon molecules. A diesel fuel is rated by its octane number which is the spontaneous ignition temperature of this particular fuel. The best diesel fuel which has the highest ignition temperature is cetane ($C_{16}H_{34}$) while that with the lowest spontaneous ignition temperature is α-methylnaphthalene. A mixture of these two yields a standard scale for assessing and expressing the spontaneous ignition temperature of a given diesel fuel. A diesel fuel having a cetane number of 40 implies that the spontaneous ignition temperature of the oil is the same as that of a mixture of 40% cetane and 60% α-methylnaphthalene. An improvement of cetane number of a diesel fuel can be brought about by adding small amounts of certain pre-ignition dopes such as acetylene, butadiene, acetone, alkyl nitrates, or methyl alcohol. The most commonly used diesel engine fuel is diesel oil or gas oil, which is essentially a fraction obtained between 250–320 °C during the fractional distillation of crude petroleum. It is the index number by which a diesel quality is expressed. The diesel index number is equal to cetane number plus three.

Kerosene is the petroleum fraction obtained between 180–250 °C during the fractionation of crude oil. Its initial boiling point may vary between 128 °C and 180 °C, while the final boiling point may range from 235 to 330 °C. Kerosene oil contains paraffins, naphthenes and aromatics. It is on the relative proportions, the structures, and the boiling ranges of these hydrocarbons that the chemical and the physical properties of kerosene depend. The specific gravity of most kerosene oils ranges from 0.775 to 0.80, while their colour ranges from water white to light green or yellow. The flash points range from 24 °C to 65 °C. A paraffinic kerosene gives rise to a high flame without smoke, while a kerosene containing a high percentage of aromatic and naphthenic hydrocarbons producers a much lower flame before the appearance of smoke. Kerosene oils are very popular for domestic purposes, and are also used in jet engines. When used in home appliances, it is always vapourized prior to combustion and, by using an excess of air, it burns with a blue flame without smoke. When used in jet engines, it is introduced into the combustion chamber, where it is mixed with vast amount of air and subjected to ignition. A low-sulfur content kerosene is needed for many duties such as jet engine fuel. A procedure involving washing with alkalies or by the action of ammonium polysulfide and concentrated sulfuric acid can reduce the sulfur content as required.

As one more common example of liquid fuels present reference may be drawn to liquified petroleum gas (LPG) or bottled gas or refinery gas. This fuel is obtained as a by-product during the cracking of heavy oils or from natural gas. It is dehydrated, desulfurized and traces of odours organic sulfides (mercaptans) are added in order to identify whether a gas leak has occurred. Supply of LPG is carried out under pressure in containers under different trade names. It consists of hydrocarbons of great volatility such that they can occur in the gaseous state under atmospheric pressure, but are readily liquifiable under high pressures. The principal constituents of LPG are *n*-butane, *iso*-butane, butylene and propane,

Table 1.31 Some of the advantages of liquified petroleum gas (LPG) over gaseous fuel and the advantages and disadvantages over gasoline as a motor fuel.

Advantages of LPG over gaseous fuel for domestic application	***Advantages of LPG over gasoline as motor fuel***	***Disadvantages of LPG over gasoline as a motor fuel***
(1) Characterized by high efficiency and heating rate, (2) Deployment of well-designed, durable and neatly made burners ensures smokeless combustion, (3) Needs little care for maintenance purpose, (4) Easy control and flexibility, (5) Easy manipulation, (6) Portability makes it admirably suitable for use in remote areas, (7) Freedom from carbon monoxide makes it less hazardous. The fire hazards are, however, as much as for any other gaseous fuel.	(1) LPG is cheaper than gasoline, (2) It affords a better manifold distribution and mixes easily with air, (3) Considerably knock resistant, (4) As a consequence of its burning cleanly, residue and oil contamination is small, (5) Crankcase oil dilution is minimal so engine life is increased.	(1) On account of its faint odour, leakage is not easily identified, (2) Handling must be under pressurized conditions, (3) Suitability under high compression ratios, (4) Exhibits a low octane number and a high load sensitivity, (5) Shows very poor response to blending. Overall LPG seems suitable as a fuel for trucks and tractors.

with a little or no propylene and ethane. The largest current use of LPG is as domestic fuel and industrial fuel. However, there is a trend for use of LPG also as a motor fuel. Some of its advantages over gaseous fuel, and its advantages and disadvantages over gasoline as a motor fuel are presented in Table 1.31.

1.10.3.1.3 **Gaseous Fuels**

Gaseous fuels are combustible in air or oxygen and provide heat for domestic/commercial use. Freedom from mineral impurities, uniformity in quality, convenience and efficiency in use are some of the important features of gaseous fuels. On commercial scale, a gas-handling system is the least costly of all the fuels. The important gaseous fuels are natural gas, manufactured gases (coal gas, producer gas, water gas, and oil gas), and by-product gases (blast furnace and coke oven gases). Some of these gaseous fuels will be dealt with here.

Natural gas and petroleum resemble each other closely in respect of their chemical compositions and geographic distributions. Both are made up mainly of hydrocarbons. Petroleum is rarely free of natural gas, and the same fields usually produce both these fuels. When natural gas occurs alongwith petroleum in oil wells, it is called wet gas. The wet gas is subjected to treatment for removal of propane, propene, butane, and butene, which are used as LPG. On the other hand, when the gas is associated with crude oil, it is called dry gas. Some natural gases contain small amounts of helium. Occasionally, wells are found in which the gas contains hydrogen sulfide and organic sulfur vapours. Sour gas is defined as a natural gas which carries in excess of 1.5 grains of hydrogen sulfide or 30 grains of total sulfur per specified volume. Natural gas is on most accounts an excellent domestic fuel. Pipelines conveniently convey it over long distances. In addition, it has other important uses; for example, it has recently been used for making several chemicals by processes that basically involve synthesis, and it is also among the standard raw materials for carbon black.

Coal gas is produced when coal is carbonized when coal is heated in the absence of air in either coke ovens in gas-producing retorts. In the gas-producing retort process, coal is fed into closed silica retorts, which are then heated to 1300 °C by burning a mixture of producer gas and air. The gas from the retort is fist scrubbed by passing through a hydraulic main. Much of the tar is then removed by cooling the gas in a condenser. The residual tar and ammonia present in the gas are removed by scrubbing with water in a scrubber. The cooled gas is subsquently scrubbed with creosote oil, which dissolves benzol and naphthalene. Next, the gas is freed from hydrogen sulfide by sending it over moist ferric oxide held in a purifier. Any hydrogen sulfide gas, if present, also is removed

$$2\,Fe(OH)_3\,(s) + 3\,H_2S\,(g) \rightarrow Fe_2S_3\,(s) + 6\,H_2O\,(l)$$

When the iron oxide of the purifier becomes exhausted, it is withdrawn from the purifier and exposed to air, whence it oxidizes to ferric oxide:

$$2\,Fe_2S_3\,(s) + 3\,O_2\,(g) \rightarrow 2\,Fe_2O_3\,(s) + 6\,H_2S\,(s)$$

Coal gas is a colourless gas. It has a characteristic odour is lighter than air, and burns with a long, smokey flame.

Producer gas is essentially a mixture of carbon monoxide and hydrogen (which are combustible components), associated significantly with nitrogen and carbon dioxide (which are non-combustible components). This gas is formed by blowing air or a mixture of air and steam through a hot bed of any solid carbonaceous fuel (coke, anthracite coal, or bituminous coal). Any fuel having 50% or more of combustible carbon can be used for the production of producer gas. The preparation process involves passing air mixed with a little steam over a red-hot coal or coke bed maintained at about 1100 °C in a refractory-lined steel reactor, known as the gas producer. The reactor is provided with a cup and cone feeder at the top, a side opening for the producer gas exit, an inlet at the base for admitting air and steam, and ash exit provision at the base. The gas producer can be divided into four zones: the ash zone, the combustion zone, the reduction zone, and the distillation zone. The ash zone is the lowest zone and consists mainly of ash. The ash protects the grate from the intense heat of combustion. Moreover, the temperature of the air and the steam supplied is increased as they pass through this zone. The combustion zone is situated next to the ash zone and is also known as the oxidation zone. The carbon burns here, leading to the formation of carbon monoxide and carbon dioxide. The temperature of this zone is about 1100 °C. In the reduction zone, carbon dioxide and steam react with red-hot coke, and free hydrogen and carbon monoxide are produced. All the reactions involved are endothermic in nature and the temperature in the zone falls to 1000 °C. If no steam is supplied the temperature of the producer further rises and this may fuse the ash and refractory lining. In order to overcome these problems and to produce a richer gas, a little steam, admixed with air, is used. In practice, a balance between the air and the steam supply is struck so as to maintain a temperature of about 1000 °C. In the distillation zone (400–800 °C) the incoming coal is heated by the outgoing gases as the gases transfer their sensible heat to the coal. The heat provided by the gases and the heat radiated from the combustion zone help to distil the fuel; thereby, the volatile matter contained in the coal becomes incorporated into the outgoing gases.

Water gas or blue gas is essentially a mixture of combustible gases, carbon monoxide and hydrogen, associated with small amounts of the noncombustible gases, carbon dioxide and nitrogen. It is produced by alternatively admitting steam and a little air through a bed of

Table 1.32 Compositions and uses of gaseous fuels.

Gaseous fuel	*Natural gas*	*Coal gas*	*Producer gas*	*Water gas*
Composition (%)	$CH_4 = 70–90$ $C_2H_6 = 5–10$ $H_2 = 3$ $CO + CO_2 =$ remainder	$H_2 = 4$ $CH_4 = 32$ $CO = 7$ $C_2H_2 = 2$ $C_2H_4 = 3$ $N_2 = 4$ $CO_2 = 1$ Rest = 4	$CO = 22–30$ $H_2 = 8–12$ $N_2 = 52–55$ $CO_2 = 3$	$H_2 = 51$ $CO = 41$ $N_2 = 4$ $CO^2 = 4$
Calorific value (kcal m^{-3})	12,000–14,000	4900	1300	23,800
Uses	Domestic fuel; chemical manufacture	Illuminant in cities and towns; fuel; metallurgical operations contributing reducing atmosphere	Heating open Earth furnaces, muffle furnaces, retorts; reducing agent in metallurgical operations	Source of hydrogen gas; an illuminating agent; a fuel gas

red-hot coal or coke, maintained at about 900–1000 °C in a reactor which is a steel vessel lined inside with refractory bricks. The constructional details are essentially the same as those of the gas producer described earlier. The steam supplied to the reactor reacts with red-hot coke at 900–1000 °C to form carbon monoxide and hydrogen

$$C + H_2O \rightarrow CO + H_2$$

The reaction is endothermic, and this brings down the temperature of the coke bed. In order to raise the temperature of the bed to its original value, the steam supply is temporarily stopped and air is admitted so that exothermic reactions

$$C + O_2 \rightarrow CO_2; \ 2\,C + O_2 \rightarrow 2\,CO$$

occur and as a result the bed temperature shoots up to about 1000 °C. The cycles of steam-run and air-blow are thus operated alternatively, and in that way the required bed temperature is maintained. The compositions of the gaseous fuels described here, along with some of their important uses, have been shown in Table 1.32.

1.10.3.2 **Refractories**

In a broad sense, a refractory is any material which withstands high temperatures, without softening or suffering a deformation in shape. It is quite unnecessary to describe the role of refractories. Most simply and most straightforwardly speaking, the refractories are singularly the most important factor in maintaining any required and desired high temperature. The principal function of a refractory is to confine heat and, at the same time, to resist the abrasive and corrosive action of molten metals, slags and gases at high operating temperatures, without undergoing softening or shape distortion. One can ill-afford to undermine the role played by refractories. Refractory failures can result in major losses of time, equipment and products, and therefore the problems of obtaining refractories that are best-suited to each branch of the industry and for each specific purpose are of supreme importance. In general, it may be said that the most appropriate refractory for a given application is not necessarily one that would have the longest life, but one which offers the best balance between initial installation cost and service performance. These balances are constantly been shifting as a result of the introduction of new processes and/or new refractories. History records that developments in the area of refractories have been driven by the pressures regenerated by the demanding requirements made by adopting progressively superior metallurgical processes. The promptness with which formidable refractory problems (which have surfaced frequently) have been solved can be attributed in large measure to the rate of advancement of many industries, including the iron and steel industry – which exemplifies an industry well known for its bulk consumption of refractories of wide and varied types. In view of the importance of refractories in process metallurgy, some of their important features, such as their classification, and their physical and chemical characteristics with special reference to their conditions, will be highlighted here.

1.10.3.2.1 **Classification**

Refractories may be classified in a number of ways. According to one classification they are categorized just as oxides and non-oxides. Another classification has been made on the basis of raw materials and altogether seven groups have been distinguished, namely, siliceous, fireclay, high alumina, magnesium–silicate, magnesia–lime, chromite, and carbon groups. According to yet another classification refractory substances, in common with compounds in general, can be of three types: acidic, basic, and amphoteric or neutral. This chemical classification has been shown in Table 1.33, which also includes rarer refractories. This classification is the oldest of all the different ways in which refractories have been classified. Theoretically, acidic refractories should not be used in situations where they may come in contact with basic slags, gases or fumes, while refractories should not be exposed to non-basic conditions. In practice, these restrictions cannot be adhered to for various reasons. With the possible exception of carbon, there is perhaps no perfectly natural refractory. There has also been an attempt to classify refractories in terms of their use, and thus one encounters such terms as blast furnace refractories, open-hearth refractories, and so on. Such a categorisation of refractories is generally somewhat diffuse and suffers from the disadvantage of being liable to frequent revisions. It is thus seen that although there have been ways in which refractories has been classified, none of these classifications have been entirely satisfactory. It may, therefore, be in order to adhere to the time-honoured chemical classification of refractories, at least for the purpose of this text.

There are generally two forms-refractory bricks and granular refractories-in which refractories are used. The bricks are used in many shapes and sizes in making furnace walls, hearths, roofs, etc. Granular refractory materials are usually tamped in place and formed in situ by sintering or burning by the furnace heat. This produces a single piece or monolithic refractory, in contrast with a jointed refractory formed by laying refractory bricks.

In general, a refractory brick manufacturing process consists of a sequence of operations. The first step involves grinding, which is carried out in such a way that a properly sized material is obtained. The next operation is mixing. The object of mixing is not only to

Table 1.33 Chemical classification of refractories.

Acid refractories		***Basic refractories***		***Neutral refractories***					***Rarer refract-tories***
Alumina–siliceous materials	Siliceous materials	Aluminum oxides	Oxides of calcium and magnesium	Forms of carbon	Naturally occurring minerals	Chemically prepared refractories	Metals	Sundry	
The use of these depends upon the infusibility of aluminum silicate. There must be as little free silica as possible, because it lowers the fusion point of this type of refractory. These materials occur in three forms: (i) natural rock; (ii) prepared mass (fireclay); and (iii) burnt brick (firebrick)	These consists mainly of SiO_2 and must be low in metallic oxides and alkalies. They are used in the following forms: (i) natural rock; (ii) prepared mass (fireclay); (iii) burnt brick; (iv) electrically fused quartz; (v) silica brick (Dinas brick); (vi) quartz furnace land (ganister); (vii) quartzite	There are two important classes of these (i) bauxite or bauxite brick; (ii) alundun (electrically fused bauxite)	The common forms are produced by calcining: (i) magnesite to give magnesia; (ii) limestone to give lime; (iii) dolomite to give a mixture of lime and magnesia	Graphite charcoal coke	Chromite Sillimanite ($Al_2O \cdot SiO_2$) Mullite ($3\ Al_2O_3 \cdot 2\ SiO_2$) Kyanite ($Al_2O_3 \cdot SiO_2$) Andalusite ($Al_2O_3 \cdot SiO_2$)	Zirconium carbide Titanium carbide Silicon carbide	Fe Cu Mo Ni Pt Ta W	Forstenite (Mg_2SiO_4) Concrete talc Serpentine	Be_2O_3 ThO_2 Y_2O_3 ZrO_2

distribute the coarse and the fine particles evenly but also to incorporate a binding material, if needed, along with some water. For example, silica has no plasticity and cannot be shaped, unless some binding material is added. The mixing process is called tempering. Tempering is carried out until a uniform paste is obtained and the mass is sufficiently plastic for moulding, which may be implemented manually or mechanically. The moulded shape is dried to remove moisture. The final operation is burning which is carried out in down-draught kilns or continuous kilns. Burning is carried out in order that vitrification is achieved and suitable mineral forms are developed. Calcination of carbonates and oxidation of ferrous forms takes place during burning. These processes may be accompanied by a significant shrinkage in volume which may cause large stresses to be developed in the refractory. To avoid shrinkage, pre-stabilization of the materials used is carried out. This pre-stabilization consists of appropriate sizing and pressing.

1.10.3.2.2 **Physical and Chemical Characteristics**

It is important to have a general appraisal of the physical and the chemical characteristics of refractories, bearing in mind their diverse and widely varying applications. The following text provides a general account of some important characteristics of refractories.

- **Refractoriness:** This is the ability of a refractory to withstand heat without appreciable softening under pertinent service conditions. Most of the common refractory materials in industrial use are hardly ever pure, but are essentially mixtures of several oxide materials and so do not have sharp melting points but rather have a softening range. It is clear that a material to be used as a refractory possesses should have a softening temperature much higher than the operating temperature of the furnace in which it is to be used. A consequence of the absence of a definite melting point of a refractory material is that it undergoes a more or less gradual transition from the solid to the liquid state, over an extended temperature range. The amount of liquid that a refractory can tolerate and still remain in a serviceable condition is governed by the viscosity of the liquid and the type of crystallization that the solid phases present undergo. For example, fireclay refractories may partially liquify and actually start softening at a temperature as low as 950 °C; however, due to high viscosity of the liquid, their limiting service temperatures may be several hundred degrees higher.

- **Strength or refractoriness under load:** Refractories invariably have to confront varying load of the products under production at high temperatures. It is, therefore, necessary that refractory materials have adequate mechanical strength, at the operating temperatures so as to withstand load without giving way. Fireclay for instance, may soften gradually over a range of temperature, but may yield under appreciable loading at temperatures far less than their fusion temperature range. Some other refractories, for example silica bricks, soften over a relatively narrow range of temperature but are possessed with good load-bearing features up to temperatures close to their fusion point.

- **Chemical inertness:** This attribute implies immunity of a given refractory in a given application to any sort of chemical reaction. It should not, for instance, form fusible products with slags, fuel ashes and furnace gases. The condition inside most furnaces is usually either acidic or basic, and on this basis an acid refractory is prohibited from coming into physical contact with alkaline materials, or vice versa.

- **Price:** The refractory must be a cheap commodity. It must, however, be appreciated that it is not the initial cost that is important, but the cost per unit weight of material treated. A refractory material may be costlier than another but if it has a longer life, it may turn out to be cheaper in the long run than the refractory with a lower initial cost. In the ultimate analysis it is the overall cost of the refractory that decides the choice in its favour or otherwise for a particular installation.

- **Dimensional stability:** This property is recognized as the resistance offered by a refractory to the volume change which may occur on its prolonged use at high temperatures. Such dimensional changes may be irreversible or reversible. Irreversible changes may lead to either in contraction or in expansion of a refractory. The contraction is the result of formation of progressively amounts of liquefaction of the low fusible components of the refractory, when held at a high temperature over a long period. This carries significant vitrification and shrinkage. The pores of the refractory body are gradually filled by the liquid (fireclay bricks typically display such a behaviour). The contraction of a refractory can also be the consequence of the transformation of its one crystalline form into another which is, of course, a denser form. In magnesite bricks, an amorphous form of MgO (which has a specific gravity of 2.05), is gradually changed to a denser (specific gravity 3.54) crystalline form, periclase. This accounts for a natural contraction of the refractory. On the other hand, the transformation of quartzite (specific gravity 2.65) in silica bricks to tridymite (sp. gr. 2.26) and to crystobalite (sp. gr. 2.32) at high service temperatures results in a considerable increase in volume. The permanent expansion of silica bricks in service is accounted from this phenomenon of transformation attended by density changes to higher sides.

- **Thermal expansion:** It is necessary that furnace designs provide for the necessary allowances of thermal expansion in view of the fact that practically all solids expand when heated, and shrink when cooled. The changes affects all dimensions (length, area, and volume) of a body. It is necessary for a refractory material to have the least possible thermal expansion as furnace capacity decreases as a result of expansion. Moreover, repeated expansion and shrinkage during the periods of heating and cooling, can be detrimental to the structural integrity of the refractory in the installation.

- **Thermal conductivity and heat capacity:** In practical applications, refractory materials processing high thermal capacity as well as low thermal conductivity are required, depending upon (of course) the functional requirements. In most situations, a refractory that serves as a furnace wall should have a low thermal conductivity in order to retain as much as heat as possible. However, a refractory used in the construction of the walls of muffles or retorts or coke ovens should have a high thermal conductivity in order to transmit as much heat as possible to the interior. The charge remains separated from flame in these specific examples of installations.

The heat transferred or conducted by a refractory at a rate Q is given by the relationship:

$$\dot{Q} = K \cdot \frac{(T_1 - T_2)\,A}{\Delta X}$$

where the temperatures on the hotter and the colder surfaces are T_1 and T_2 respectively, the area of the refractory is A, and its thickness is ΔX, and K is its thermal conductivity. From this relationship it follows that if the refractory wall is made thicker, the heat loss will be decreased. Alternatively, if the refractory brick is backed by an insulating layer, the same result ensues. These provisions tend to cause the refractory material to be at a higher average temperature. The increased temperature tends to soften the refractory and to enhance the chemical attack on it. In this scenario, a choice must be made between increased heat savings and a reduction in the life of the refractory material. This particular problem has drawn considerable attention in the design of open-hearth furnaces for steel making. The question of insulating the roofs of these furnaces has been the subject of a great deal of deliberation.

The high thermal conductivities of metals such as iron or copper make them very useful materials in some particular applications. These metals are cooled by a circulating current of water (air in some cases) and thus are maintained at a relatively low temperature. The hearths of arc and electron beam melting furnaces are constructed exclusively of copper, invariably with a provision retained for water cooling. The cooling effect results in the formation of a skin of solidified metal being melted in these furnaces. In essence, the metal melts in the crucible formed of the metal itself, thereby eliminating completely any contamination from any refractory, if used. Nonmetallic refractories that are exposed to very high temperatures are often cooled by incorporating hollow wedges or plates in the refractory wall and by circulating water through these. Most nonferrous blast furnace walls are made entirely of hollow metal water jackets.

The porosity of refractory bricks has a direct bearing on the thermal conductivity. The densest and the least porous bricks have the highest thermal conductivity owing to the absence of air voids. On the other hand, in porous bricks the entrapped air in the pores acts as a nonconducting material.

The heat capacity of a furnace unit at a given temperature depends on bulk density, specific heat and thermal conductivity of the refractory. The heat capacity and thermal conductivity of a refractory increase with increasing bulk density, and decrease with increasing porosity. A refractory with a high bulk density and a high thermal conductivity is desirable from the point of view of certain applications. With refractories used for heat storage and transmission, such as checker bricks, no conflict between properties arises, since high density is a desirable criterion both for stability and for increased heat storage and conductivity.

- **Porosity and permeability:** All normally produced refractories possess a certain amount of voids, their amount, size and continuity of which influence the behaviour of the refractory. The apparent porosity indicates the percent of the total volume which is open pore space, and provides a measure of the surface area available interaction with slags and gases. The total porosity is the percentage of the total void volume which is equal to the total volume of all the pores, whether open or closed. The apparent porosity can be slightly less than the total porosity or can be twice as less depending upon the nature of the material, the manufacturing method and the degree of firing. Increasing porosity counter-productively influences the cold strength, the resistance to attacks deformation under hot loading, the heat capacity, the thermal conductivity, and the resistance to slags and gases. As a general rule, it can be gainful in performance from refractories having the least possible porosity.

Porosity bears but little connection to permeability. The permeability is a measure of the rate of diffusion of liquids and gases through the refractory. It is understandable that the process of diffusion is governed by the size and the number of connected pores or channels which are continuous from one side of the refractory to the other. Permeability to liquids increases with increasing temperature. In the case of gases, however, the opposite is true since the viscosities of gases increase at higher temperatures unlike those for liquids for which viscosities decrease with increase of temperature.

- **Bulk density and true specific gravity:** Like porosity, the bulk density of refractories is utilized as an indication of the voids to solids ratio, and is meaningful in this sense only with reference to the true specific gravity of the refractory. Thus, the bulk density of chromite bricks having a true specific gravity of 4, but a porosity of 25% is still much greater than that of dense fireclay bricks whose porosity is 10%, but whose true specific gravity is only 2.6. Expressed as the mass of the refractory material in a given volume (g mm^{-3}), an increase in the bulk density of a given refractory improves a number of its qualities, as for instance, the strength, the volume, the stability, the heat capacity, and the resistance to slag penetration.

The true specific gravity of a fired refractory may differ from that obtained by the raw materials from which it is prepared. This is a consequence of the transformation of the mineral constituents during firing. As an example, it may once again be mentioned here that quartzite, with a specific gravity of 2.65, transforms on heating first to tridymite, with a specific gravity of 2.26 and then on further heating to crystobalite, with a specific gravity of 2.32. The resultant specific gravity of fired silica bricks reflects the extent of conventions or transformation. It is a most dependable test for the correctness of the firing procedure. As another example, mention may be made of the transformation of kyanite to mullite.

- **Resistance to thermal shock (spalling):** One of the major causes of deterioration of a refractory is spalling, which is the breaking away of pieces of the refractory from the hot face, thus baring fresh surfaces. There are three types of spalling: thermal, structural, and mechanical. Thermal spalling is due to too rapid an expansion or contraction of the hot face of the refractory consequent to sudden temperature changes, which leads to the development of internal stresses and strains. Structural spalling is due to changes in the hot face brought about by flux absorption or vitrification; this may lead to the formation of the brick which differ in expansion and insensitivity to thermal shock from the original brick or contraction may result, so that separation of pieces takes place. Mechanical spalling is due to mechanical abuse, as in removal slag collections from refractory surfaces.

Thermal expansion characteristics, elasticity (implying thereby the ability to yield to stress without rupture), and strength are among the most important properties of refractories which influence their resistance to spalling.

- **Resistance to abrasion or erosion:** For a refractory to last longer, it is desirable that it does not become extensively abraded by the descending hard charge, the flue gases ascending to escape at great speeds, the particles of carbon or grit, etc. The resistance of a refractory to abrasion and erosion is primarily a function of its strength. Since strength is governed by the degree of burn, some correlation also exists between abrasion loss and porosity and bulk density. Resistance to erosion is of paramount importance for such constructions as by-product coke oven walls, linings of the discharge end of rotary kilns, and many other areas with similar functional requirements.

- **Electrical conductivity:** The electrical conductivity of refractories is important when they are used in electric furnaces. Except for graphite and metals, all other refractories are poor conductors of electricity. Graphite is a highly refractory material, and is used for electrodes and furnace linings in all high-temperature electric furnaces. Metals are not important as refractories in electric furnaces, but copper wires or busbars, for example, are utilized to carry current to the graphite electrodes.

1.11
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2
Mineral Processing

2.1
Introduction

Mineral processing may be comprehensively described as the physical or chemical processing methods or their combinations, which may or may not lead to changes in the physical and/or chemical properties of a mined mineral resource, and which ultimately result in the production of a processed mineral product that can either be ready for use or be better suited for further processing. Mineral processing operations can be grouped into front-end and back-end operations as shown in Figure 2.1. The front-end operations essentially comprise processes leading to material severance and the back-end operations, to separation of the severed material into two parts – one that is valuable (called the concentrate), and the other that is not (called the tailings). Since most of the mineral processing operations are conducted wet, dewatering forms very much an integral part of the whole scheme. The content of the present chapter consists primarily of the two cited ends which best describe or convey quite succinctly all the essential ingredients that make mineral processing a subject in its own right.

The need for mineral processing is not at all difficult to comprehend. There is virtually no mineral in the mined condition that is suitable for immediate application for chemical treatment to a final product; rather it needs some sort of physical processing. There are a number of reasons for this. Particle size control is one. Second, there often arises a need to expose a constituent mineral for subsequent processing. This task is performed by comminution. Exposure of valuable mineral is a necessity for the purposes of leaching. Adequate liberation of the constituent minerals from each other is clearly a prerequisite for obtaining a separation between them. A third reason can be to control composition, whereby the aim is to get rid of the material that will be detrimental to subsequent chemical processing, as for example, in smelting. As a typical example in this context, mention may be made of the production of a concentrate, containing the bulk of the valuable mineral, with the removal of gangue minerals. These introductory points are amply elaborated in the following text.

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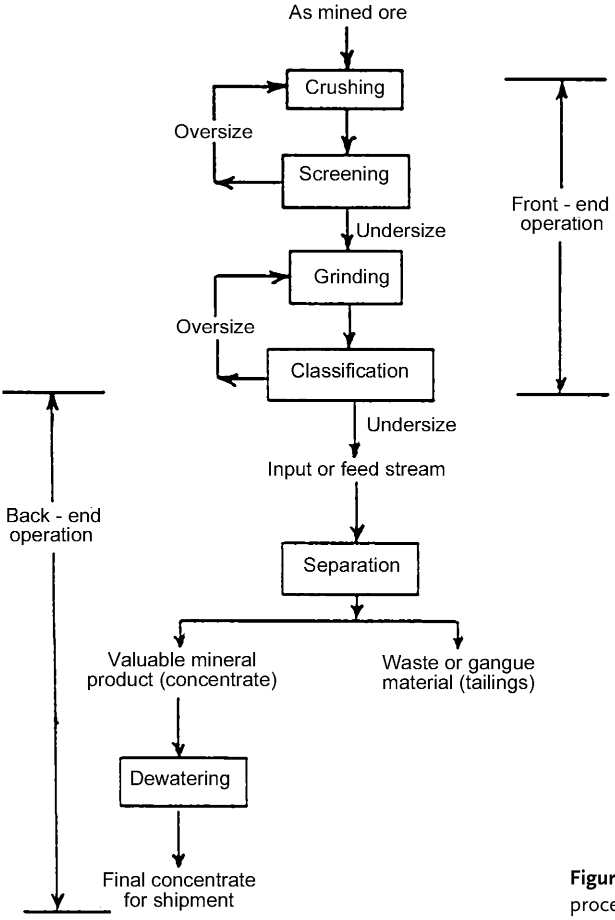


Figure 2.1 Sequence in mineral processing flowsheet.

2.2
Particles

Mineral processing works mainly with finely divided or particulate materials. A particle is a discrete unit of matter which is a useful working unit. The word particle, in its most general sense, refers to any object having definite physical boundaries, without any limit with respect to size. The characteristics of a set of particles can be obtained, to a large extent, in terms of those of the individual particle. Individual solid particles are characterized by their density, shape, and size. Particles of homogeneous solids have the same density as the bulk material. Particles derived from breaking up a composite solid, as for example, a metal-bearing ore, have various densities, commonly different from the density of the bulk material. Shape and size are easily specified for regular particles; such examples are spheres and cubes. However, the distinction between the terms “shape” and “size” are less clear-cut for irregular particles, as for example, sand grains or mica flakes and an arbitrary definition must apply in these instances. It must be appreciated that the study of particle characteristics bears considerable significance, and this stems from the fact that all separators employ differences in particle characteristics to influence a separation. Particles are characterized by such parameters as their shape, size, size distribution, and surface area. Particle shape characteristics can be considered independently of size (though there are linkages in comminution), but particle size is intimately related to surface area. This presumably accounts for presenting in sequence first shape, then size, and then surface. It may be mentioned however that because there is available a voluminous body of open literature on particle shape, size and surface, it is only possible herein to outline some principal features of the subject. In particular, the measurement of particle size and surface is regarded as subject in its own right, and readers are directed to appropriate references, a listing of which is provided at the end of the chapter. However, this chapter does provide descriptions of some methods which may be taken as illustrative and indicative examples of the wide diversity of available and known measurement methods.

2.2.1
Particle Shape

The shape of an object is a descriptor of the outline of its external surface only. Thus the shape of an object is a property that reflects the recognized pattern of relationships among all the points that constitute its external surface. The difference between the shapes of two objects arises from the differences between the patterns of relationships among these point coordinates corresponding to the two shapes. While the size of an object, for example a material particle, is an indicator of the quantity of matter contained in it, its shape is concerned with the pattern according to which this quantity of matter is assembled together. Shape is an intrinsic rather than an extrinsic characteristic in that it is not additive.

The importance of particle shape can be emphasized by providing some examples. Inks, paints and cosmetics with flaky particles contained therein have better covering power and optical properties than those containing round particles. Granular particles are required for reinforcement of rubber. This is so because if the particles are elongated, they tend to form a grain pattern which may tear the rubber preferentially in the direction in which the particles have aligned. Plastics, however, prefer elongated reinforcements such as fibers over granular shapes, this being due to the fact that plastics need high impact strength and not high tensile strength. The explosives industry welcomes smooth spherical grains as irregular particles make the initiators chemically unstable, especially if they have sharp edges and corners. The abrasives industry calls for highly angular grains and not flat particles; this is because flat particles have a tendency to slide rather than roll and hence have a low chance of providing their sharp features to the surface to be abraded. Particle shape exerts a marked control on the packing characteristics of mineral powders in bins and hoppers. It is, therefore, important to have a knowledge of the size reduction conditions which will give rise to the various desired shapes to meet the requirements of different specific application areas.

2.2.1.1 Shape Factor

The shape of an individual particle is expressed in terms of a shape factor, f. This is independent of particle size, and bears connection with the major defining dimension of a particle. May a reference be drawn to a length of an arbitrarily chosen dimension, d_p, and may this be identified as the diameter of a particle. May the length of a side of a cube and of a diameter of a sphere be chosen to explain the matters pertaining to dimensions. According to the choice being taken into account presently the volume and the surface of the cube are d_p^3 and $6\, d_p^2$; those of the sphere are $(\pi/6)\, d_p^3$ and $\pi\, d_p^2$. For both shapes (cubical and spherical) the ratio of surface to volume is $6/d_p$.

The volume (V_p) of a particle of any shape can be generally expressed as:

$$V_p = a\, d_p^3$$

and the surface (surface area, S_p) generally as:

$$S_p = 6\, b\, d_p^2$$

where a and b are geometric constants. These constants are dependent only on the particle shape. The ratio of volume (V_p) to surface (S_p) is derived from the above equations.

$$\frac{V_p}{S_p} = \frac{d_p}{6\,(b/a)} = \frac{d_p}{6\, f}$$

where the ratio of the constants (b/a) represents the shape factor (f). The shape factor f is unity for cubes, spheres, and cylinders for which the diameter equals the length. Irregularly shaped particles have f greater than unity. It is found to be between 1.5 and 1.7 for many severed substances. Commercial tower packings are so constructed as to have high surface-to-volume ratios, and f for such particles is large (in the range of 3 to 5). Two general statements are worth recording as general but practically important issues in the present context of shape factor: (i) when the dimensions of a particle are approximately the same in all the three dimensions the shape factor has a minimum value; and (ii) when the shape is either flattened or elongated, the shape factor increases.

2.2.1.2 **Qualitative and Quantitative Definitions**

Particle shapes influence properties such as surface area, bulk density, flow, and so on. A number of methods are available for describing shape; from simpler qualitative descriptions, through property ratios, to techniques that employ fast Fourier transformations to describe the projected perimeter of the particle. The measurement of the shape and the relevance of the data obtained are generally the two difficulties associated with particle shape. Fortunately, in the processing of materials physically unlike those in chemical processing, shape is perhaps is less significant and is more often than not inherently accounted for in the nominal diameter.

Some of the common terms used for defining or describing particle shapes in a qualitative way are presented in Table 2.1. It is by now quite clear that particle shape cannot be very precisely defined. However, it is fortunate that mineral particles occur in a variety of generally simple shapes; some are acicular, several are plate-like, most are convex, others are mildly concave, and in this manner a phraseological descriptive list is built for the different shapes that are formed or produced or generally encountered of powders of fragments of

Table 2.1 Some terms used to describe the shape of particles (qualitative definition).

Terms	*Description*
Acicular	needle-shaped
Flaky	plate-like
Modular	having a rounded irregular shape
Granular	having approximately equidimensional but irregular shape
Spherical	globule-shaped
Dendritic	having a branched crystalline shape
Irregular	non-symmetrical or lacking any symmetry
Angular	sharp-edged or having roughly polyhedral shape
Fibrous	regularly or irregularly thread-like
Crystalline	of geometric shape, freely grown and developed in a fluid medium

materials. The behaviour of these particles in fluids depends considerably on the specific surface area between the solid and the fluid, and this in turn depends on factors such as: (i) the amount of solids and the size distribution of these solid particles in the fluids; (ii) the densities of the particles; and (iii) the shapes of the particles. As an example mention may be made of particles of fine grained ferrosilicon. These are frequently used to form the heavy media used in industry to separate minerals according to their densities. Alterations in the shape of the ferrosilicon particles can markedly change the viscosity of a dense medium and can thus seriously influence the efficiency of an intended separation. A presentation of classification of the methods of particle shape assessment is given in Figure 2.2.

While the shape factor, introduced in the previous section, provides a quantitative definition or description of particle shape, there are other descriptors such as flakiness ratio, flakiness index, elongation index and angularity number which are also found to be in vogue.

The particle shape is related to the measured distance between tangents parallel to the outline of the particle. For a particle of any shape, three dimensions, namely, thickness (t), breadth (b), and length (l) may be considered. The thickness is given by the minimum distance between two planes tangential to the opposite surfaces of the particle and parallel to each other. The breadth is taken to be the minimum separation between two parallel planes that are normal to the planes defining the thickness. Finally, the length denotes the distance between two parallel planes which are perpendicular to the sets of planes defining thickness and breadth and which touch opposite surfaces of the particle tangentially. From the measured values of t, b and l, two ratios, which give an idea of the shape of the particle, can be obtained: elongation ratio (l/b), and flakiness ratio (b/t).

Aggregates are categorized as flaky when they possess a thickness (smallest dimension) of less than 0.6 of their nominal size as determined by two confining square screen openings. From a given screened size fraction of mass m_s, the mass fraction m_g which clears through a slot screen of special design is obtained. Then the flakiness index is given by 100 m_g/m_s. It is thus seen that the term flakiness ratio, which is applied for an individual particle, is replaced by the term flakiness index when aggregates are considered. This index is of considerable relevance in choosing aggregates for road construction.

Aggregates are categorized as elongated when they possess a length which exceeds 1.8 times their nominal size (largest dimension). From a given sized square mesh fraction of

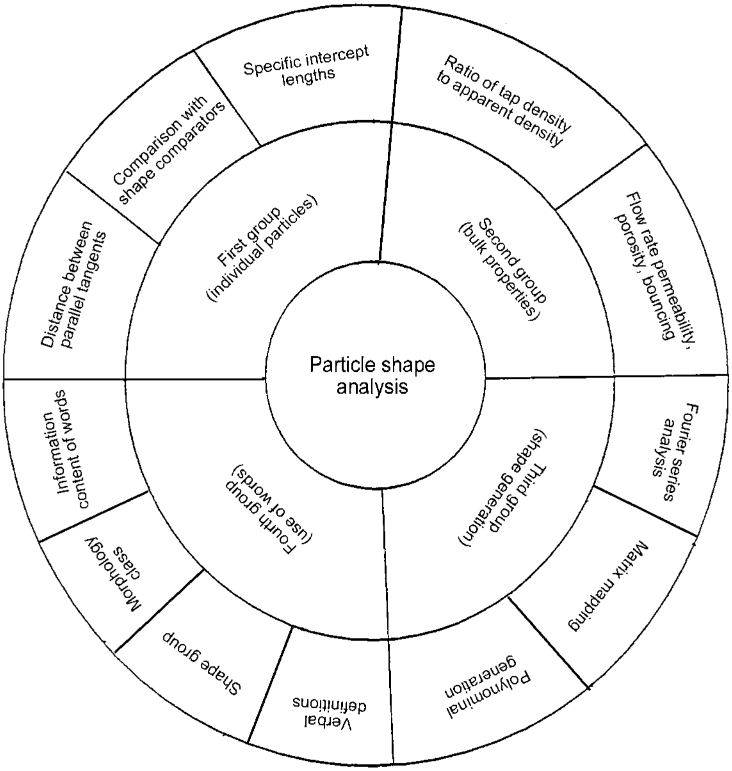


Figure 2.2 Classification of the methods of particple shape assessment.

mass m_s, the mass proportion m_e is found for which the longest particle dimension clears between appropriate stages in an apparatus of special design. Then the elongation index is 100 m_e/m_s. In this case, the term elongation ratio used for an individual particle may be said to have changed to the term, elongation index when it pertains to aggregates. There exists a relationship between the elongation and the flakiness indices. However, the elongation index is rarely indicated and it is only the flakiness index that is generally specified.

Angularity, i.e., the absence of rounding of particles in an aggregate, influences the ease of handling mixtures with binders and is meaningful in abrasive cutting. It is determined from the proportion of voids in a sample of the aggregate when it is subjected to a standard system of tamping in a standard dimensioned cylinder. The values of angularity vary, ranging from zero for a rounded shape to as much as 12 for an angular product, with the most commonly encountered values lying between 6 and 9.

2.2.2
Particle Size

The topic on particle size may be presented with an interesting example of a cigarette packet and a scale. The task assigned is to find its size. There goes the ready reply; the packet is

$25 \times 15 \times 5$ mm. It would not be correct to say "the packet is 25 mm" since this dimension represents only one aspect of its size. It is really impossible to specify the size of a three-dimensional object like the packet in the present example by just one number. Obviously, the situation is more difficult for a complex shape like a grain of sand or pigment particle in a can of paint. A quality assurance manager would prefer to have one number only to describe the particles. He or she needs to know if the average size has increased or decreased since the last production operation, for example. This forms the basic problem of size analysis in that one number cannot describe a three-dimensional object.

Any equidimensional particle may commonly be specified by "diameters". Nonequidimensional particles, or in other words, those which are longer in one direction than in others, are commonly characterized by the second longest major dimension. For needle-like particles, for instance, d_p would represent the thickness of the particles, not length.

Another method of describing particle size is in terms of "equivalent diameter" or the "equivalent sphere" $d_{p,e}$, which is the diameter of a sphere possessing the same ratio of surface to volume as the actual particle. Thus, from the equation, $V_p/S_p = d_p/6f$, the equivalent diameter ($d_{p,e}$) is

$$d_{p,e} = \frac{6\,V_p}{S_p} = \frac{d_p}{f}$$

The size of an individual particle having a regular geometric figure can be described quite conveniently. There is only one shape that can be described by one unique number, and that is the sphere. If one has a 20 μ sphere, this describes the object exactly, but the same be said cannot for a cube, where 20 μ may refer to an edge or to a diagonal. In the example taken of the cigarette packet, there are a number of its properties that can be described by one number. For instance, its weight can be expressed as a single unique number; the same is true of its volume and its surface area. So if one has a technique that measures the weight of the cigarette packet, one can then convert this weight into the weight of a sphere and, remembering that the weight is given by $4\,\pi\,r^3\,\rho$, (where ρ is the density of the packet), one can calculate a unique number ($2\,r$) for the diameter of the sphere of the same weight as the cigarette packet. This is the equivalent sphere theory. Some property of the particle in question is measured, and assumes that this refers to a sphere and proceeds to derive a unique number (diameter of this sphere) to describe the particle. This ensures that it is quite unnecessary to describe three-dimensional particles by three or more numbers, a procedure which, although doubtlessly more accurate, is not convenient for management purposes.

Particle sizes are conventionally described in different units depending on the size range involved. Coarse particles are measured in inches or centimeters; fine ones, in terms of sieve size; very fine ones in microns or millimicrons. The sizes of ultrafine particles are sometimes specified in terms of their surface per unit mass, this being commonly expressed in square meters per gram.

2.2.2.1 **Particle Size Measurement**

The methods by which particle size determination is carried out have been presented in Figure 2.3. The methods are observed to be broadly classified into two groups: static meth-

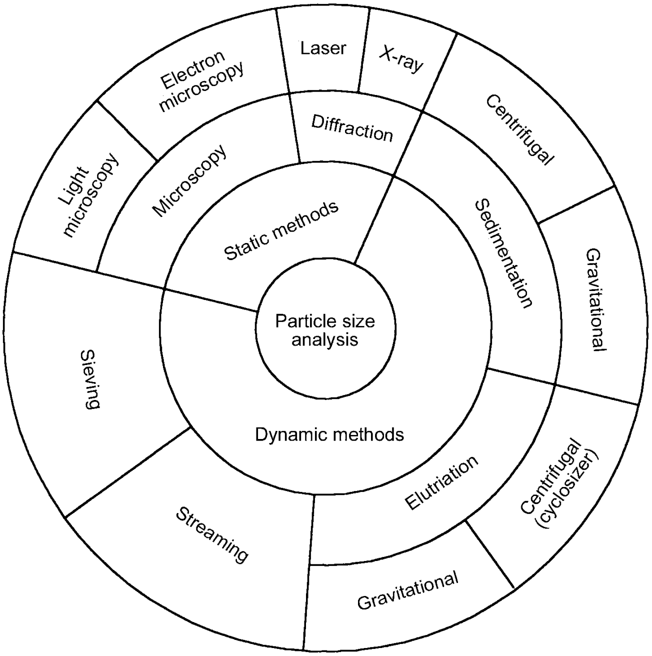


Figure 2.3 Classification of the methods of particple size analysis.

ods; and dynamic methods. The static methods as compared with the dynamic methods are seen to be fewer in number.

The *static methods* simply imply that they are fundamentally static and are essentially observational in character. An extremely popular method to metallurgists, microscopy, may be cited as one of the leading examples of static methods.

It is an excellent technique and constitutes the only method in which the individual particles are directly observed and measured. It also provides the analyst with information regarding the shapes and the sizes of the particles being examined. The microscopy techniques involve the sizing of particles by direct measurement of their enlarged images. Whether a scale is used in the ocular of a microscope or a photograph is taken, enlarged, and the measurements are carried out on it, a preselected dimension of the particle is measured and the particle is assigned that size. A difficult problem in microscopic sizing is the decision as to what is to be measured as the diameter of a particle which has an irregular shape. The image of a particle seen in a microscope is two-dimensional. From this image an estimate of particle size has to be made. With reference to the image, the different diameters used can be divided into two groups: the physical diameters, and the statistical diameters. The area diameter, the average diameter and the perimeter diameter belong to the category of physical diameters. The area diameter represents the particle's diameter as that of a circle whose area equals the projected area of the image of the particle. The average diameter is the average of the maximum and the minimum linear dimensions of the particle. The perimeter diameter represents the particle's diameter as that of a circle whose circumference is equal to the perimeter of the projected image of the particle. Martin's diameter and Feret's diameter belong to the category of statistical diameters. The former is the length of the line, measured parallel to a fixed direction, that bisects the projected area of the particle into two equal parts, and the latter is the distance between two tangents on opposite sides of the particle, perpendicular to a fixed direction. The principal tools used in microscopy are the light microscope, the transmission electron microscope, and the scanning electron microscope.

In a light microscope, the particle must be magnified to a size at least as large as the resolving power of the unaided human eye. The resolving power of microscope equals $1/d$, with

$$d = \frac{0.5\,\lambda}{n\,\sin\theta}$$

where λ is the light wave length, θ is the angle subtended at the lens, and μ is the refractive index of the medium between the lens and the object being examined. The quantity, $n\,\sin\theta$, is called the numerical aperture. Substitution of typical values in the expression for d leads to a d value of nearly 0.5 μm. Since the resolving power of the human eye is about 200 μm, it is obviously mandatory to magnify the object to a level at which the human eye can resolve the image formed. This means that the magnification required is around 200/0.5 or about 400 ×. While all these go as general guiding principles of microscopic examination, it may be mentioned that even the best quality instruments are restricted by many limitations to particles larger than about 0.5 μm. The use of ultraviolet light or phase-contrast attachments may extend this limit down to the neighbourhood of 0.2 μm.

The *dynamic methods* involve the placement of particles to be measured in an environment which is subsequently disturbed. The members belonging to the particle set react differently to these imposed environmental impulses. These different reactions are observed and therefrom deductions are made as regards the size characteristics. As examples of dynamic methods mention may be made of sieving, streaming, elutriation, and sedimentation.

Probably one of the oldest, the cheapest, the simplest and certainly the most popular method of size analysis is sieving. This has the advantage that it is readily usable for large particles which are generally encountered in the mining of minerals. It has, however, some drawbacks: (i) it is not amenable for measurement of sprays or emulsions; (ii) it is not very suitable for measurement of sizes below 38 μm (400 mesh); (iii) it is difficult to use for measuring cohesive and agglomerated materials (as for example, clays); (iv) the measurement depends on the operating parameters, thus requiring a rigid standardization of measurement times and operating methods (e.g., tapping); and (v) a true weight distribution is not produced; rather the method relies on measuring the second largest dimension of the particle (this can give some strange results with rod-shaped particles).

The simplest and the most common method of separating mixtures exclusively by size alone is to make a screen analysis using testing sieves. A set of standard screens is arranged serially in a stack, with the smallest mesh at the bottom and the largest at the top. The analysis is carried out by placing the sample on the top screen. The stack is agitated manually or mechanically for a definite period. The particles retained on each screen are removed and weighed, and the masses of the individual screen increments are converted to mass fractions or mass percentages of the total sample. The particles that clear the finest of the screens are accepted in a pan at the bottom of the stack.

The results of a screen analysis are tabulated to display the mass fraction of each screen increment as a function of the mesh size range of the increment. Since the particles on any one screen are cleared by the screen immediately preceding it, two numbers are necessary to specify the size range of an increment: one for the screen through which the fraction clears; and the other for the screen on which it is retained. Thus, the notation 10/14 means "through 10 mesh and on 14 mesh". An analysis tabulated in this way is called a differential analysis. Besides differential analysis there is a second type of screen analysis called cumulative analysis. This type of analysis is obtained from a differential type by adding, cumulatively, the individual differential increments, beginning with that retained on the largest mesh, and tabulating or plotting the cumulative sums against the mesh dimension of the retaining screen of the last to be added.

In particle size analysis it is important to define three terms. The three important measures of central tendency or averages, the mean, the median, and the mode are depicted in Figure 2.4. The mode, it may be pointed out, is the most common value of the frequency distribution, i.e., it corresponds to the highest point of the frequency curve. The distribution shown in Figure 2.4 (A) is a normal or Gaussian distribution. In this case, the mean, the median and the mode are found to lie in exactly the same position. The distribution shown in Figure 2.4 (B) is bimodal. In this case, the mean diameter is almost exactly halfway between the two distributions as shown. It may be noted that there are no particles which are of this mean size! The median diameter lies 1% into the higher of the two distri-

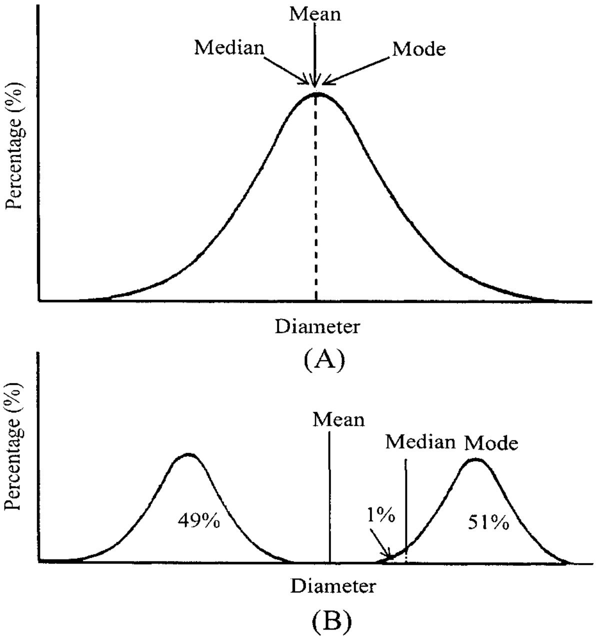


Figure 2.4 (A) Normal or Gaussian distribution; (B) bimodal distribution.

butions because this is the point which divides the population into two equal halves. The mode corresponds to the top of the higher curve because this gives the most frequently occurring value of the diameter (only just!). This example illustrates that there is no reason why the mean, the median and the mode should be identical or even close to each other. Their relative values depend on the symmetry of the distribution.

It may be mentioned here that the mode which represents the most commonly occurring size in a given distribution is not of much use in mineral processing since it does not describe fully the characteristics of a group of particles. The arithmetic mean diameter suffers from the same limitation except when the distribution is a normal one. The harmonic mean diameter is related to the specific surface area. It is, therefore, useful in such mineral processing operations where surface area is an important parameter.

2.2.3
Surface

There are two widely used methods for the determination of the specific surface area of particles. One is based on permeability and the other on gas adsorption.

2.2.3.1 Permeability

The determination of the specific surface area of a powder by air permeability methods essentially involves the measurement of the pressure drop across a bed of the powder under carefully controlled flow conditions. The data obtained are substituted in the Kozeny-Carman equation to estimate the specific surface area. Permeability methods have certain advantages, one of them being that the equipment used for carrying out the measurements is cheap and robust. Another advantage is that sample problems are minimized because a large sample of powder is required to be used for analysis.

Two types of instruments are employed to determine the specific surface area by permeametry. Those of the first type are called constant pressure systems, and the Fisher subsieve sizer is a typical example that belongs to such systems. Instruments of the second type are known as constant volume permeameters, and the apparatus devised by Blain is an example.

2.2.3.2 Gas Adsorption

A commonly used method of determining the specific surface area of a solid is by the adsorption of a gas onto the solid and the determination of the monolayer capacity. Most methods make use of the Brunauer, Emmett, and Teller equation, commonly referred to as the BET equation, for calculating the surface area on the basis of monolayer adsorption. The BET equation can be written as

$$\frac{1}{V\left(\frac{P_0}{P}-1\right)} = \frac{1}{V_\mathrm{m}\,C} + \frac{C-1}{V_\mathrm{m}\,C} \cdot \frac{P}{P_0}$$

where P is the absolute gas pressure, P_0 is the saturation vapour pressure of the adsorbate at the temperature of adsorption, V_m is the volume of gas adsorbed at complete monolayer coverage, V is the volume of gas adsorbed at pressure P, and $C = \exp\,(Q_1 - Q_2)/R\,T$, Q_1

being the heat of adsorption of the first layer and Q_2 the heat of liquefaction of the bulk liquid. A plot of $1/V\,(P_0/P-1)$ against P/P_0 should give a straight line of slope $(C-1)/V_m\,C$, with an intercept $1/V_mC$. In this way V_m can be determined and by knowing the molecular area of the adsorbate, the specific surface area can be calculated from the relation

$$S=\frac{N\,\sigma\,V_\text{m}}{M}$$

where S is the specific surface area ($\text{m}^2\ \text{g}^{-1}$), N is Avogadro's number ($6.023 \cdot 10^{23}$ molecules/gram molecule), σ is the area occupied by one adsorbate molecule (m^2/molecule), V_m is the monolayer volume (ml), and M is the gram molecular volume (22410 ml).

The instruments used to carry out specific surface area determination are based on two types of methods: volumetric methods, and gravimetric methods. Most instruments based on the former use conventional nitrogen adsorption, or some modification of it, and basically follow the original instrumental design of Emmett. These instruments are best suited for the analysis of high surface area powders. Other instruments have been developed for the analysis of low surface area powders; these usually make use of krypton or ethylene gas. The gravimetric methods have a great advantage over the volumetric methods in that the volume of the adsorption system is quite immaterial. The quantity of gas adsorbed is obtained directly by measuring the increase in weight of the solid substance upon exposure to the gas. The main disadvantages of the gravimetric methods are: (i) the instrument is much less robust and correspondingly more difficult to make and maintain as compared with a volumetric instrument; (ii) the apparatus needs calibration; and (iii) there is a need to apply the buoyancy correction. In the gravimetric methods, single spring balances, multiple spring balances, and beam balances are used for weight determination.

2.3
Comminution

The word "comminution" encompasses all the terms, crushing, grinding and other words or phrases associated with the size reduction or severance of ores and rocky materials. It will be recalled (Figure 2.1) that comminution forms the first step of the front-end operations of mineral processing. Throughout the process industries solids are reduced by different techniques for different purposes. Huge chunks of crude ore are crushed to manageable size that they can be further worked on, while synthetic chemicals are ground to powder. These are some among the many examples that can be cited. Commercial products are often required to meet strict specifications as regards the size and sometimes also the shape of the particles they contain. Reducing the particle size also enhances the reactivity of solids; it allows separation of undesirable constituents by mechanical means; and it reduces the bulk of fibrous substances for easy working.

Comminution essentially produces a suit of particles in different sizes, and a quantitative description of comminution relates the sizes of particles in the feed with those in the product. Simply stated, comminution modifies only the particle size distribution between the feed and the product.

Table 2.2 Major purposes of comminution.

1. Liberation of one or more economically important minerals from the gangue components in an ore matrix.
2. Exposure of a large surface area per unit mass of material to facilitate some specific chemical reaction, such as leaching.
3. Reduction of the raw material to the desired size for subsequent processing or handling.
4. Satisfaction of market requirements concerning particle size specifications.

A crusher or grinder does not produce a uniform product, whether the feed is uniformly sized or not. The output always consists of a mixture of particles, ranging in size from a categorized maximum to a submicroscopic minimum. Some machines, especially in the grinder category, are designed to control the magnitude of the largest particles in their yields. The fine sizes, however, are not under control. In some types of grinders the fines are minimized but they are not eliminated. If the feed is homogeneous, both in the shapes of particles and in chemical and physical structure, the shapes of the individual units in the product may be quite uniform; otherwise, the grains in the various sizes of a single product may vary significantly in proportions.

The smallest grain in a comminuted product may be comparable in size to that of a unit crystal, which is the smallest unit of the material that can exist as an independent crystal. This size is of the order of 10^{-3} micron (1 micron is equal to 10^{-3} mm, or $10^{-4\,\mathrm{cm}}$). If for example, the biggest particle in a product just clears a screen having 1-mm apertures, the ratio of the diameters of the biggest and smallest particles is of the order of $10^{-1} : 10^{-7}$, or 10^{6}. Because of this extreme variation in the sizes of the individual particles, relationships adequate for uniform sizes must be modified when applied to such mixtures. The term "average size", for example, has no meaning until the method of averaging is pronounced, and, as it happens that there are several different sizes which can be calculated.

The major purposes of comminution or size reduction operations can be summarized in four categories as shown in Table 2.2. Comminution is almost invariably performed in two or more stages. It starts with the crude mined or quarried product; this is progressively taken to the desired final size by a step-by-step process. As the process of fracture is involved throughout this procedure, a brief discussion on the fracture of materials is appropriate at this point.

2.3.1
Fracture of Materials

The term fracture implies fragmentation of a solid body into two or more bodies under the action of stress. Two main types of fracture mode are observed in solids. The first is *ductile fracture* which is the failure of a material after it has undergone a considerable amount of plastic deformation. The other is *brittle fracture* which is the failure of a material without undergoing practically any plastic deformation. The type of failure which occurs depends largely on the nature of the material and its condition; however, failure is also affected by other factors, including the type of stressing, the rate of application of stress, temperature and environment. Brittle fracture should generally be avoided in structural materials since it can occur without notice or warning and can lead to catastrophic consequences. However, brittleness is a desirable property for comminution: the more brittle a material the more easily it fragments. The strain is proportional to the applied stress up to the point at which fracture occurs in the case of a brittle material.

The principle behind the phenomenon of fracture of materials can be described by having recourse to Griffith's theory. Alternatively, this can be done by introducing the concept of fracture toughness.

In the study of fracture, a basic problem is to explain why it takes place at only a small fraction of the theoretical stress calculated for the fracture of a perfect crystal. It is believed that this happens due to the occurrence of inherent flaws such as cracks in the material. Fracture is the separation of a load-bearing body into two or more parts by the extension of a crack, and leading to a reduction in the load-bearing capacity to zero. These cracks cause the local concentration of stress to attain values as high as the theoretical (i.e., cohesive) strength; this results in the propagation of such cracks and eventually in the fracture of the material in a brittle manner. In Griffith's theory an energy balance is considered for estimating the stress required to cause a crack to propagate. The surface energy associated with a flat crack of length 2 L and unit thickness is 4 $L\,\gamma$, where γ is the surface energy per unit area of the crack surfaces. In general there will also be some plastic deformation of the surfaces of the crack, requiring an energy P per unit area, so that the total energy required for the creation of the crack is

$$W_L = 4\,L\,(\gamma + P)$$

This energy is considered to be supplied by the elastic strain energy, W_e, that is released per unit thickness by the formation of the crack and is given by

$$W_e = \frac{\pi\,L^2\,\sigma^2}{E}$$

where σ is the tensile stress acting normal to the crack and E is the Young's modulus. Now, an existing crack will grow spontaneously under the action of a given stress, if the change in W_e with increase in L, dW_e/dL, is at least equal to the corresponding change in W_L, dW_L/dL. From the two relationships provided, this equality can be expressed as

$$\frac{2\,\pi\,L\,\sigma^2}{E} = 4\,(\gamma + P)$$

The value of σ obtained from this equation is the critical value of the applied tensile stress normal to the crack (also known as the Griffith stress) necessary to cause the crack to propagate and is given by

$$\sigma_f = \left[\frac{2\,E\,(\gamma + P)}{\pi\,L}\right]^{0,5}$$

This result indicates that the stress necessary to cause brittle fracture is lower, the longer the existing crack and the smaller the energy, *P*, expended in plastic deformation. The quantity σ_f represents the smallest tensile stress that would be able to propagate the crack of length 2 *L*. The term $\sigma_f\ (\pi\ L)^{0.5}$ is generally denoted by the symbol *K* and is known as the stress-intensity factor (for a sharp elastic crack in an infinitely wide plate). Fracture occurs when the product of the nominal applied stress and the stress concentration factor of a flaw attains a value equal to that of the cohesive stress.

To sum up, failure of materials by crack propagation, according to Griffith, takes place when it is energetically possible, i.e., when the energy of the new surfaces produced is less than the energy released by the relaxation of strain in the surrounding material. The second criterion for crack propagation is that there should be a mechanism whereby it can occur, i.e., that plastic flow is inadequate to relieve the stress, which is the case with brittle materials. In these materials the strain energy is relieved by crack propagation in contrast to tough materials which relieve the strain energy mainly by plastic deformation. For brittle materials, P is small and the influence of the surface energy term, γ, becomes very significant. Once the applied stress reaches the level σ_f, small internal cracks can propagate; as the cracks increase in size the value of *L* increases with a corresponding reduction in the value of σ_f. In such a situation the cracks spread in a catastrophic manner. This failure mode applies to all brittle solids.

In providing an overall picture of the Griffith theory applied to the comminution process, it must be pointed out that the theory requires that a tensile stress should exist across a crack to open it further. While a uniform compressive force can close a crack, a nonuniform one can lead to the occurrence of localized tensile stresses. In a comminution process the particles are subjected to nonuniform loading, and therefore it can be surmised that they normally break in tension and not in compression. However, the tensile component of loading in comminution does not form the major loading component and this contributes towards a lowering of the overall energy efficiency of comminution.

All materials have a statistical distribution of cracks in them. The longest crack that is most favourably oriented with respect to the applied stress axis is the most effective one in that it propagates first to cause fracture, as the applied stress is increased. If a second test is carried out on one of the broken pieces, the strength is usually higher as a direct result of the elimination of the most effective crack in the first test. This, coupled with the fact that the probability of cracks being present in a particle decreases as the particle size decreases, explains the progressively higher energy requirements as the ore particle sizes come down in comminution.

In the context of crack propagation, a quantity, β, which is a function of temperature and the crack velocity and is known as the fracture surface energy, is often used. The ranges of the values of β, obtained from the results of fracture tests, for different types of materials are (in ergs. cm^{-2}) 10^3–10^4 for glasses, 10^4–10^6 for plastics and 10^6–10^8 for metals. The free surface energy of solids is of the order of 10^2–10^3 ergs. cm^{-2}. This implies that the free surface energy is quite insignificant in fracturing. For comminution to occur, energies commensurate with the fracture surface energy must be expended.

Besides Griffith's theory, the fracture of materials can be described in terms of a property known as fracture toughness. The fracture toughness of a material refers to its resistance to fracture in the presence of cracks or discontinuities. Fracture toughness is represented by the symbol K_{IC} (pronounced "kay-one-cee") and is the critical value of the stress intensity factor (K) at a crack tip necessary to produce catastrophic failure under simple uniaxial loading. In general, the value of fracture toughness is given by

$$K_{IC} = Y\sigma\,(\pi\,L_C)^{0,5}$$

where Y is a dimensionless geometric factor and L_c is the critical crack length. The initiation of unstable fracture in a material takes place as soon as the applied stress intensity (K) attains the critical value, K_{IC}, either because of increasing stress or due to increasing crack length, or both. It should be noted that a properly determined value of K_{IC} represents the fracture toughness of the material under consideration irrespective of crack length, geometry or loading system; K_{IC} is a material property in the same sense that yield strength is a material property.

2.3.1.1 **Fracture Mechanisms**

The manner in which a particle fractures depends on (i) the nature of the particle; and (ii) the manner in which the fracture force is applied. A number of terms have been used to describe the different mechanisms of single particle fracture. The different terms considered here are abrasion, cleavage, shatter, and chipping. It may be pointed out that in practice these events do not occur in isolation. Real breakage involves a combination of these processes, with the proportions changing, depending on the equipment, and on the manner each particle is stressed within it.

Abrasion fracture occurs when sufficient energy is not supplied to cause significant fracture of the particle. In such circumstances only a localized stressing occurs and a small area is fractured to result in a distribution to be essentially the original particle, together with a small amount of very fine particles.

Cleavage fracture is said to take place when the applied energy is just sufficient to load a few regions of the particle to the point of fracture. Only a few particles result, and their size is comparatively close to that of the original particle. This situation typically arises under conditions of slow compression where fracture immediately relieves the loading on the particle.

The term *shatter fracture* applies to a situation where the applied energy is well in excess of that necessary for fracture. Many regions of the particle are overloaded under these conditions, yielding a comparatively large number of particles with a wide distribution of sizes. This type of fracture occurs under conditions of rapid loading such as those obtained in a high-velocity impact.

The term *chipping* implies breaking of the edges or the corners of a particle. The process may be considered to be a special case of cleavage. It should not be overlooked that the principal terms, abrasion, cleavage, and shatter used here have been so arranged as to qualify the order of increasing energy intensity.

2.3.2
Energy and Power Requirements

Comminution is mechanically a very wasteful process. It has been seen that most of the energy is lost, and this is so because of the difficulty in transmitting the applied forces to the particles in the mill contents that most need to be broken down. The culprit in this regard is interparticle friction. This is coupled with the fact that most materials processed by comminution are substantially weaker in tension than in compression and, for the most part, the operating forces in comminution are not tensile in nature. During comminution, the particles of feed material are first distorted and strained. The work required to strain them is stored temporarily in the solid as mechanical energy of stress. As additional force is applied to the stressed particles, they are distorted beyond their ultimate strength, and their rupturing into fragments takes place all on a sudden. New surface is produced. Since a unit area of solid has a definite amount of surface energy, the production of new surface requires work, which is supplied by the release of energy of stress when the particle fragments. By conservation of energy, all energy of stress in excess of the new surface energy produced must appear as heat. Rock breaking is a good example of a comminution process. According to an estimate, only about 3% of the total energy input is actually used to comminute, and a very substantial portion appears as heat. The rock-breaking operation can be made more efficient provided that ways and means are found to put to use the heat energy evolved in the process. No advance has taken place as yet in this direction.

2.3.2.1 Energy Size Relationship

In the past, considerable efforts have gone into finding correlation between the energy input and the amount of size reduction induced. Widely known as laws, these correlations are mostly empirical relationships of the general form:

$$\mathrm{d}E_0 = \frac{-K\,\mathrm{d}d_s}{d_s^n}$$

where E_0 is specific energy necessary to supply the surface energy of the new surface, d_s is particle size, and K is constant. It is through the use of appropriate values of n, that the correlations of Kick, Rittinger, and Bond can be developed from above equation. Among them, only the relationship of Bond (developed from above equation with $n = 1.5$) has found wide practical use.

2.3.2.2 Bond Law

Bond presented the equation in the form

$$W = W_i\left(\frac{\sqrt{100}}{d_0} - \frac{\sqrt{100}}{d_p}\right)$$

where d_p, d_0 = the 80% passing size of feed and product, respectively; W = total work; W_i = total work for reduction of a particle from infinite size to 100 µm.

The work index, W_i, is basically an indication of ore hardness, but also includes equipment efficiency. The Bond method has been the mainstay of size reduction circuit. It still holds a value, specially for initial design calculations, and for simple checks on efficiency.

2.3.2.3 Crushing Efficiency

The ratio of the surface energy produced by crushing to the energy consumed by the solid is the crushing efficiency, and is represented by η_c. If e_s is the surface energy per unit area, and A_{wb} and A_{wa} are the areas of product and feed, respectively, and the energy consumed by the motor W_n, than

$$W_n = \frac{e_s\,(A_{wb} - A_{wa})}{\eta_c}$$

The surface energy produced by fracture is small when compared with the total mechanical energy stored in the material at the time of fracture, and most of the latter is transformed into heat. This leads to the crushing efficiencies to be low and results show them range between 0.1 and 2%.

2.3.3
Liberation

The two fundamental operations in mineral processing are release or liberation or freeing of the valuable minerals from waste gangue minerals from each other and concentration, which involves separation of the liberated product. Comminution is the cause, and liberation is its effect. This has also been listed as the first among the different purposes of comminution. It may be pointed out that occasionally, as in beach sands, alluvial deposits and soils, the constituent minerals in these deposits already occur in the form of discrete, single-phase particles, and are usually completely liberated from each other. This job is done by natural agencies. More common however is the rocky material in which the individual mineral grains are firmly bound together. The valuable minerals in such rocks can be released (or in other words liberated) in commerce by comminution implementing breakage of rocks into small fragments.

Figure 2.5 provides a schematic representation of an ore recovery process embedded in a rocky material through a liberation process. It is of interest to present graphically the result of fracturing a lump of ore consisting of gangue in which valuable mineral particles are embedded. The original ore lump is a mixed particle, and after breaking it up into smaller particles, it is virtually certain that some of those particles are entirely gangue, some entirely valuable mineral, while some are mixed. The percentage of mixed particles as a function of the mean particle size, on breaking the lump into finer and finer particles, has been sketched in Figure 2.6. This figure illustrates the fact that the fraction of mixed particles containing both gangue and valuable mineral particles declines during comminution. As the sketch conveys, for mean particle sizes not much smaller than the original size, the majority of the particles is mixed. As the mean particle size begins to approach the valuable mineral particle size, or the separation between the valuable mineral particles (whichever is greater), particles that are not mixed appear and when well below the valuable mineral particle size, almost none of the particles are mixed. This physical liberation of the valuable mineral particles is also facilitated by the tendency of the ore to fracture along the interfaces separating the mineral and the gangue.

To provide an understanding of the optimum results in the linearation process from the elementary level, breakage in an unbroken rock fragment consisting of two mineral grains is considered as an example. The starting point is the unbroken fragment consisting of minerals X and Y. A single random break accomplishes no liberation. Multiple random

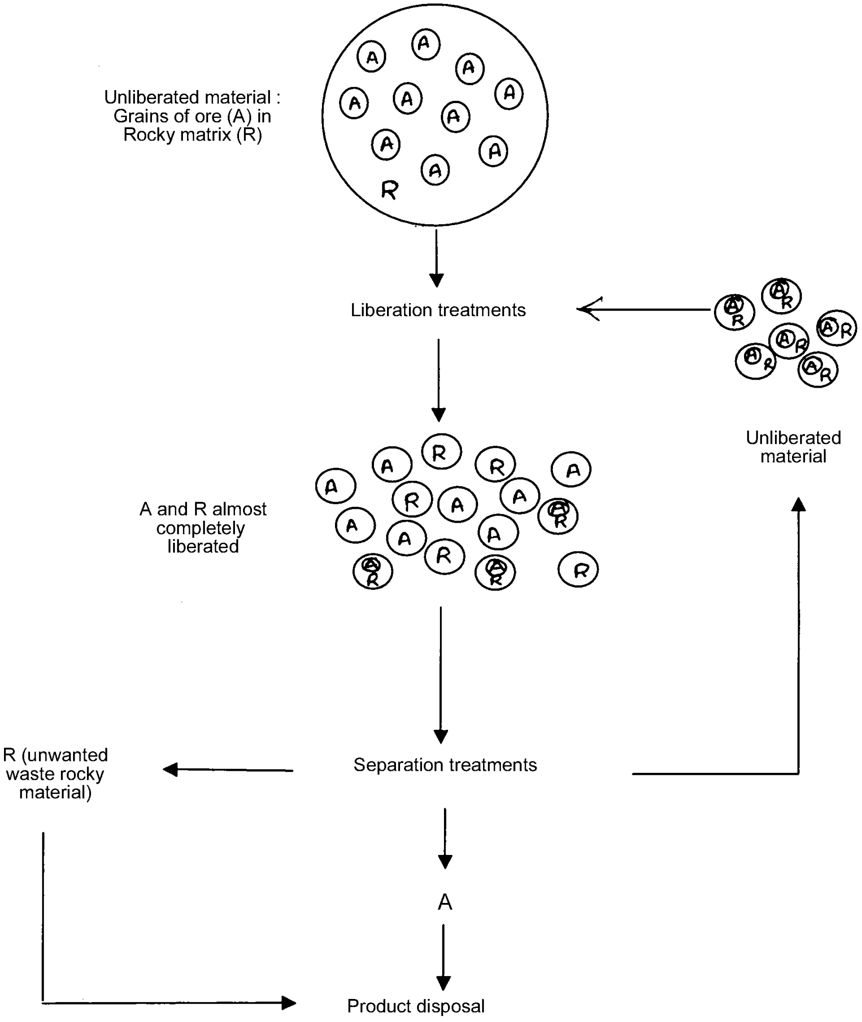


Figure 2.5 Schematic representation of ore recovery process (and the accompanying separation treatments).

breaks liberate some of mineral Y; some particles are liberated of Y, and some are composite particles containing both X and Y. A single nonrandom break along a grain boundary yields perfect liberation of both X and Y. This example substantiates the fact that an ideal kind of liberation would be achieved if a hard rock could be broken along the boundaries between the valuables mineral grains and the gangue. This type of breakage is very difficult, but it is not impossible to achieve. It is well known that it is continually being realized by the natural agencies which give rise to alluvial deposits and beach sands to which reference has been made above. Liberation is accomplished by randomly breaking a rock into progressively smaller fragments. Liberation initializes when the fragment size becomes

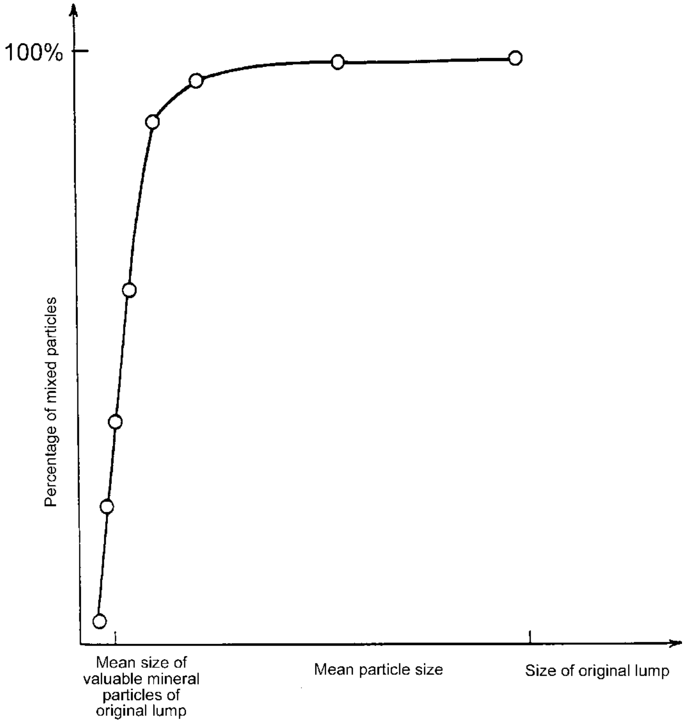


Figure 2.6 Qualitative presentation of liberation versus particle sizes after fracturing.

smaller than the original size of either the gangue or the valuable mineral. Since the gangue is normally present in much greater amounts than the mineral, it may be possible to liberate some of the rocky matrix at a coarser size than the valuable mineral. This type of liberation through random breakage will, unfortunately, only achieve 100% liberation when the rock is severed to zero particle size.

It is important to bear in mind that the grain size distribution of a mineral determines, to a considerable extent, the ease with which that mineral can be liberated from its rocky matrix. Minerals occurring as large grains are liberated at comparatively large sizes, while small grains can only be liberated at very fine sizes. If a mineral allows itself to be free at coarse particle sizes, then the liberated process involved will be comparatively cheap. Moreover, minerals that are coarsely sized are far more easy to concentrate into market products than those finely sized. Consequently, good estimates of grain size distributions of the various minerals in a deposition must be obtained. This information has an important bearing in the assessment of the value of a deposit.

2.3.4
Machine Selection

There are many variables or factors that must be considered while attempting to decide what type of equipment should be chosen for any particular size reduction operation.

The hardness and mechanical structure of the material and its moisture content are among the physical properties which guide selection of the machine. Hardness dictates the size and design of the machine in order that it may have sufficient strength to crush the material. The harder the material, the greater is its abrasive action, and the machine must be so designed as to contain the fewest possible wearing parts. In order to illustrate the importance of the mechanical structure, it may be mentioned that if a material is of a fibrous nature, it cannot be crushed by pressure or by shearing action, but must be torn apart. Wood, for example, is a soft material but on account of its fibrous nature it has to be cut or torn apart. Machines used for subdividing such fibrous materials are often called disintegrators. Moisture also plays an important role in the selection of crushing and grinding machinery. If the moisture content is more than about 4–5%, the material becomes sticky and presents problems in maintaining a free crushing. On the other hand, if the moisture content exceeds about 50%, the material is quite fluid, and under such circumstances the water may actually be used to aid free crushing by washing and carrying away the finely ground product.

The fineness of the material being processed governs the selection of machines. Both the feed and the product sizes are involved in the selection process. Some machines, by their very design, can treat only coarse material, while some others can treat only fine material. Some machines produce a very uniform product, whereas some others, by virtue of their construction, produce a product with considerable variations in size.

Tonnage is a vital factor in determining the economic balance between fixed charges (interest, depreciation and taxes) and operating costs (labour, power and maintenance). The higher the tonnage, the more the money that may have to be spent for the initial installation in order to cut down operating costs such as power and maintenance. The higher the tonnage, the more necessary it is to use machines where operating costs are low.

The chemical reactivity of the material to be processed for size reduction can pose a great problem. For example, the plant construction itself may be exposed to the threat of corrosion. The size reduction process generally raises the temperature of the material in question and this effect may alter the material in some undesirable way.

One very basic factor worth listing perhaps in the very beginning is the necessity of size reduction. It is a costly process not only in terms of money, but also in terms of energy. It may be more advantageous to buy already sized material or to alter some other stage of processing, in order to avoid the size reduction operation altogether.

2.3.5
Machine Types

Alternative terms for size reduction to describe the operations that subdivide solids mechanically are crushing and grinding. An ideal crusher or grinder should (i) have a large capacity; (ii) require a small power input per unit of the product; and (iii) yield a product of the size and/or the size distribution desired.

In the very initial stages of size reduction, when the particles are large, the fracture energy for each particle is high, even though the energy per unit mass is low. The crushers dealing with these initial coarse particles have to be massive and structurally strong. As the particle size decreases the fracture energy for each particle also decreases, but the energy

Table 2.3 Principal types of size reduction machine.

I *Crushers (coarse and fine)*	*II* *Grinders (intermediate and fine)*	*III* *Ultrafine grinders*	*IV* *Cutting machines*
1. Jaw crushers 2. Gyratory crushers 3. Crushing rolls	1. Hammer mills; impactors 2. Rolling-compression mills a) bowl mill b) roller mills 3. Attrition mills 4. Revolving mills a) rod mills b) ball mills; pebble mills c) tube mills; compartment mills	1. Hammer mills with internal classification 2. Fluid energy mills	1. Knife cutters; dicers; slitters

These machines have distinctly different modes of action. The characteristic action of crushers is slow compression. Grinders apply impact and attrition, sometimes combined with compression; ultrafine grinders function mainly by attrition. Cutters, dicers and slitters are characterized by their cutting action.

per unit mass increases more rapidly. This explains why the energy requirement goes up in operations involving size reduction to finer dimensions. This happens in various grinders and other machines used to produce materials in finely divided states. Experience has shown that stage-by-stage crushing and grinding are usually more efficient than attempting to implement a specified size reduction by means of a single machine.

Size-reduction machines are of various types. They may broadly be divided into crushers, grinders, ultrafine grinders and cutting machines. Grinding implies subdividing to a product finer than that obtained by crushing. A listing of size-reduction machines is shown in Table 2.3. Solid materials may be broken in as many as eight or nine ways, but only four of them are commonly used in size-reduction machines: (i) compression; (ii) impact; (iii) attrition; and (iv) cutting. Compression or impact results due to forces applied almost normally to the particle surface. The type of mechanical action, compression, is exemplified by a nut cracker and that of impact by a sledge hammer. The crushers, which are concerned with coarse reduction, use slow compression. In general, compression is used for coarse reduction of solids, to give relatively few fines. Attrition yields very fine products from soft, nonabrasive materials. Cutting gives particles of definite size and sometimes a definite shape, with few (or free of) fines. In the given listing, chipping may also be mentioned as an additional way of breaking solids. Chipping primarily occurs due to oblique forces. All these mechanisms distort the particles and alter their shape beyond certain limits governed by their degree of elasticity, and this causes them to break. Impact action yields coarse, medium, or fine products. The mechanical actions, attritions and cutting, are exemplified respectively by a file and a pair of scissors, or cutters, or slicers.

2.3.5.1 **Crushers**

One important fact about crushers is that their working surfaces do not make contact with each other during size reduction. The size reduction operations, as has been pointed out, are carried out in stages. The first stage is called coarse or primary crushing or primary breaking. The crushers used in this stage take up the run-of-mine ore material and reduce it to a size small enough to be treated by the next crusher, called the secondary crusher. The secondary crushers consume more power as compared with the primary crushers. This is because the work essentially on finer material and yield more new surface than would a primary crusher for an equal reduction ratio. A classification of crushers into primary and secondary crushers has been depicted in Figure 2.7. Crushers are slow-speed size reduction machines for coarse reduction of large amounts of solid materials. The main types are jaw crushers, gyratory crushers, smooth-roll crushers, and toothed-roll crushers. The first three operate by compression and can break huge chunks of hard solids, as in the primary and secondary reduction of rocks and ores. *Toothed-roll crushers* tear the input materials apart as well as crushing it; they usually operate on softer materials such as coal, and soft shale.

Jaw crushers occupy a very important position in the field of mineral processing. Their simplicity of operation and repair, combined with their ruggedness, enable them to be widely used as primary crushers. The three general forms of the jaw crusher are: Blake, Dodge and Universal. These are distinguished by the manner in which the movable jaw is moved in relation to the stationary jaw. In the Blake-type crusher, which is the most common type of jaw crusher, the movable jaw is pivoted at the top so that it has a fixed receiving area and a variable discharge opening. The greatest amount of motion is at the bottom of the V, which implies that there is little tendency for a crusher of this kind to “choke” (by which it is meant that it becomes filled with partially crushed material that will not drop out the discharge). These crushers produce fewer fines than Dodge crushers, and can handle stickier materials; they are also made in much larger sizes than Dodge crushers. In the Dodge-type crusher, the movable jaw is pivoted at the bottom of the V, and thus it has a variable feed and a fixed discharge opening. This design also implies that the greatest amount of motion is at the top of the jaws. This type of crusher yields little oversize product and a great many fines. It also tends to “choke”. On this account, these crushes operate only on moderate amounts of dry, free-flowing solid materials. In the Universal-type crusher, the movable jaw is pivoted at an intermediate position, with the result that it has variable discharge and receiving areas. Apart from jaw crushers, gyratory crushers also occupy an important position in the list of primary crushers.

There are several crushers referred to as secondary crushers. Examples of these (shown in Figure 2.7) are the cone crusher, the roll crusher, and the hammer mill.

A *cone crusher* can be regarded as a modified gyratory crusher. The cone crusher is made in two types: the standard and the short-head, these differing chiefly in the shape of the crushing cavities. It is now a general practice to install ahead of the secondary crusher a vibratory type of screen in order to screen out all the material that has already been crushed fine enough by the primary crusher, thereby increasing the capacity of the secondary crusher. *Roll crushers* operate by the rotation of spring-loaded horizontal rolls which revolve towards each other, drawing the feed material into the rolls. The rolls, as shown in Figure 2.7, have smooth surfaces, but they may also sluggers or protruding teeth. *Hammer mills* form the group of crushers called impact crushers in which the crushing is carried out predominantly by impact. In the mill, the material is fed into the path of fast-moving hammers which swing freely from a central rotor. The feed material is shattered either on impact

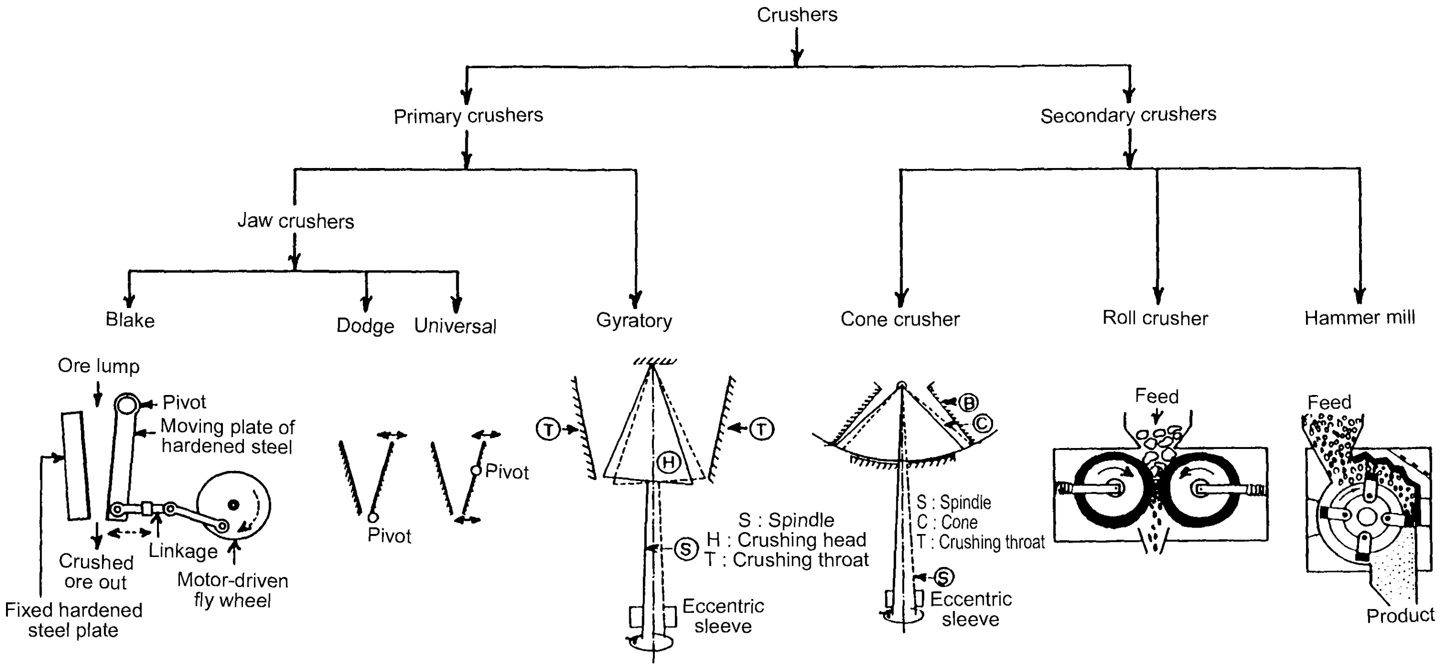


Figure 2.7 Classification of crusher.

with the hammers or during subsequent collisions of the particles with impact plates within the machine. The material stays in the machine until it is fragmented small enough to escape through the gap between the hammers and the machine housing.

In the context of crushing mainly by impact (as in some crushers, including the hammer mills) it may be pointed out that there is a subtle difference between this mode of crushing and that performed by compressive forces, as used in many other crushers. The states of material broken by pressure differ from those broken by impact. Materials broken by pressure have internal stresses which can lead to cracking later. Materials subjected to impact, on the other hand, fracture immediately and there are no residual stresses. This stress-free condition is a desirable feature in some specific situations, as for instance, in stones in such utilities as brick making, building and road construction, in which binding agents (such as bitumen) are subsequently added to the surface. The impact crushers, therefore, have a wider use in the quarrying industry than in the metal mining industry. They are also well suited for crushing those metallic ores which tend to have plasticity and pack when the crushing forces are applied slowly, as in the jaw and the gyratory crushers.

2.3.5.2 **Grinders**

The reduction of ore or similar raw materials to particle sizes smaller than the practical limits attainable by crushing machinery is accomplished in grinding. Infact, grinding is the ultimate stage in the process of comminution. Unlike crushing equipment, the working surfaces of grinding equipment make contact with each other during size reduction. The grinding operations in mineral processing are carried out in what are called are the tumbling mills. The general term tumbling or revolving mill includes the rod mill, the ball mill, the pebble mill, the autogenous mill, and the tube mill.

2.3.6
Circuits

The residence time of ore pulp in a given mill largely determines the mill capacity. If there is a need to grind 150 mm ore to 2 mm, a charge can be loaded in a closed ball mill and there is a need to continued grinding until the entire material attains the required size. However, much of the material would be found to be underground, so that a major portion of the product would be much smaller than 2 mm. The ball mill does not restrict its crushing action exclusively to the large particles, but continues to act on particles that are fine enough (2 mm in the present example under description), grinding them still smaller. Ideally speaking, communition for concentration is reduction of the particle size to a sufficient degree to liberate the ore minerals from the gangue with minimum overgrinding. If 2 mm represents the stage at which liberation is complete, then the batch grinding carried out in the manner stated would have two harmful effects: (i) a large amount of overgound mineral would be contained in the discharge, which would then be difficult to treat by concentration processes; and (ii) there would be expenditure of a large amount of energy in performing this unwanted and harmful overgrinding. However, if an attempt is made to avoid overgrinding by using a continuous process (open-circuit grind) and to have the ore discharged from the mill after it had been ground for a short period, then the product would be considerably oversized.

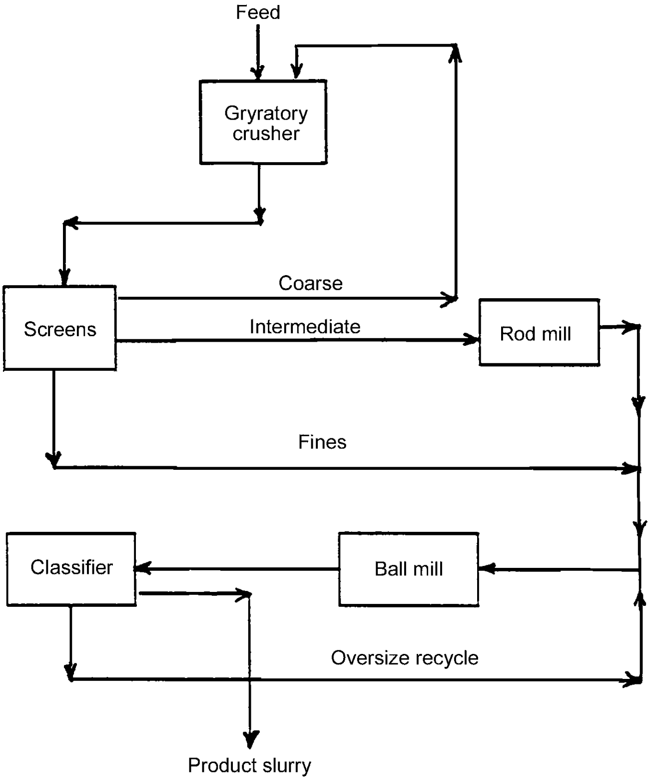


Figure 2.8 Flowsheet for closed-circuit size reduction.

In order to avoid oversize in the product yet at the same time minimize the extent of overgrinding, most ball mills operate in closed circuit with a classifier or a screen. The classifier takes the ball mill discharge and separates it into two portions. One portion is the finished product, which is ground as finely as needed. The other portion is the oversize material, which goes back to the mill for further grinding, and this is identified as the circulating load of the system. It is in this manner that the material can be made to traverse through the ball mill rapidly enough to prevent any serious overgrinding; this leads almost to what is called sliming, but the classifier must prevent the accompanying oversize material from going out of the circuit. The ball mill and classifier combination, then, results in a continuous operation, the output of which is a product of required size. The ball mill, of course, tends to work on coarse material as much as possible. A flowsheet for closed-circuit size reduction is shown in Figure 2.8.

2.3.7
Operational Aspects

There are a number of operational aspects of size reduction, the important points being feed control, mill discharge, and thermal effects.

A mill should preferably operate with feed of properly sized particles. It goes without saying that particles should not be so greatly sized that cannot be ground by the mill. In cases where there are associations of too many fines the effectiveness of many machines, especially intermediate crushers and grinders, are seriously jeopardized. With some solids, certain pretreatments (for example pre-compression or chilling) of the feed before it enters the mill may greatly increase the ease with which it may be comminuted. In those mills which are continuous it is necessary that the feed rate be controlled within close limits in order to avoid choking or erroneous behaviours in load, yet make thorough use of the machine capacity.

In the case of a continuous mill the rate of mill discharge is required to equal the rate of feed in order to avoid build-up of material. Furthermore, the rate of discharge needs to be such that the working parts of the mill can operate most effectively on the substance to be broken. In a jaw crusher, for example, particles may be collected in the discharge opening and subjected to crushing many times before they clear. As has been pointed out earlier, this is an unnecessary expenditure of energy if many particles are so disposed that they are subjected to crushing to an extent beyond what is required or necessary. With fairly coarse products, as many machines produce, gravitational force is mostly sufficient to provide free discharge. Usually the product clears from the bottom of comminuting machines, but other types of discharges also exist, such as circumferential discharge and trunnion charge, which are used in particular types of machines used for communition. In discharging mills used for fine and ultrafine grinding, the gravitational force is replaced by the drag of a fluid carrier which may be a liquid or a gas. Wet grinding with a liquid carrier is common in revolving mills. It results in more wear on the chamber walls and on the grinding medium than does dry grinding. However, it economizes energy, enhances capacity, and simplifies handling and product classification operations. A sweep of air, steam, or inert gas removes the product from some machines, as for instance, attrition mills, fluid-energy mills, and many hammer mills. The powder is extracted from the gas stream by employing bag filters or cyclone separators.

In dealing with thermal effects it may firstly be pointed out that only a very small portion of the energy supplied to the solid substance in a grinding mill is utilized in creating a new surface. The major portion of the energy, therefore, is transformed into heat, which may raise the temperature of the solid substance inside by several degrees. The solid may melt, decompose, or may even explode, depending of course on the material in question and its characteristics, unless this heat is removed. For this reason cooling water or refrigerated brine is often circulated through the coils or jackets in the mill. Sometimes the air blown through the mill is refrigerated, or solid carbon dioxide (dry ice) is made to accompany the feed to the mill. Still more severe reduction of temperature is attained with liquid nitrogen, to provide grinding temperature below about –38 °C. The objective of using such low temperatures is to charge the fracture features of the solid substances, commonly by making them more brittle. While heat removal on some occasions becomes a necessity, there are also occasions when heat addition becomes a necessity. Heat addition to the mill is commonly carried out by circulating hot air or flue gas through it. In this mode the mill simultaneously grind and dry a moist solid.

2.4
Mineral Separation

In general, the necessity that frequently arises to separate the components of a mixture into individual fractions needs little elaboration. The fractions may differ from each other in particle size, in phase, or in chemical composition. It is important in this context to examine Table 2.4, which lists the different objectives with which mechanical separations are performed. A number of methods have been invented for accomplishing such separations and several unit operations are devoted to them. In practice, many separation problems are encountered, and the best suited method must be applied to the problem. Procedures for separating the components of mixtures fall broadly into two categories. One category includes methods, called *diffusional operations*, that involves phase changes or transfer of material from one phase to another. The second category includes methods, called *mechanical separations*, which are useful in separating solid particles or liquid drops. Mineral separation may be regarded as simply another name for mechanical separation as specifically applied. Mechanical separations are applicable to heterogeneous mixtures, but not to homogeneous solutions. Colloids, which are an intermediate class of mixtures, are not usually treated by the methods described in this present section, which is concerned primarily with particles greater 0.1 micron in size. The techniques described are based on physical differences among the particles such as size, shape, or density. They are applicable to separating solids from gases, liquid drops from gases, solids from solids, and solids from liquids. This indeed a varied list, but two general methods are used for the purpose. One is the use of a sieve, septum, or membrane, such as a screen or a filter, which holds one component and allows the other to clear. The other method is the utilization of differences in the rate of sedimentation of particles or drops as they move through a liquid or gas. For special problems, other methods exploit differences in the wettability or electrical or magnetic properties of the substances, and these form the subject matters for later sections of this chapter.

Once the comminution process is completed, the succeeding operations in mineral processing are taken over by what is known as separation. Regardless of the method or methods used, the aim is always the same-to take a natural aggregate of minerals (an ore) and separate it into two or more mineral products. In general, the products of separation are (i) the concentrate which contains the valuable minerals; and (ii) the tailings which contain primarily materials of little or no value. It may be borne in mind that minerals have been liberated, either by grinding or by chemical means, must usually be “sized” prior to

Table 2.4 A representative listing of wide and varied aims of mechanical separations.

1. Purification of a crude product by removing from it any contaminating impurities.
2. Separation of a mixture of two or more products into the individual pure products.
3. The stream discharged from a process step may consist of a mixture of product and unconverted raw material, which must be separated and the unchanged raw material recycled to the reaction zone for further processing.
4. A valuable substance, such as a metallic ore, dispersed in a mass of inert material must be liberated for recovery and the inert material discarded.

their separation from each other because the efficiencies of most separation methods are improved when closely sized fractions are used.

A common feature of all separation processes is that they are imperfect – some of the materials of no value contaminate the concentrate to some extent, and some of the minerals of value are always present in the tailings in small amounts.

It is now necessary to consider some parameters which qualify a separation method in mineral processing. The term “recovery”, which is frequently used, refers to the percentage of the total metal contained in the ore that is recovered in the concentrate. Thus, a recovery of 70% implies that 70% of the metal in the ore has reported to the concentrate, and the balance to the tailings. The purpose of calculating the recovery is essentially to determine the distribution of the metal value contained in the feed (or heads) among the various products of the separation operations. Another term which is used often is the “ratio of concentration” which is the ratio of the weight of the feed (heads) to the weight of the concentrates. Thus, if 1 kg of concentrate is obtained from 50 kg of ore, the ratio of concentration is 50 to 1. This ratio of concentration is a measure of the efficiency of a concentrating operation, and it is related to the grade (or assay) of the concentrate; the value of the ratio of concentration will generally increase with grade of concentrate. The ratio of concentration and the recovery are essentially independent of each other. It is necessary to know both the quantities for the purpose of evaluating a given operation. One may, for example, obtain a very high grade of concentrate and ratio of concentration simply by picking a few pieces of pure sphalerite from a kilogram of zinc ore. However, the recovery in such a case is obviously very low. On the other hand, a concentration process might show a recovery figure of over 90% of the metal, but it might also put well over 50% of the gangue minerals into the concentrate. To cite an extreme example, one can obtain 100% recovery by not concentrating the material at all! The recovery and the grade generally bear an inverse relationship in any concentration process. If one attempts to obtain a very high grade concentrate, the tailings assays are higher and the recovery is low. On the other hand, if one attempts to recover as much metal as possible, there will be more gangue in the concentrate, and the grade of the concentrate and the ratio of concentration will both come down. A concentration ratio of 2 to 1 might be acceptable for certain high-grade nonmetallic ores, but a ratio of 50 to 1 might be considered too low for a low-grade copper ore; ratios of concentration of several million to one may be the common place for diamond ores. The objective of milling operations is to keep the values of ratio of concentration and recovery as high as practicable.

For a general analytical approach, reference may be made to Figure 2.9, showing the input stream breaking into two separation streams: the concentrate and the tailings. The weights of the feed, the concentrate and the tailings have been shown as W_f, W_c and W_t respectively and their corresponding assays are f, c, and t. The following two relations obviously hold

$$W_f = W_c + W_t$$
$$f\,W_f = c\,W_c + t\,W_t$$

The first of these two equations states that the weight of the input equals the sum of the weights of the products, while the second equation states that the weight of one constituent in the feed equals the sum of the weights of that constituent in the products.

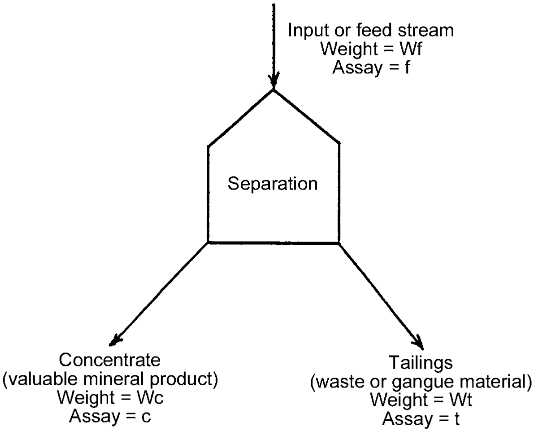


Figure 2.9 A two product separation process.

Multiplying the first equation by t, the following relationship is obtained:

$$t\,W_f = t\,W_c + t\,W_t$$

Subtracting this third equation from the second, one obtains

$$W_f\,(f - t) = W_c\,(c - t)$$

or

$$\frac{W_f}{W_c} = \frac{c - t}{f - t}$$

As defined earlier, the ratio of the weight of the feed to the weight of the concentrate is called the ratio of concentration. Denoting this by k, the following relationship can now be written:

$$k = \frac{c - t}{f - t}$$

From the relative weights of the concentrate and the tailings and their assays, that fraction of a certain mineral or gangue contained in the feed or input material which is recovered in the concentrate can be obtained. This, defined earlier, is known as the recovery (R). When expressed as a percentage,

$$R = 100 \cdot \frac{W_c \cdot c}{W_f \cdot f}$$

or

$$R = 100 \cdot \frac{1}{k} \cdot \frac{c}{f} = 100 \cdot \frac{c\,(f - t)}{f\,(c - t)}$$

Thus R and k can be obtained from data pertaining only to the assays of the materials involved in the process. This relationship is very useful when the weights of the feed and of the concentrate are not available. It may be mentioned here that the quantity R, by itself, gives no information about the quantities of the concentrate and the tailings. However, R and k, when considered jointly, can adequately express metallurgical results. The enrichment ratio is c/f which is the ratio of the grade of the concentrate to the grade of the feed.

Separation processes, as could be seen from Figure 2.1, position themselves at the back end of the sequence in operations in the mineral processing flowsheet. The front-end operations has been found virtually to terminate with the liberation or the size-reduction processes involving crushing and grinding. It is important to limit the amount of size reduction to that at which adequate liberation is accomplished. The term adequacy is related to the cost involved in comminution and to performance of the concentration methods that follows. The concentration is obtained by separation processes which rely on differences in the properties of the particles, the physical and physico-chemical characteristics of minerals. In this context, it will only be relevant to refer to Table 2.5 which presents a summary of the processes along with the properties of the minerals that are exploited.

Broadly speaking, separation processes can be divided into two main categories: sizing separation, and concentration separation. In some cases, sizing separation is carried out with a view to obtaining a product which must meet a size specification. More importantly, however, sizing separation is applied to control the size of material to be fed to other equipment. Such control is necessary because each equipment has an optimum size of material that it can handle in an efficient manner. The two basic operations in a sizing separation process are classification and screening. The chief objective of concentration separation is to obtain valuable minerals in more concentrated forms. The processes employed for accomplishing this objective rely on both physical and surface chemical properties of the minerals. The main concentration separation processes are gravity concentration, magnetic separation, electrostatic separation, and flotation. Later in the chapter the sizing separation and the concentration separation processes are described. However, before dealing with these a diversion is taken into the mechanics of movement of particles in a fluid medium.

It will be both interesting and instructive to describe the separation process principles for two substances: one a quartz–magnetite, and the other a quartz–hematite. The quartz–magnetite when ground would consist of liberated quartz particles, liberated magnetite

Table 2.5 Separation processes.

Physical and physico-chemical properties	*Comminuted size, diameter (d), mm*	*Separation process employed*
Shape and size	$d > 0.04$	Screening and classification
Specific gravity	$d > 0.1$	Wet or dry gravity separation
Electrical charge	$0.05 < d < 5$	Electrostatic separation
Magnetic susceptibility	$0.1 < d < 5$	Wet or dry magnetic separation
Surface properties	$0.001 < d < 1$	Flotation
Colour	$d > 50$	Sorting
Radioactivity	$5 < d < 1000$	Radiometric sorting

particles and some quartz-magnetite composite particles. The magnetite particles differ from the quartz particles in density, magnetic response and surface chemistry, and any one or combination of these processes could be made the basis of a separation technique that would provide mineral fractions consisting largely of clean magnetite or clean quartz. Unfortunately, the composite quartz–magnetite particles processes a range of property values between those for clean magnetite and those for clean quartz, and these must be returned for further comminution and further liberation. In this context reference may be drawn to Figure 2.5 which depicts this sequence of events.

The quartz-hematite combination presents a different picture. In this case, the differences between the magnetic properties of the liberated hematite and the liberated quartz would not be adequate to constitute the basis of development of an adequate separation procedure. It is necessary to devise a method for altering a property of one or both minerals in order to bring an adequate property difference. In the present example of quartz and hematite, the magnetic properties of the two are similar, but if they are thermally treated in a reducing atmosphere then the hematite is converted into magnetite, while the quartz remains unaltered. Thus, following the indicated thermal treatment, the magnetic properties of the two minerals would be vastly different and a magnetic separation process can readily separate quartz from magnetite.

2.5

Fluid Dynamic Principles

Many mechanical separations involve the movement of solid particles or liquid drops through a fluid. The fluid may be gas or liquid, and it may be flowing or static. As some assortment of examples mention may be made of the removal of dust and fumes from air or flue gas, the removal of solids from liquid wastes to permit discharge into public domain, and of the recovery of acid mists from an acid plant gaseous wastes.

In many problems in the field of mineral processing, the influence of fluids on solids is of considerable interest. The fluid may be static with the solid moving through it, or the solid may be static with the fluid flowing past it. Two typical unit operations can be cited as examples involving liquids flowing through beds of solid particles. One is filtration in which the bed of solids consists of small particles that are removed, by a filter cloth or fine screen, from the liquid. The other example is ion-exchange, in which a single liquid flows through a bed of granular solids. These examples essentially represent the flow of a single fluid phase through a column of stationary particles. The situation where the solid is immersed in, and surrounded by, fluid is in essence the subject to which this particular section of the present text remains principally addressed. It is generally of not much concern which phase, solid or fluid, is considered static. It is only the relative motion between the solid and fluid phases that is of importance. The different phenomena or principles involved with settling of particles in a liquid as the fluid medium, and their treatment in their application mode in accomplishing separation of materials, will now be described.

2.5.1
Particle Settling Phenomena

A particle falling freely in vacuum is subjected to a constant acceleration, and its velocity increases continuously. The velocity at any point depends only on the distance from the starting point, and is independent of the size and the density of the particle. Thus a heavy stone and a feather fall at exactly the same rate in an evacuated system. However, in the event of a particle falling in a fluid medium, there is resistance to this fall or movement. The resistance increases as the velocity of the particle increases, and this continues until the forces tending to accelerate the particle and the fluid resistance forces become equal. The particle is then said to have attained its terminal velocity; it continues to fall, but with a uniform velocity.

The nature of resistance which a particle encounters during its descent in a fluid medium is the viscous resistance and the turbulent resistance. The relative magnitudes of these resistances depend upon the velocity of the descending particle. When it moves slowly in the fluid medium, the motion is smooth; this is because the film of the fluid medium in contact with the particle moves with it, while the fluid medium is motionless beyond a certain short distance. There exists a zone of intense shear in the fluid medium all around the descending particle between these two positions. Effectively, all resistance to motion is due to the shear forces or the viscosity of the fluid medium and this resistance is therefore called *viscous resistance*. The viscous resistance predominates when the particle is small and its surface to volume ratio is large. The nature of the flow of the fluid medium around the slowly descending particle is streamline flow (also referred to as laminar flow). When the particle moves with a high velocity, the viscous resistance is relatively small and the main resistance to its motion arises from the displacement of the fluid medium by the particle. This is known as *turbulent resistance* and the corresponding flow is called turbulent flow which causes vortices and eddies to form at the back of the particle in motion. This effect is due to the rapid displacement of the fluid medium, brought about by the rapidly descending particle. As has already been mentioned, when only viscous resistance is present, the fluid medium flows around the particle in a streamlined fashion and the formation of eddies does not occur. Unlike viscous resistance, turbulent resistance is predominantly experienced by fast-moving, large-sized particles. Whether viscous or turbulent resistance predominates, the acceleration of particle in a fluid quickly falls and the terminal velocity is rapidly attained.

The movement of a particle through a fluid demands that a density difference exists between the particles and the fluid. An external force is also required to induce motion to the particle relative to the fluid. The external force is usually gravity, but when gravity is not adequately strong, centrifugal force (which can be many times that of gravity) is employed. If the particle is of equal density of that of fluid, the buoyant force from the immersion of the particle in the fluid will counterbalance an external force, however large, and the particle will not move through the fluid. The greater is the difference in density, the more pronounced is the effectiveness of the process.

There are essentially three forces that act on a particle moving through a fluid. They are: (i) the external force, gravitational or centrifugal; (ii) the buoyant force, which acts parallel with the external force, but in the opposite direction; and (iii) the drag force which appears whenever there is relative movement between the particle and the fluid. The drag force acts to oppose the motion and acts parallel with the direction of movement but in the opposite direction.

In the general case, the direction of movement of the particle relative to the fluid may not be parallel with the direction of the external and buoyant forces, and the drag force then creates an angle with the other two. This is known as two-dimensional motion. In this situation, the drag force must be resolved into two components, which complicates the treatment of particle mechanics. This presentation considers only the one-dimensional case in which the lines of action of all forces acting on the particle are collinear.

Thus as pointed out above, further treatment on the mechanics of particle motion remains confined only to one-dimensional motion of particle through fluid. A particle of mass m moving through a fluid under the action of an external force F_e is considered. The velocity of the particle relative to the fluid is taken to be v. The buoyant force on the particle is taken to be F_b, and the drag force be F_D. Then, the resultant force on the particle is $F_e - F_b - F_D$, the acceleration of the particle is dv/dt, and the resulting equation of motion is given by

$$m \frac{dv}{dt} = F_e - F_b - F_D$$

The external force can be expressed as a product of mass and the acceleration a_e of the particle from this force, and

$$F_e = m\, a_e$$

The buoyant force is, by the well-known Archimedes principle, the product of the mass of the fluid displaced by the particles and the acceleration from the external force. The volume of the particle is m/ρ_s, where ρ_s is the density of the particle, and the particle displaces this same volume of fluid. The mass of fluid displaced is $(m/\rho_s)\,\rho_f$, where ρ_f is the density of the fluid. The buoyant force is, then,

$$F_b = \frac{m\, \rho_f\, a_e}{\rho_s}$$

If the external force is gravity, a_e is g, and the above equation takes the form:

$$F_b = \frac{m\, \rho_f\, g}{\rho_s}$$

When the terminal velocity is reached, $dv/dt = 0$. With the mathematical expressions thus far expressed, and substituting them in the equation of motion originally given, one obtains the following expression:

$$F_D = m\, g - \frac{m\, \rho_f\, g}{\rho_s}$$

substituting for a spherical particle

$$m = \frac{\pi\, d^3\, \rho\, s}{6}$$

into the above equation one finally obtains the following expression:

$$F_D = \frac{\pi}{6}\, g\, d^3\, (\rho_s - \rho_f)$$

It may be added that a centrifugal force appears whenever the direction of movement of a particle is changed. The acceleration from a centrifugal force from circular motion is $a_e = r\,\omega^2$, where r is radius of path of particle and ω is angular velocity. These values of a_e may be substituted in the relationships for F_e and F_b and equation for dv/dt can be evaluated. The equation for terminal velocity v_t is finally obtainable, for centrifugal settling by taking $dv/dt = 0$ in the same way as was performed for gravitational settling. Reference may be drawn to the drag force, F_D; this is given by the expression

$$F_D = 0.5\, f_D\, \rho_f\, v^2\, A$$

where f_D is the drag coefficient and A is a characteristic area taken to be that obtained by projecting the particle on a plane perpendicular to the direction of flow. The drag coefficient, f_D, is commonly expressed as a function of Re, which is a dimensionless number known as Reynolds number and is given by

$$\mathrm{Re} = \frac{d\, \rho_f\, v}{\eta}$$

where η and ρ_f are respectively the viscosity and the density of the fluid medium, and d is the particle diameter. For nonspherical solids the drag coefficient f_D must be used for a given value of Ψ, where Ψ is the ratio of the surface area of a sphere which has the same volume as the particle to the actual surface area of the particle.

The relationship between f_D and Re is shown graphically in Figure 2.10. The graph can be divided into three regions: a laminar flow or Stokes region; an intermediate region; and a turbulent flow or Newton region. It was Stokes who assumed that under laminar flow conditions (when $\mathrm{Re} < 0.2$) the drag force acting on a particle is entirely due to viscous forces within the fluid and derived the following expression for this drag force on a spherical particle of diameter *d*,

$$F_D = 3\, \pi\, d\, \eta\, v_t$$

where v_t is the terminal velocity. Substituting this expression for F_D in the last equation involving F_D ($F_D = \pi/6\, g\, d^3\, (\rho_s - \rho_f)$) one obtains the following relationship:

$$v_t = \frac{d^2}{18} \left(\frac{\rho_s - \rho_f}{\eta} \right) g \quad \text{(laminar flow, Re < 0.2)}$$

This expression for the terminal velocity (i.e., the constant velocity that the particle ultimately attains), is called Stokes' law. When the Reynolds number is high, say usually greater than of the order of 800, the flow becomes turbulent flow and eddies form. It was Newton

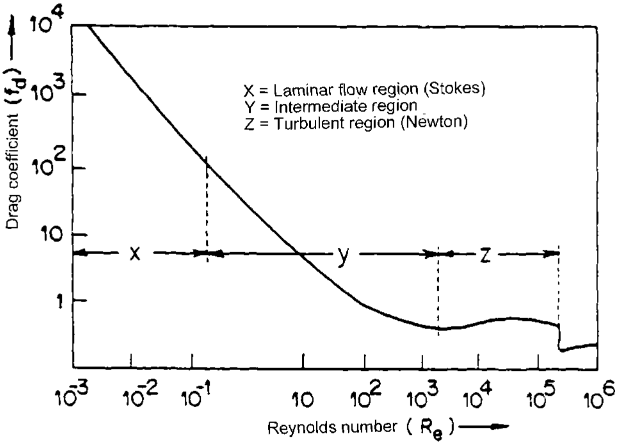


Figure 2.10 Relationship between drag coefficient (f_d) and Reynolds number (Re) for a spherical particle settling in a liquid.

who assumed that in such a situation the drag force is entirely due to turbulent resistance. He deduced the following expression for this drag force:

$$F_D = 0.055\, \pi\, d^2\, v_t^2\, \rho_f$$

Substituting the above relationship into the equation involving F_D one arrives at the following expression for the terminal velocity:

$$v_t = \left[\frac{3\, d\, g\, (\rho_s - \rho_f)}{\rho_f}\right]^{0.5} \quad \text{(turbulent flow, Re > 800)}$$

This expression for terminal velocity is called Newton's law. Stokes' law for the terminal velocity (laminar flow) in a particular medium can be expressed in simplified form as

$$v_t = k_1\, d^2\, (\rho_s - \rho_f)^{0.5}$$

Likewise, Newton's law for terminal velocity (turbulent flow) can be expressed in simplified form as

$$v = k_2\, [d\, (\rho_s - \rho_f)]^{1/2}$$

where k_1 and k_2 are constants, and ($\rho_s - \rho_f$) is known as the effective density of the particle of density ρ_s in a medium of density ρ_f.

To sum up, reference is drawn to Table 2.6 which presents expressions for the terminal velocity in the laminar range as derived from Stokes' law and that in the turbulent range as derived from Newton's law, and their simplified versions. It may be noted that Stokes' law contains the factor η, which is the viscosity of the medium, but that this factor is absent in Newton's law. Both laws indicate that the terminal velocity of a particle in a particular fluid

Table 2.6 Terminal velocities based on Stokes' and Newton's laws.

Conditions	***Terminal velocity (v)***		***Simplified versions of terminal velocity (v)***	
	Stokes' law	Newton's law	Stokes' law	Newton's law
Particles moving down in the medium with a low velocity; relatively small particles (< 0.01 cm in diameter); laminar flow; viscous resistance; Reynolds' number low (Re < 2)	$\frac{d^2}{18}\frac{(\rho s - \rho f)}{\eta} g$	–	$k_1 d^2 (\rho s - \rho f)$	–
Particles moving down in the medium with a high velocity. Relatively large particles (> 0.5 cm in diameter); turbulent flow; turbulent resistance, Reynolds' number high (Re > 800)	–	$\left[\frac{3 d g (\rho s - \rho f)}{\rho f}\right]^{\frac{1}{2}}$	–	$k_2 [d (\rho s - \rho f)]^{\frac{1}{2}}$

is a function of its size and density. The dependence of the terminal velocity on the particle size is considerably different in the two flow conditions. Under laminar flow conditions the velocity varies as d^2, whereas under turbulent flow conditions it varies as $d^{0.5}$ However, regardless of the law that applies, the following two observations can be made: (i) if two particles have the same density, the particle with the larger diameter (size) will have the larger terminal velocity; and (ii) if two particles have the same diameter (size), the particle with the greater density will have the larger terminal velocity.

It will now be appropriate to describe the applications of these laws in the context of particles settling under different conditions, that lead to their separation.

2.5.2
Free Settling and Hindered Settling

Free settling means that the particle is at a sufficient distance from the boundaries of the container and from other particles, and that the density of the medium is that of a pure fluid, as for example, water. If two different mineral particles of densities ρ_1 and ρ_2 and diameters d_1 and d_2 respectively fall in a fluid of density ρ_3 with the same settling rate, then their terminal velocities must be the same. From Stokes' law this gives for the laminar range

$$d_1^2(\rho_1 - \rho_3) = d_3^2(\rho_2 - \rho_3)$$

so that

$$\frac{d_1}{d_2} = \left(\frac{\rho_2 - \rho_3}{\rho_1 - \rho_3}\right)^{1/2}$$

The above expression is known as the free settling ratio of the two particles (minerals) under laminar conditions. In a similar way the ratio under turbulent conditions can be obtained from Newton's law as

$$\frac{d_1}{d_2} = \frac{(\rho_2 - \rho_3)}{(\rho_1 - \rho_3)}$$

The above two expressions for the ratio d_1/d_2 essentially give the ratio of particle sizes required for the two minerals to fall at equal rates under the two specified flow conditions, laminar and turbulent. As an example, let us consider a mixture of particles of the two minerals calcite (with $\rho_1 = 2.7$) and scheelite (with $\rho_2 = 6.0$) to be classifying in water ($\rho_3 = 1.0$). From calculations, one obtains that in the laminar region $d_1/d_2 = 1.71$ and in the turbulent region $d_1/d_2 = 2.94$. The free settling ratio for particles obeying Newton's law is, therefore, larger than that for particles obeying Stokes' law. It is also known that Newton's law is obeyed by coarse particles and Stokes' law by comparatively finer particles. All these amount to saying that the free settling ratio is larger for coarse particles obeying Newton's law than for fine particles obeying Stokes' law. This means that the density difference between mineral particles has a more pronounced influence on classification at coarser size ranges. This is an important consideration where gravity concentration is being used. Overcomminution of the mineral matter should be avoided, and the particles should be fed to the separator in as coarse a condition as feasible so that a rapid separation can be accomplished, thus exploiting the enhanced influence of the density difference. The increased gravity influence does, however, imply that fine heavy minerals are more prone to be overground in conventional ball-mill-classifier systems, so it is better where practicable to employ rod mills for the primary coarse grind.

From the above two expressions for the ratio d_1/d_2, a general expression for the free settling ratio can be written down as

$$\frac{d_1}{d_2} = \left(\frac{\rho_2 - \rho_3}{\rho_1 - \rho_3}\right)^{n}$$

In the above expression, n is 0.5 for small particles obeying Stokes' law and 1 for large particles obeying Newton's law.

Hindered settling refers to a situation where settling takes place in a carrier liquid with a high concentration of solids. In this situation the particles are so close together that collision among them is practically continuous, and the relative fall of particles involves repeated pushing apart of the lighter by the heavier particles. The system begins to behave as a heavy liquid whose density is that of the pulp rather than that of the carrier liquid. Taking the density of the medium now as 1.5 (instead of unity as in the previous case of free settling) and considering the minerals calcite and scheelite as before, the hindered settling ratio in the laminar range for the particles obeying Stokes' law is

$$\frac{d_1}{d_2} = \left(\frac{6.0 - 1.5}{2.7 - 1.5}\right)^{1/2} = 1.93$$

while in the turbulent range, for the particles obeying Newton's law, this ratio is

$$\frac{d_1}{d_2} = \left(\frac{6.0 - 1.5}{2.7 - 1.5}\right) = 3.75$$

It is seen that these hindered settling ratios are larger than the corresponding free settling ratios. This example also highlights the fact that hindered settling reduces the effect of size, while increasing the effect of density on classification. This is an important point in classifier design.

2.5.3

Particle Separation

Particle separation based on differential-settling methods utilize the difference in terminal velocities that can occur between materials of different density. The density of the medium is less than that of either material. The shortcoming of the method is that, since the mixture of materials to be separated covers a range of particle sizes, the larger, light particles settle at the same rate as the smaller, heavy ones. This gives rise to a mixed fraction. In differential settling, both light and heavy materials settle through the same medium. This method brings in the concept of equal-settling particles to which reference has already been made in the previous section dealing with the phenomenology on particle settling in a liquid. It may, however, be recounted that although a denser particle of definite size settles faster than a less dense particle of the same size, a larger less dense particle can have the same velocity as a smaller denser particle. It may also be recounted that a relationship between the diameters of such equal-settling particles is found by assuming the terminal velocity of material 1, v_1, to be equal to the terminal velocity of material 2, v_2 ($v_1 = v_2$). As a consequence the general expression that is derived is shown below:

$$\frac{d_1}{d_2} = \left(\frac{d_2 - d_3}{d_1 - d_3}\right)^{1/(1+n)}$$

Particles of materials 1 and 2 whose diameters conform to the above equation are called equal-settling particles:

If the particles settle in the Stokes' law range, $n = 1$, and the equation above becomes

$$\frac{d_1}{d_2} = \left(\frac{d_2 - d_3}{d_1 - d_3}\right)^{0.5}$$

which is same as shown earlier.

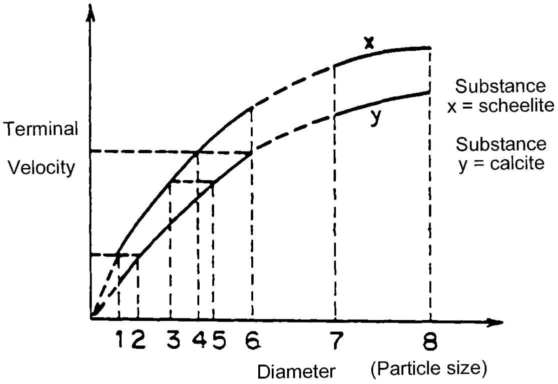


Figure 2.11 Equal-settling particles.

The significance, in a separation process, of the equal settling ratio of diameters is shown by Figure 2.11, in which curves of terminal velocities against particle diameters are plotted for two components x and y, for Stokes' law settling. Substance x is assumed to have the higher density and a mixture of x and y particles in the size range indicated by 7–8 is considered. It is observed that the slowest (and the smallest) particle of x moves faster than the fastest (and the largest) particle of y; hence all material x will settle faster than all material y. In this case separation is possible. On the other hand, a mixture of x and y particles in the size range 1–6 is considered. In this case, it is apparent that the slowest x particle (of diameter 1) is considerably slower than the fastest y particle (of diameter 6), and that every particle of x in the size range 1–4 has the same velocity as a larger particle of y in the size range 2–6. Thus, there are three fractions possible: (i) a fraction comprising entirely y, every particle of which is in the size range 1–2; (ii) a fraction comprising entirely x, every particle of which is in the size range 4–6; and (iii) an intermediate mixed fraction comprising x and y particles, the x particles of which are in the size range 1–4, and the y particles in the range 2–6. The heavier substance x can be considered to be scheelite, or alternatively, galena and the lighter substance y to be calcite, of alternatively, quartz.

Inspection of the general equation shown above for equal settling particles shows that the sharpness of settling is enhanced provided the density of the liquid medium is increased. Since, in hindered settling, the apparent density of the medium ρ_3 is that of the entire suspension and is greater than the density of the liquid itself, hindered settling is more effective in separation than is free settling. The rate of hindered settling is less, however, than that of free settling. it is also clear from Figure 2.11 that intermediate fraction can be decreased or eliminated by closer sizing of the feed. For example, if the size range of the feed is from 7 to 8 in Figure 2.11, complete separation is feasible.

2.6
Classification

It will be recalled from the earlier section that classification is one of the sizing separation processes, the other being screening. The two differ in that while screening does not take into consideration the specific gravity of the particles, it is as important a parameter as the particle size in classification. Classification, generally, is a practice in which a material aggregate of mixed sizes and different specific gravities is allowed to settle through a medium, which may be either in motion or at rest, with the result that the material is separated into two or more products. Differential settling causes the separation. The medium ordinarily used is water, though other liquids, and air or other gases may also be used.

The efficiency of a classifier is represented by a performance or partition curve, similar to that used for screens, which relates to the particle size to the percentage of each size in the feed that reports to the underflow. The most important industrial application of classifiers is to reduce overgrinding in a mill by separating the milled product output into coarse and fine fractions in order that the fines can be removed as they are produced and the coarse returned for further comminution.

Classification is more suitable for particles in the finely divided state where screens perform poorly. A classifier may consists of a column with rising fluid and descending particles. Particles either sediment or settle (sink) or are carried upward with the fluid. This phenomenon occurs based on the terminal velocities as discussed earlier. Particles undergo either free or hindered settling depending upon the solid to fluid ratio. Classification is pronouncedly influenced by density differences at coarser size ranges, and size differences play a dominant role at fine size ranges. Free settling conditions emphasize the influence of size. The hindered settling, on the other hand, emphasizes the influence of density. Thus, the classifiers are capable of separating smaller heavier particles from larger lighter ones, or relatively coarse from relatively fine particles.

2.6.1
Classifier Machinery

A common problem in both chemical and metallurgical practice is that of separating relatively coarse particles, which are called sands, from a slurry of fine particles, which are called slimes. The most common method is to use continuous settling equipment called classifiers.

As representative examples of the various machineries used for classification mention may be made of mechanical classifiers, hydraulic classifiers, and hydrocyclones. Simplified sketches of these have been shown in Figure 2.12 (A–C).

2.6.1.1 Mechanical Classifiers

A typical mechanical classifier for coarse particles is shown in Figure 2.12 (A). In this device the settling vessel is an inclined through with a liquid overflow at the lower end. Slurry is continuously fed to the trough at an intermediate point. The flow rate and slurry concentration are adjusted so that the fines do not have time to settle but are carried out with the liquid leaving the classifier. Larger particles sink to the floor of the trough, from which they must be removed. Different types of classifiers differ chiefly in the means by which they perform this. In the crossflow classifier in Figure 2.12 (A), the trough is semicylindrical, set at an angle of about 12° with the horizontal. A rotating helical conveyor moves the settled solids upward along the floor of the trough, out of the pool of liquid and up to the sands-discharge chute.

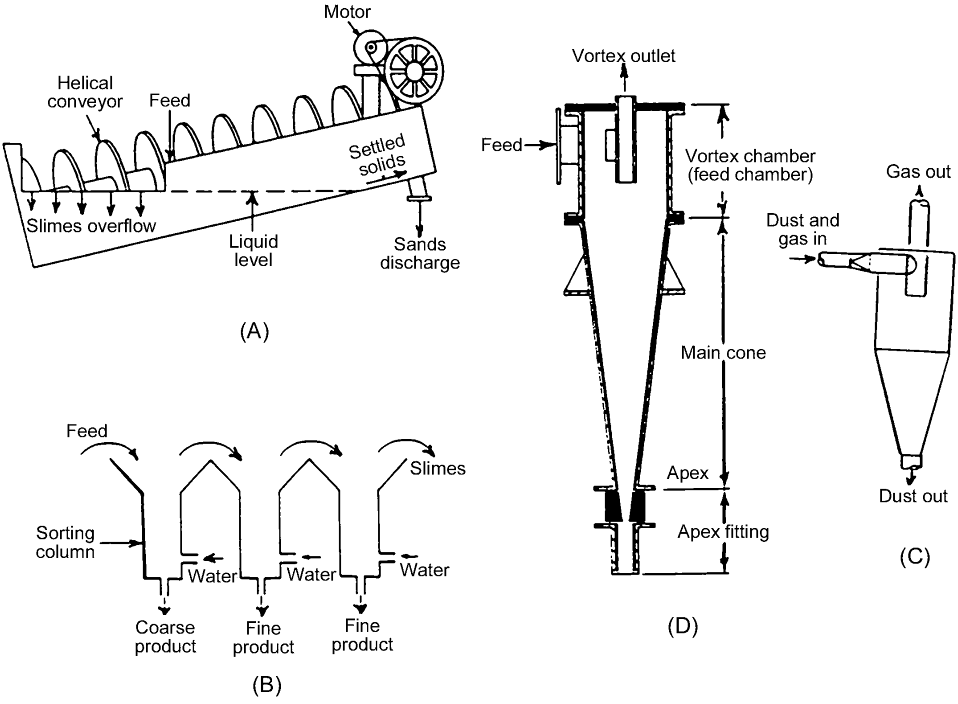


Figure 2.12 Some different types of classifiers:
(A) crossflow classifier; (B) hydraulic classifier; (C) hydrocyclone; (D) cyclone.

The classifier described above works very well with coarse particles where exact splits are not needed. Typical applications are in connection with ball or rod mills for reduction to particle sizes between 8- and 20-mesh. These classifiers have high capacities; they lift coarse solids for return to the mill, so that auxiliary conveyors and elevators are not required. There are other types of classifier that must be usual for close separations with fine particles. One such device is the centrifugal classifier; its action bears a strong resemblance to that of the crossflow classifier, but the settling is greatly accelerated by the substitution of centrifugal force for gravitational force.

The centrifugal classifiers may in the first instance be treated as one of the important centrifugal settling processes for mechanical separations based on the motion of particles through fluids. In centrifugal processes, during passage of the liquid through a centrifugal bowl the heavier, larger solid particles are thrown out of the liquid. Finer, lighter particles may not settle in the time available and be carried out with the liquid effluent. As in a gravity hydraulic classifier, solid particles can be sorted according to size, shape or specific gravity.

2.6.1.2 Hydraulic Classifiers

Hydraulic classifiers are devices that are characterized by the use of water additional to that contained in the feed pulp, and introduced so that its direction of flow opposes that of the settling particles. These classifiers contain a number of vertical sorting columns in each of which a current of water is made to rise, as shown in Figure 2.12 (B). When an ore pulp is brought above one of these columns, those particles whose terminal velocities are greater than the upward velocity of the rising water sink in the column and are discharged as a spigot product at the bottom of the classifier. A series of spigot products can be obtained by making the pulp flow through a launder over a series of such sorting columns, in which rising water has successively smaller upward velocities. The fraction (slime) which is in a finely divided state and does not settle in any of the sorting columns overflows at the end of the classifier. Based on the conditions of settling, hydraulic classifiers are grouped into free settling and hindered settling types. Generally, the pulp densities in the sorting columns decide the settling condition: free or hindered settling. A free settling classifier is characterized by the fact that the sorting column is of the same cross-sectional area throughout its length. A hindered settling hydraulic classifier, on the other hand, is characterized by the fact that the sorting column is constricted at the lower end. Free settling as well as hindered settling classifiers may be again grouped into two categories: launder-type and tank-type. In contrast to mechanical classifiers which mostly give two products, hydraulic classifiers yield several products. The principal use of these classifiers is in the preparation of feed for concentrating tables, since a table operates well with a feed that has been classified. These classifiers are effective for coarse material and are not meant for fine material (size range: –100 mesh and finer).

2.6.1.3 **Hydrocyclones**

The hydrocyclones are primarily regarded as nonmechanical sedimentation-type clarifying units. They have no moving parts, and they have become the workhorse of most mineral operation because of their simplicity, short residence time, compactness, and low cost of operation. A cyclone separator is the device most intimate with a hydrocyclone. These two do not differ in any major way in construction, operation and principles except for the fact cyclones operate on solids in gases (Figure 2.12 C) whilst hydrocyclones operate on solids in liquids (Figure 2.12 D). They both belong to the category of centrifugal separators. A typical hydrocyclone consists of a short cylindrical section (the vortex chamber) closed at one end and fitted with an axially mounted overflow pipe (the vortex outlet) protruding into the body of the cyclone (Figure 2.12 D). There is a tangential feed opening as shown. A conical section is connected at the other end of the cylinder and terminates in a circular opening at its apex. For operation, a suspension of solid particles in a liquid is introduced under pressure through the feed opening. The tangential entry induces the liquid to spin within the cyclone, and the design of the apparatus results in a portion of the liquid (together with the faster-settling particles) being discharged through the apex opening. The remainder of the liquid, together with the slower-settling particles, is discharged through the vortex outlet.

A considerable interaction among particles generally occurs in a classifier. As has been pointed out, the operation of the separation process is influenced by particle size as well as by particle density. This implies that the heavy fraction is an admixture of large particles of minerals, large particles of gangue, and smaller mineral particles. A classifier is suitable for open-circuit operation in which the product is to be subjected to another process such as tabling, where the large-gangue particles can be separated. The application of hydraulic classifiers in conjunction with tabling is an example in this context. While talking about the mechanical classifier and the hydrocyclone, it may be mentioned that the latter installation, including its feed pump, requires lower capital costs and less floor space. A hydrocyclone generally produces an overflow product of higher solids content as compared with that of a mechanical classifier. These advantages of the hydrocyclone have to be weighed against certain advantages gained by using the mechanical classifier. The latter requires less power and lower maintenance cost than the hydrocyclone and its feed pump. The underflow product from a mechanical classifier, because of its very nature of operation, contains less undersize particles than a comparable product from a hydrocyclone. This justifies the application of a mechanical classifier in conjunction with a tumbling mill when classification by size alone is desired for a closed-circuit grinding. It should be mentioned that when a sharper separation is desired between mineral and gangue, methods other than classification must be adopted.

2.7
Screening

Screening (continuous, commercial) and sieving (batch, laboratory test generally confined for size determination) are essentially mechanical separations of particles based on size, accomplished by using a perforated surface that serves as a go–no-go gauge. Both processes, like all other separation processes, have the drawback that a complete separation is seldom obtained, and some potential oversize/undersize particles are always left in the undersize/oversize fraction.

In industrial screening the solids are dropped onto, or thrown against, a screening surface. The undersize, or “fines”, pass through the screen openings while the oversize, or “tails”, do not. A single screen can make only a single separation into two fractions. These are called unsized fractions, because although either the upper or the lower limit of the sizes of the particles they contain is known; the other limit is unknown. Those materials passed through a series of screens of different sizes are separated into sized fractions, i.e., fractions for which both the maximum and the minimum particle sizes are known. Although wet screening is carried out sometimes, dry screening is much more commonly used.

Screening is generally carried out on relatively coarse material, primarily due to the poor efficiency with fineness. Fine screens are very fragile and expensive, and tend to be blinded rather easily with retained particles. Screening is, therefore, performed on substances over 250 μm in size. Although classification generally works well with finely sized materials, the dividing line between screening and classification methods depends on a number of factors, such as the type of ore, the plant throughput and certain others. The trend towards finer crushing prior to grinding has also imposed the need to use screens that have the capability of recovering fine products at high efficiency and capacity. To the mineral industry the main purposes of screening are: (i) prevention of the entry of undersize into crushing units in order to increase their capacity and efficiency; (ii) prevention of oversize substance from passing on to the next stage in closed circuits fine crushing and grinding operations; (iii) preparation of a closely sized feed for some gravity concentration processes; and (iv) production of a closely sized end product (this is of considerable importance in quarrying, where the final product size is an important aspect of the specification).

2.7.1
Passage of Particles

The rate of passage of undersize material through a screening surface depends on many factors such as: (i) the absolute size of the opening; (ii) the ratio of open surface area to the total surface; (iii) the relative size of the particle as compared to the size of the opening; (iv) the angle and the speed at which the particle strikes the screening surface; and (v) the moisture content of the material. The main objective of screen design is to obtain a separation unit that permits the passage of as great a proportion of undersize as possible at the highest possible rate per unit of surface.

The passage of particles through a screen aperture is primarily a statistical problem. When a particle is presented to the screen, it may strike the screen frame rather than passing through the aperture. The probability, P, of a spherical particle of diameter, d_0, passing through an aperture, assuming that the particle does not touch the screen surface before passing through, can be calculated from geometrical considerations. If a square aperture has a side of length, D_a, and if the thickness of the wire surrounding the aperture is D_W, it can be shown that

$$P = \left(\frac{D_a - d_0}{D_a + D_w} \right)^2$$

The probability of passage decreases as the particle size tends to approach the size of the aperture. Thus, to ensure that efficient screening of particles takes place, many opportunities to pass through the screen must be provided to them. This is accomplished by moving the screen. For efficient screening both horizontal and vertical movements are required. The vertical movement is intended to lift the particles out of the blocking positions in the apertures and the horizontal movement ensures that when the particles fall they are presented at different positions on the screen surface. For any given aperture size the optimum conditions of the horizontal movement (vibration frequency) and the vertical movement (stroke) of the screen are related.

2.7.2
Ideal and Actual Screens

An understanding of the process of screening requires that ideal screening and actual screening are studied comparatively. The aim of a screen is to receive a feed consisting of a mixture of particles of different sizes and separate it into two fractions, an underflow that is cleared through the screen, and an overflow that is refused by the screen. Either one, or both, of these streams may be a "product", and in the presentation that follows no discrimination is made between the overflow and underflow streams.

An ideal screen in essence sharply separates the feed mixture in such a fashion that the smallest particle present in the overflow would be just bigger that the biggest particle present in the underflow. Such an ideal separation defines a cut diameter D_{pc} which points the separation between the fractions. The cut diameter D_{pc}, for convenience, is chosen to be nearly equal to mesh opening of the screen.

The performance of an ideal screen in terms of the screen analysis of the feed is shown in Figure 2.13 (A). The cut point is the point *C* in the curve. Fraction A comprises all particles bigger than D_{pc}, and fraction B comprises all particles smaller than D_{pc}. The fractions *A* and *B* are the overflow and underflow respectively. Screen analyses of the ideal fractions *A*

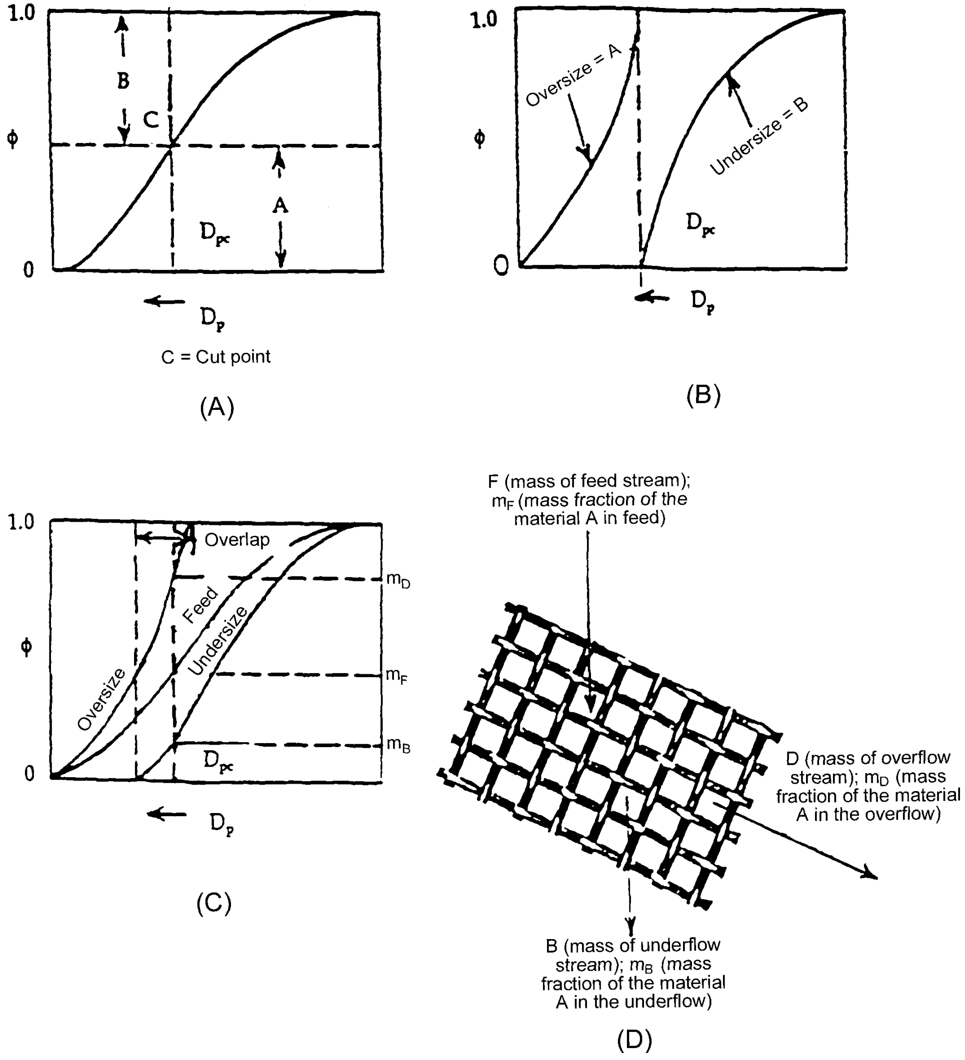


Figure 2.13 Ideal versus actual screening. (A) Ideal screening; (B) screen analysis of products from ideal screening; (C) actual screening; (D) mass balance across a screen.

and *B* are plotted in Figure 2.13 (B). The first point on the curve for *B* has the same abscissa as the last point on the curve for *A*, and there is no overlap of these curves. In these figures the diameter D_p increases from right to left.

Actual screens do not or provide an incisive separation. Rather, the screen analyses of the overflow and the underflow are like those shown in Figure 2.13 (C). The overflow contains a good amount of particles smaller than the desired cut diameter, and the underflow contains particles bigger than the cut diameter. The two curves overlap, as shown in Figure 2.13 (C). It may also be added that the mass of the two outgoing streams will not equal the individual masses of *A* and *B* unless it occurs that the undersize material in the overflow is equal to the oversize material in the underflow.

The closest separations are acquired by standard testing screens and with spherical particles. Even in this case, an overlap occurs between the largest particles in the underflow and the smallest particles in the overflow. The overlap is particularly marked when the particles are needlelike or fibrous, or where the particles tend to form collections or groups that act as big particles. Some long, thin particles may hit the screen sidewise and be retained. Industrial screens commonly provide poorer separations as compared to testing screens of the same mesh opening while working on the same mixture.

2.7.3
Material Balances

The equations derived from consideration of material balances over a screen are found to be useful in calculating the ratios of feed, oversize, and underflow from the screen analysis of the three streams and knowledge of the desired cut diameter. Let *F* stand for the mass of the feed flow, *D* for the mass of the overflow flow, *B* for the mass of the underflow flow, m_F for the mass fraction of material, *A* in feed, m_D for the mass fraction of material *A* in the overflow and m_B for the mass fraction of material *A* in the underflow. The mass fractions of material *A* are shown in Figure 2.13 (C). The mass fractions of material *B* in the feed, the overflow, and the underflow are $1 - m_F$, $1 - m_D$, and $1 - m_B$ respectively. Since the total material fed to the screen must exit either as underflow or as overflow,

$$F = D + B$$

The material *A* in the feed must also exit in these two streams, and

$$F\,m\mathrm{F} = D\,m\mathrm{D} + B\,m\mathrm{B}$$

The elimination of *B* from these two foregoing equations gives the following:

$$\frac{D}{F} = \frac{m_F - m_B}{m_D - m_B}$$

Likewise, the elimination of *D* results in the following relationship:

$$\frac{B}{F} = \frac{m_D - m_F}{m_D - m_B}$$

2.7.4
Screen Efficiency and Capacity

The performance of screens is assessed on the basis of two criteria: efficiency, and capacity.

The screen efficiency of a screen (known also as effectiveness of a screen) is a measure of the success of a screen in closely separating materials A and B. Provided the screen works perfectly, all of material A would be in the overflow, and all of material B would be in the underflow. An usual measure of screen effectiveness is the ratio of oversize material A that is actually in the overflow to the amount of A entering with the feed. These amounts are $D\, m_D$ and $F\, m_F$, respectively. Thus

$$E_A = \frac{D\, m_D}{F\, m_F}$$

where E_A the screen effectiveness based on the oversize. In a similar way, E_B, the screen effectiveness based on the undersize is provided by

$$E_B = \frac{B\,(1 - m_B)}{F\,(1 - m_F)}$$

Defining the product of the two individual ratios as the combined overall effectiveness and denoting it by E, one has the following relationship:

$$E = \frac{D\, B\, m_D\,(1 - m_B)}{F^2\, m_F\,(1 - m_F)}$$

Substituting D/F and B/F from the earlier equations into the above equation, the final relationship is obtained as:

$$E = \frac{(m_F - m_B)\,(m_D - m_F)\, m_D (1 - m_B)}{(m_D - m_B)^2\,(1 - m_F)\, m_F}$$

In industrial screening, capacity is important in addition to efficiency. The capacity of a screen is measured by the mass of the material fed per unit time to unit area of the screen.

Efficiency and capacity oppose each other, and in order to obtain maximum efficiency the capacity must be small. A large capacity is achievable only at the expense of a reduction in efficiency. In practice, a reasonable balance between capacity and effectiveness is struck. Although accurate correlations are not obtainable for judging or calculating these operating characteristics of screens, certain principles apply, and these can be used as guidelines in grasping the basic features of screen performance.

The capacity of a screen is controlled simply by varying the rate of feed to the unit. The effectiveness obtained for a given capacity depends on the nature of screen performance. The overall likelihood of the passage of a given undersize particle depends on the number of times the particle hits the screen surface and the chance of passage during a single contact. If the screen is overloaded, the number of contacts is small, and the likelihood of passage on contact comes down due to the intervention of the other particles. The improvement in effectiveness accomplished at the expense of capacity is a consequence of more contacts per particle and a better chance of passage on each contact.

In an ideal situation a particle would have the greatest probability of clearing through the screen if it hits the surface in a direction normal to the surface, if it were so oriented that its minimum dimensions were parallel with the screen surface, if it were unobstructed by any other particles, and if it did not cling to (or wedge into) the screen surface. None of these conditions apply to actual screening, but this ideal situation can be employed as a basis for judging the influence of mesh size and wire dimensions on the functioning of screens.

If the width of the wire in a screen were negligible in comparison with the size of the screen openings, the wires would not meddle with the passing of the particles, and practically the entire screen surface would be active. The prospect of the passage of a particle that hits the screen would then be nearly unity. In an actual screen the diameter of the wire, or the fraction of the surface that is not in openings, is appreciable, and the solid meshes strongly influence the functioning of the screen, especially by hampering the passage of particles almost as large as the screen openings.

The probability of the passage of a particle through a screen depends on (i) the fraction of the total surface represented by openings; (ii) the ratio of the diameter of the particle to the width of an opening in the screen; and (iii) the number of contacts between the particle and the screen surface. When these parameters are all constant, the average number of particles passing through a single screen opening in unit time is constant, independent of the size of the screen opening. If the size of the largest particle that can pass through a screen opening is taken to be equal to the width of a screen opening, both dimensions may be represented by D_{pc} for a series of screens of different mesh sizes, the number of openings per unit screen area is proportional to $1/D_{pc}^2$. The weight of one particle is proportional to D_{pc}^3. The capacity of a screen, in mass per unit time, divided by the mesh size should be constant for any specified conditions of operation. This is a practical rule of thumb.

The foregoing analysis is useful in analyzing the basics of screen functioning. In practice, however, a number of perplexing factors surface and those cannot be treated theoretically. Some of these upsetting factors are (i) the intervention of the bed of particles with the motion of any one; (ii) binding; (iii) bonding of particles to each other; (iv) the cohesion of particles to the screen surface; and (v) the direction of approach of the particles that is oblique to the surface. When big and small particles coexist, the big particles are inclined to segregate in a layer adjacent to the screen and thus prevent the smaller particles from arriving at the screen. All these tend to decrease capacity and reduce effectiveness. An important factor is the moisture content of the feed. Either dry particles or particles running in a stream of water screen more readily than do moist particles, which are likely to cohere to the screen surface and to each other and to screen retardly and with difficulty. As the particle size decreases, screening becomes progressively more difficult, and capacity and effectiveness are, in general, low for particle sizes smaller than about 100-mesh.

2.7.5
Types of Screens

Most screens are characterized by the fact that the particles drop through the screen opening by gravity. Few designs are found where the particles are pushed through by a brush or by centrifugal force. The key element in the screening method of particle sizing is obviously the screening surface, the medium that contains the apertures for the passage of undersize material. This surface must be: (i) strong enough to support the material meant to be screened; (ii) flexible enough to cope up with the forces of vibration that it is subjected to; and (iii) light enough to provide a reasonable amount of open area to yield a practical throughput. The surfaces are of a variety of types, shapes, sizes, and materials of construction. The three general types of screening surfaces are: (i) woven wire cloth (woven out of a wire of steel, copper, bronze, morel, or some other alloy); (ii) fabric, such as silk bolting cloth; (iii) perforated plate (made of sheet steel punched by dies); and (iv) parallel bars or rods (usually made of steel bars, steel rails, cast iron, or wood).

In the screening process, coarse particles drop quickly and easily through large openings in a stationary surface. The screening surface must be agitated in some way with finer particles. Common ways are by revolving a cylindrical screen about a horizontal screen; or, with flat screens, by shaking, gyrating, or vibrating them mechanically or electrically. Industrial screens are of many types, but can be divided broadly into stationary and moving screens. Typical examples of the stationary variety are the grizzly and sieve bends, while those of the moving variety are revolving screens, shaking screens, reciprocating screens, gyratory screens and vibrating screens.

2.8
Gravity Concentration

Gravity separation is a concentration separation process in which particles of mixed sizes, shapes and specific gravities are separated from each other by the force of gravity or by centrifugal forces. The nature of the process is such that size and shape classification is an inherent part, in addition to separation on the basis of specific gravity – a feature from which the process derives its name. This process of mineral concentration has occurred widely in Nature, and the concentration of heavy minerals such as gold, platinum, cassiterite, ilmenite, zircon, and diamonds in placer or beach sand deposits are examples that can be cited in this context. Gravity concentration dates back to the early days of mineral processing, and can be credited to be the first mineral concentration process used in situations where selective mining and hand-sorting methods were no longer adequate to produce the quality of concentrate desired. The introduction of the flotation process has caused the gravity concentration methods to lose much of their importance. However, nonsulfide ores such as cassiterite, chromite and wolframite, and certain nonmetallics do not respond well to economic flotation, and so gravity methods are still used for their treatment. The need effectively to separate particles showing only small specific gravity differences and the need to develop efficient, high-capacity devices for the treatment of mineral fines constitute the two basic challenges that must be met adequately if gravity concentration techniques are to be used more widely.

An estimate of the applicability of gravity concentration to the separation of a mineral pair of differing specific gravity can be obtained by making use of what is called the concentration criterion, which makes use of the ratio $(\rho_1 - \rho_2)/(\rho_3 - \rho_2)$, where ρ_1 is the specific gravity of the heavy mineral, ρ_3 is the specific gravity of the light mineral, and ρ_2 is the specific gravity of the fluid medium. This criterion helps in gaining some idea of the type of separation possible. In very general terms, when the absolute value of the ratio is larger than 2.5, then gravity separation is relatively easy. As the absolute value of the ratio decreases, so does the efficiency of separation, and at values smaller than about 1.25 gravity concentration is generally not feasible commercially.

2.8.1
Gravity Separation Machines

The devices used for the gravity concentration of minerals are many in number. Typical examples include devices such as jigs, spirals, tables, and heavy medium separators.

2.8.1.1 **Jigs**

Jigs are mechanical devices used for accomplishing separation between materials differing in their specific gravities. In order to understand the principle of separation by jigging, reference may be drawn to the motion of a particle settling in a viscous fluid. The equation of a motion of a particle settling in a viscous fluid is given as:

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = mg - m'g - F_{\mathrm{D}}$$

where, as indicated earlier, m is the mass of the particle, $\mathrm{d}v/\mathrm{d}t$ is its acceleration, g is the acceleration due to gravity, m' is the mass of the fluid displaced, and F_{D} is the drag force or the fluid resistance opposing the downward movement of the particle. At the start of particle movement, since the velocity v is quite small, F_{D} can be ignored as it is a function of particle velocity. The equation of motion then simplifies to the following:

$$\frac{\mathrm{d}v}{\mathrm{d}t} = \left(\frac{m - m'}{m}\right)g$$

Since the volume of the particle is equal to the volume of the fluid it displaces the following is the final relationship:

$$\frac{\mathrm{d}v}{\mathrm{d}t} = \left(1 - \frac{\rho_2}{\rho_1}\right)g$$

where ρ_1 and ρ_2 are the respective specific gravities of the particle and the fluid.

This expression shows that, unlike the terminal velocity of the particle, its initial acceleration is independent of the particle size and depends only on the densities of the solid particle and the fluid. This type of acceleration, known as differential acceleration, may be exploited by designing equipment which provides frequent opportunities for accelerating the particles from rest. If a particle is allowed to accelerate from rest for a brief period of time and then arrested and subsequently allowed to fall once more, the total distance travelled by it will be influenced more by the differential acceleration and, therefore, by the specific gravities of the particle and of the liquid, than by its terminal velocity, or in other words, by its size. In this way, as the preferential movement of dense particles to the bottom of a bed of particles occurs, the bed becomes stratified and physical separation of the top and the bottom fractions is possible.

The movement of individual particles in concentrated slurries is influenced by the movement of neighbouring particles, and so the situation is different from that corresponding to dilute slurries. In deriving the expression,

$$\frac{dv}{dt} = \left(1 - \frac{\rho_2}{\rho_1}\right) g$$

it was assumed that as a particle falls through the fluid, it displaces the fluid in a direction opposite to that of its motion. Neighbouring particles must, therefore, be moving in a moving fluid and this may act against the settling of the particles in the slurry. The magnitude of this effect, referred to as hindered settling, is clearly dependent on the voidage of the bed. Although hindered settling favours the settling of denser particles, the movement of particles can also be affected by differences in particle size. In order to improve the performance of processes in which selection is on the basis of particle density, some form of size selection is necessary prior to density selection. The phenomenon of hindered settling plays an important role in the jigging process.

Besides differential acceleration and hindered settling, a third process must be considered, and this becomes important when the bed begins to compact. At this stage the movement of the larger particles tends to be restricted by the neighbouring particles. Small dense particles, however, can still move downwards through the interstices between the large particles under the influence of gravity. This leads to the recovery of fine heavy particles. This stratification process is called consolidation trickling.

Considered all in all, there are therefore three different effects that contribute to the process of stratification that operates in jigs. These are: (i) differential acceleration at the start of descent; (ii) hindered settling; and (iii) consolidation trickling at the end of descent. A jig essentially consists of a tank or hutch which is divided by a wall into two main sections (Figure 2.14). One section contains the support screen, and a fluid pulse is generated in the other. In operation, a mixture of ore particles supported on the screen is subjected to an alternating rising and falling (pulsating) flow of fluid. The particles of high specific gravity travel to the bottom (concentrate), while the particles of lower specific gravity (tailing) collect at the top of the bed. The operation is carried out by continuously removing the light tailing from the top of the bed to permit the layer of concentrate to build up. After a sufficient quantity of concentrate has accumulated, it may be removed manually or automatically. The layer of large heavy particles at the bottom of the bed controls the rate at which the fine concentrate particles penetrate and percolate through the bed to the hutch. In some cases there are enough coarse heavy fractions to provide this layer. With fine materials it is necessary to provide an added layer of coarse heavy material to form the bed, and so an artificial bed or ragging is used. This is made of steel shot, lead shot, coarse galena, or some other heavy material. In general, the ragging particles must be heavy enough to remain at the very bottom of the bed, but light enough for dilation on the upstroke. The size must be greater than the screen openings and large enough to provide spaces between the particles to permit smaller particles to percolate through on the down-stroke into the hutch, and the entire concentrate is made in the hutch. Jigs do not usually produce in one opera-

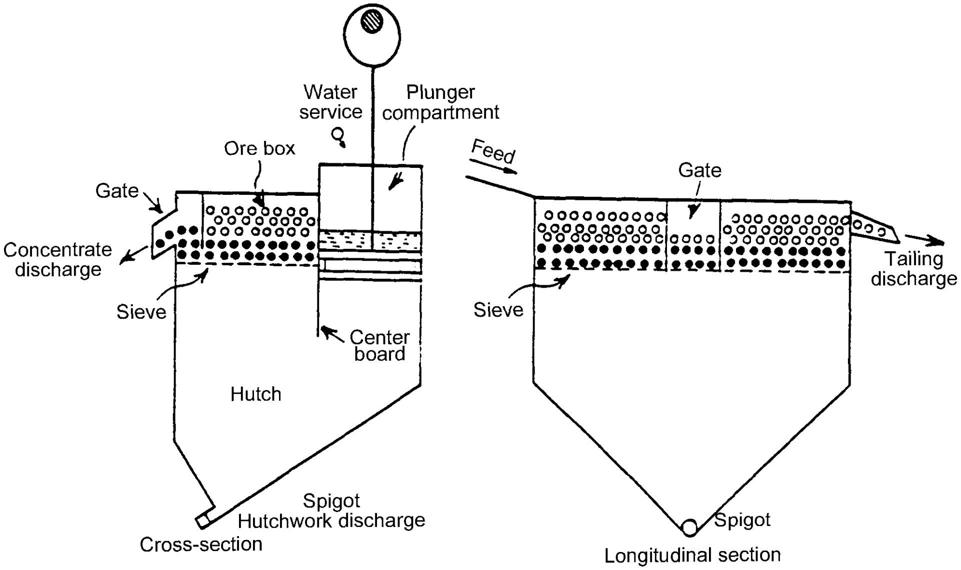


Figure 2.14 Essential features of jigging appliance.

tion a finished concentrate as well as tailing. They are normally used either to reject rock, i.e., a tailing, and produce a middling for further treatment, or alternatively to make a middling and a finished concentrate.

Jigs are relatively cheap with regard to construction, operation, and maintenance, and are relatively unaffected by the grade of the feed. They are basically designed for handling material that is too coarse for table feed (380 mm in diameter down to 2 mm). The cleaning of coal and the production of tin mineral concentrate can be cited as two major examples where jigging is found to be in use even today.

2.8.1.2 Spirals

As in all the gravity concentration processes, spiral concentration is based mainly on specific gravity differences of the materials to be separated. The best known spiral-type concentrator is the Humphreys spiral concentrator. This appliance is composed of a helical conduit (commonly consisting of five turns) arranged around a vertical axis. The working of the spiral starts with the slurry entering through a feed box and on to the spiral surface. Once on the spiral surface, mineral grains settle and become sorted according to size, shape and specific gravity. A specific gravity difference of 1.0 or more is required to make a separation of different minerals.

Particles with the lowest specific gravity are carried with the water towards the outside wall of the spiral. The spiral separates at its greatest efficiency when used in the size range of 10 to 200 mesh. Some particles will be recovered both above and below these size ranges, but occasionally, ultrafine and very coarse heavies will be lost in the tailings, as will be middlings or unliberated ore particles. The spiral will benefit, therefore, from the use of hydraulic classification as a feed preparation step.

Figure 2.15 (A) presents the cross-sectional profile regions of a spiral concentrator. As shown, there are altogether six regions which can be distinguished. The first region consists mainly of water and fine particles, most of which are "trapped" here from the discharge of the feed box. The water in this region moves in a counter-clockwise direction. No separation occurs in this region due to the low pulp density and the high velocity of the slurry, which hinders any settling of dense particles. The second region is that with maximum water velocity and, therefore, is associated with the maximum centripetal force of the water. Because there is no counter-force, the water moves down this plane and disrupts any movement between the first and third regions. The third region is considered to be the upper portion of the high velocity of the water and is carried towards the next region. The fourth region is where the third and fifth regions overlap. This serves as a reference point to the operator and assists in making adjustments. This allows for the maximum recovery of the more dense particles without loss in grade. The fifth region is where the more dense particles are encountered. The less dense particles in this region work themselves to the top of the slurry bed and are then washed away by the water on the surface of this bed. This

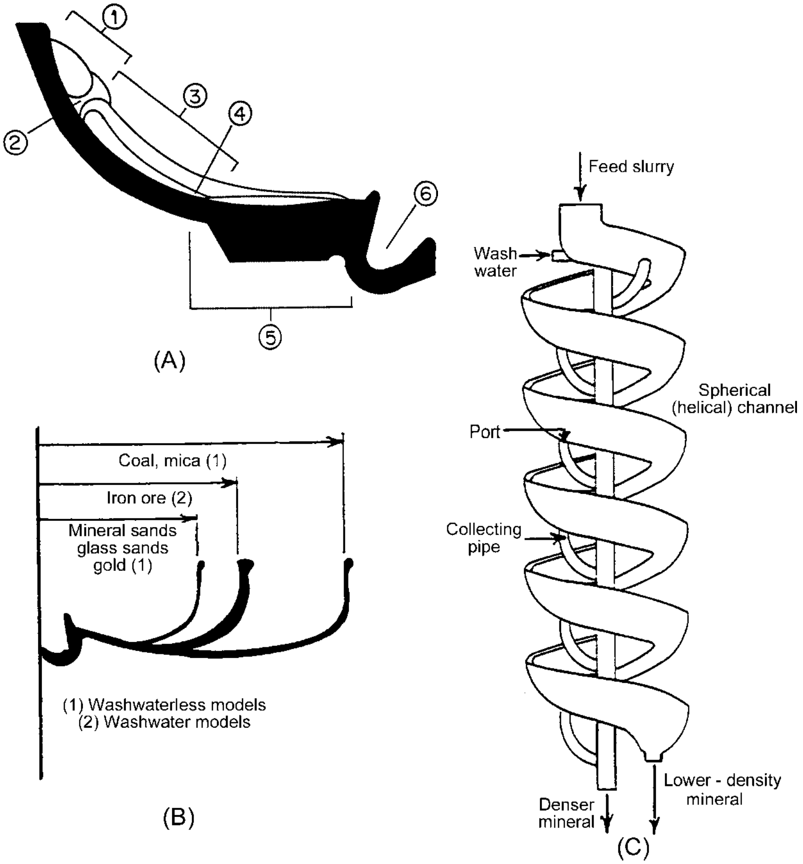


Figure 2.15 (A) Cross-sectional profile regions (for description of the regions marked refer text); (B) spiral diameter versus application; (C) a view of the spiral concentrator.

"washing away" of the less dense particles is enhanced by the washwater introduced into the sixth region.

The spiral concentrator is one of the most effective, low-cost devices for the treatment of ores. Manufactured from lightweight, corrosion- and abrasion-resistant materials, spirals require a minimum of maintenance and upkeep. The list of spiral types includes washwaterless, washwater and coal/mica spirals. The wash waterless type is used in most applications, particularly for concentrating low-grade ores. The only water required is added with the solids prior to introducing the feed onto the spiral. Concentrates are removed either at the bottom, directly into the product box, or at several intermediate take-off points down the spiral. Washwater spirals require extra water at stages down the spiral which provides for more efficient washing of the concentrate and for transporting away silica or other gangue materials. Units with diameters larger than those of the mineral spiral series, known as coal/mica spirals, are designed to take advantage of the particle shape differences. Take off spitters at different points down the helix give this spiral a high capacity to remove refuse or siliceous contaminants from coal or mica. Figure 2.15 (B) illustrates the ranges of spiral diameters used for different applications.

Some examples of materials suitable for being subjected to spiral concentration are: (i) beach sands that are processed for the recovery of chromite, ilmenite, rutile, zircon, tin, and iron ore minerals; (ii) iron ores; (iii) some mica and phosphate rocks; (iv) tailings from concentrating plants that carry heavy mineral components not amenable to processing by flotation and other methods; and (v) some fractions of coal. The spiral concentrator is very well suited for treating tailing streams. An outstanding example is that of a Colorado molybdenum ore processing plant where spirals recover tungsten, pyrite and tin concentrates from huge amounts of flotation plant waste. There is no other known processing method which can economically extract tin and tungsten values from this source. The crude ore contains only 0.03% tungstic oxide (tungsten occurs as the mineral hubnerite) and a trace of tin (tin occurs as the mineral cassiterite). A view of the spiral concentrator is shown in Figure 2.15 (C).

2.8.1.3 **Tables**

A shaking table is a very useful concentrating device. It consists of a substantially plane surface which is inclined slightly from the horizontal along its breadth and is shaken with a differential movement in the direction of its length. This longitudinal movement usually comprises a slow forward stroke, followed by a rapid return. The surface or the deck of the table is washed by a stream of water flowing in the direction perpendicular to the direction of motion and along the slope. When water flows over a flat inclined surface, as in the case of a shaking table, it produces a flowing film. The velocity of water in this film varies with the depth with respect to the film surface. In regions close to the table surface (i.e., furthest from film surface) the motion of water is obstructed due to friction against the adsorbed layer on the surface, whereas in regions close to the film surface there is no such obstruction. As a result of this, water velocity decreases with increasing depth in the film. This implies that a very small particle would not wash down the table surface as rapidly as a larger particle of the same density because it would be submerged in the slower-moving regions of the film. Likewise, if two equal-sized particles of different densities are placed in the flowing film, the heavier particle will be washed down more slowly because it will have a greater tendency to sink in the film. Thus, the effect of the flowing film of water on the shaking table on the motion of particles placed on it would depend on the sizes and the densities of the particles. Any mineral particle on the table will be subjected to two mutually perpendicular forces-one along the length of the table (due to the motion of the table) and the other down the slope of the table. It follows that under the action of these forces the particles would move diagonally across the deck. If a mixture of particles is fed to the upper right-hand corner of the deck, they would fan out and gradually move towards the lower left-hand corner, arranging themselves according to their sizes and densities. An idealized arrangement of such particles is illustrated in Figure 2.16. The larger, low-density particles would traverse the maximum distance in the direction of the flowing water stream and would constitute the tailings while the smaller, high-density particles would traverse the minimum distance and constitute the concentrate. The middlings would be made up of high density particles which are large in size and low-density particles which are small in size. Thus, the shaking table is very efficient in separating small particles of heavy minerals from large particles of light minerals.

In modern types of shaking tables, the deck is generally provided with a number of thin wooden strips or riffles. In the most common arrangement, the riffles are placed parallel to the length of the table. Usually they are made thickest near the feed end and taper down toward the discharge end. Since the riffles lie parallel to the direction of motion of the table, the water film flows across them. Depending on the nature of the material being handled, the riffles may cover the entire table surface or only a part of it.

The shaking action of the table causes the minerals to stratify in the spaces between the riffles, with the light minerals rising to the top and the heavy ones sinking to the bottom. The former are exposed to the flowing water film while the latter travel along the length of the table, parallel to the riffles.

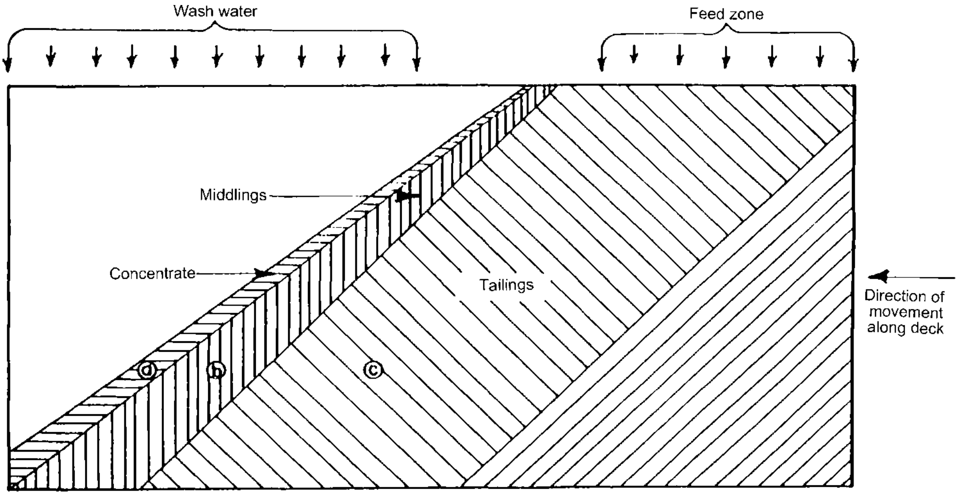


Figure 2.16 Idealized arrangements of particles on a shaking table: a = smaller, higher-density particples; b = high-density particles, large in size and low-density particles, small in size; c = lesser, low-density particles.

The flow of mineral particles on the deck of a riffled table results in a distribution that is essentially similar to that obtained with a smooth table. However, some additional features are introduced due to the action of the riffles. In the case of a smooth table, a hydraulically classified fraction usually makes a better feed as compared with an unsized mixture. However, a classified feed does not always work best on a riffled table, and screen-sized or unsized feed is often used. The maximum particle size that can be treated in a riffled table is generally larger than that corresponding to a smooth table.

2.8.1.4 **Heavy Medium Separators**

Heavy medium separation involves the following stages:

- introduction of a suitable feed;
- separation into floats and sinks in a bath containing dense media;
- withdrawal of products, and removal from them of adherent dense media; and
- cleaning, reconstitution, and return to bath of clean dense media.

These stages are usually merged into a continuous process. The process performs one or more of the following functions: (i) production of a finished waste product and an enriched concentrate for further concentration; (ii) production of a finished concentrate and a rejectable waste; and (iii) production of a finished concentrate and a low-grade reject, plus a middling for additional treatment.

The feed must not contain colloidal minerals, primary slimes, or fine ores. The separation process depends neither on the rate of fall nor on the particle size, but only on the particle density. The process is most widely applied when the density difference is pronounced at a coarse particle size, since the separation efficiency decreases with decreasing particle size due to the slower rate of settling of smaller particles. It is preferable that the particle size be greater than about 10 mesh, in which case separation can be effective even on a difference in specific gravity of 0.1 or less. The dense media can be of three types: (i) solution of salts in water; (ii) organic liquids; and (iii) suspension of solids in water. Among these the third type is the industrially accepted one. The substance chosen to provide the dense medium should have the following main qualities: (i) it should possess adequate hardness in that it should not easily break or wear down into a slime under the working conditions; (ii) it must not be chemically corrosive, or liable to react with the ore minerals undergoing treatment; (iii) it must form a fairly stable pulp without having to be ground very fine, or the medium would be too viscous; (iv) it should have a specific gravity high enough to provide the required bath density under reasonably nonviscous conditions, (v) it must lend itself to easy cleaning; and (vi) it should be nonfouling (a certain amount of the medium stays in the cracks and crevices of the lumps of the cleaned and washed ore, and it must not be of such a composition as to adversely influence the subsequent treatment due to be applied to the ore).

Among the dense media the best which are able to meet the requirements cited above are galena, magnetite, mill scale, ferrosilicon, pyrites, and sand. The most widely used substance now is ferrosilicon. With a silicon content of 10% the material has a specific gravity of 7.0, and with 25% silicon the specific gravity is 6.3. When the silicon content exceeds 22% it is feebly magnetic, and at silicon contents below 15% the material becomes prone to rusting. Ferrosilicon containing 15% silicon does not rust and has good magnetic qualities, lending itself to regeneration by magnetic separation. Ferrosilicon containing about 15% silicon can be used to prepare dense media with specific gravities upto 3.5, but the more usual working range is 2.5 to 3.2. Where the separation is to take place between particles of specific gravities of 2.65 and 2.9, the ferrosilicon is usually ground to –100 mesh and is mixed with between 10% and 20% of magnetite. At higher working ranges of the bath density (above 3.0), –65 mesh ferrosilicon is used. As an example of other substances used for making dense media, reference may be drawn to galena. In the pure state it can provide a bath density of about 4.0. Above this level, ore separation is found to slow down by the viscous resistance. Froth flotation (which is a costly process) when deployed to clean the contaminated medium, is found to be not without problems. Galena is fairly soft and tends to slime easily; it also has a tendency to oxidize. All these effects adversely influence the flotation efficiency. On account of this, galena – which was used earlier for making heavy media – is now confronted with a tendency towards an increased use of magnetic materials. Magnetite is used where bath densities below 2.5 are suitable. This is rather low for many uses, but magnetite is increasingly being used in cleaning coal.

Cleaning the media, together with the regulated return of the cleaned media adjusted to the correct bath density, constitute the critical control parameter in the heavy media separation process. The usual sequence of operations consists of: (i) drainage of media from ore leaving the bath; (ii) washing of ore products to remove the balance of adherent media; (iii) collection of foul media, and cleaning it by a suitable process (flotation for galena, magnetic separation for magnetic media, hydraulic separation for sands); and (iv) reconstitution and return to circuit of reclaimed media.

The most important application of this method is in coal cleaning where the low-ash coal is removed from the heavier high-ash discard and the associated shales and sandstones. There are three basic types of vessels that are commonly used for carrying out heavy media separation; these are: (i) cone-type vessel; (ii) drum-type vessel; and (iii) trough-type vessel. The cone- and the drum-type vessels have been used extensively in treating high-gravity solids such as iron ores and lead-zinc ores. The trough type vessel is used in coal treatment. A cone type vessel for coal washing, using sand suspension in water as the heavy medium, is shown in Figure 2.17.

2.9
Magnetic Separation

It may be recalled from the first chapter that one of the ways of classifying materials is based on their magnetic characteristics. On this basis, materials can be classified into two broad categories: (i) paramagnetic materials; and (ii) diamagnetic materials. Paramagnetic materials exhibit positive magnetization, implying thereby a greater magnetic flux density in the material than in the applied field. In contrast, the diamagnetic materials exhibit a negative magnetization, implying thereby a lower magnetic flux density in the material than in the applied field. Very strongly paramagnetic materials can be regarded to belong to a separate category called ferromagnetic materials. In an applied magnetic field, the magnetization of ferromagnetic materials changes until saturation magnetization is reached. If

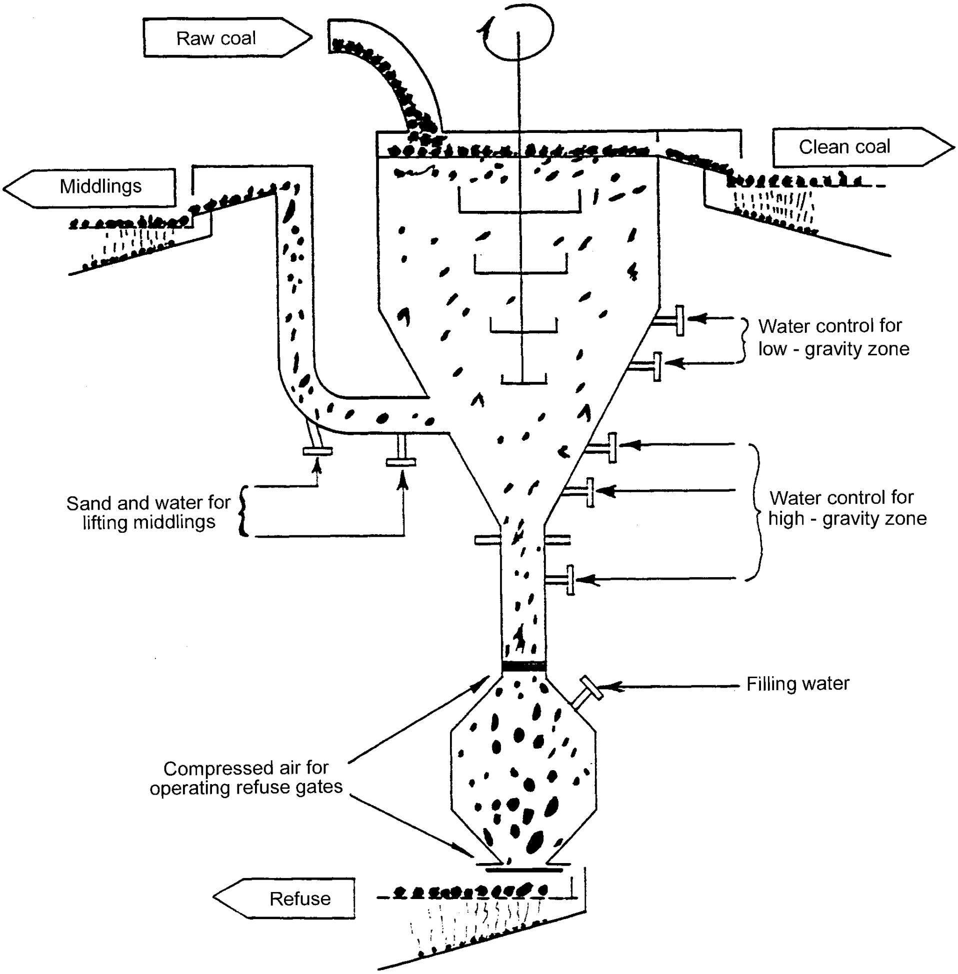


Figure 2.17 A simplified sketch of heavy medium separator for coal cleaning.

the applied field is reduced, the magnetization decreases but does not revert to its original value. Such a nonreversible process of magnetization is called hysteresis. The residual magnetization of the material is called magnetic remanence. The main ferromagnetic mineral is magnetite, but among other minerals, only pyrrhotite is attracted to a bar magnet. There are a number of other minerals which possess sufficient paramagnetism to be potentially amenable to magnetic separation. The list of such minerals includes magnetic minerals such as chromite, garnet, hematite, ilmenite, siderite, and wolframite, and weakly magnetic minerals such as spinels, including franklinite, and the constituents of monazite sands. The capacity of a magnet to lift a particular mineral depends not only on the value of the field intensity, but also on the field gradient (the rate at which the field intensity increases towards the magnet surface). Since paramagnetic minerals have higher magnetic permeabilities than the surrounding media (usually air or water) they concentrate the lines of force of an external magnetic field. The higher the magnetic susceptibility, the higher is the field density in the particle and the greater is the attraction up the field gradient towards increasing field strength. Diamagnetic materials have lower magnetic susceptibility than the surrounding media and hence expel the lines of force of the external field. This expulsion is in the direction down the gradient of the field towards decreasing field strength. It is understandable, therefore, as to why the magnetic property of the greatest interest to mineral processing engineers is the magnetic susceptibility. Magnetic separations depend on a particle magnetic susceptibility in a magnetic field. The force, F, acting on a particle is proportional to the product of the field strength, H, and the field gradient $\mathrm{d}H/\mathrm{d}l$ (i.e., $F \propto H\,\mathrm{d}H/\mathrm{d}l$). For producing a given lifting force, there are thus a large number of available combinations of field and gradient which will yield the same effect. The production of a high field gradient as well as a high field intensity, therefore, becomes an important design consideration in magnetic separators. In order to attract and hold a paramagnetic particle, a high magnetic field as well as a high gradient are required to be produced by suitably designed separators.

Besides the incorporation of a high field gradient, a magnetic separator design should have:

- A provision for regulating the intensity of the magnetic field to deal with various types of material, this being achieved in electromagnetic separators by changing the current, and in separators using permanent magnets by varying the interpole distance.
- A provision for the collection of the magnetic and the nonmagnetic fractions.

In the context of the second provision it may be pointed out that the magnetics are not allowed to contact the pole pieces because this would create the problem of detachment. The design provides for the magnetics to get attracted to the pole-pieces, and to make physical contact with a conveying device which transports them out of the influence of the field and puts them into a bin or a belt. Apart from all these, some other important elements in the design of a magnetic separator are: (i) control of passage of ore through the magnetic field; (ii) avoidance/correction of occlusion of nonmagnetic material between or within magnetic flocs; and (iii) elimination (or reduction to a minimum) of moving parts. Elaborating on the second point listed it may be added that in a magnetic separation device the particles themselves behave as magnets, resulting in mutual attraction. This leads to flocculation, or agglomeration of the particles, especially if the particles are small and possess high values of susceptibility, and if the field is intense. The separating machine design must attend to this aspect because these magnetic flocs can entrap gangue and can bridge the gaps between magnet poles, thereby adversely affecting the efficiency of separation. In dry separating machines which work on finely sized material, flocculation is of considerable concern. This effect is less serious if the ore is fed into the magnetic field in one layer. This, however, reduces the capacity of the machine drastically. Flocculation can be minimized by passing the material through consecutive magnetic fields, which are usually arranged with successive reversal of polarity. This causes the particles to turn, and the turning action frees entrapped gangue particles. However, this procedure suffers from a major disadvantage in that the flux tends to leak from pole to pole, and this cuts down the effective field intensity.

2.9.1
Magnetic Separators

Magnetic separators are commonly classified into two broad categories: dry, and wet. Depending upon the strength of the magnetic field used, each is further categorized into low intensity and high intensity. In addition to these four types there is also a type identified by its application for tramp iron removal. Bulk materials often contain varying amounts of unwanted ferrous-type materials (nails, bolts, machinery parts, etc.), and it is necessary to remove these in order to provide protection to the magnetic separation machinery. One of the simplest and most easily installed tramp iron protection devices is a magnetic pulley.

The family of dry magnetic separators as has been mentioned consists of low- and high-intensity separators.

The high-intensity dry magnetic separators group may be cited as consisting of induced roll, crossbelt and ring-type separators.

In order to illustrate how magnetic separation in a dry category functions, we can consider the details of a low-intensity dry magnetic separator. This separator generally makes use of a rotating drum inside which are stationary permanent or electromagnets. The magnets are generally oriented axially and are equally spaced with alternating polarity so that a tumbling action is introduced in the particles. This turning-over action of the magnetic particles helps in releasing any nonmagnetic particles physically trapped in them. With devices of this type it is possible to recover a middlings fraction. The middlings particles are less strongly attracted by the magnetic force than the concentrate particles, and hence may be made to fall into product streams between the concentrate and the tailings streams. These middlings are generally composed of partially liberated particles and contain both magnetic and nonmagnetic components. Since grinding is expensive, it is usually economical to treat the entire starting resource initially with a dry drum separator, and then to regrind the middlings prior to retreating them magnetically. The separators are built in various models that differ in the field strength and the number of poles used. The standard intensity magnetic separators are mainly used for ferromagnetic materials (magnetite). They are also used for paramagnetic materials with high magnetic susceptibility.

Like dry magnetic separation, wet magnetic separation is practiced at two levels: low and high intensity. Low-intensity wet magnetic separators use drums for separation and comprise basically three types: co-current, counter-rotation, and counter-current. In the co-current type, the slurry feed is passed through a trough in the same direction as the direction of rotation of the drum. Whilst the nonmagnetic particles sink in the trough, the magnetic fraction is carried on the drum surface to a point where it is taken off into a separate processing stream. A high-grade concentrate is produced by this separator. However, tailings contain significant amounts of magnetics. In the counter-rotation type, the feed flow takes place in the direction opposite to the direction of drum rotation. In the counter-current type, the tailings are freed to travel in the direction opposite to that of drum rotation and are discharged into the tailings chute.

2.9.2
Principles

In a dry drum-type magnetic separator, the magnetic force, F_m, acting on a particle on the drum surface is given by

$$F_m = \frac{3\,\pi\,\nu\,V\,B^2}{\mu_0\,\theta\,R}$$

where ν is volume fraction of ferromagnetics in the particle, V is volume of the particle, B is the magnetic induction at the drum surface, μ_0 is the magnetic permeability of free space, θ is the angular spacing between the magnet poles, and R is the drum radius.

The centrifugal force, F_c, acting on the particle is given by

$$F_c = \rho\ V\,\omega^2\ R$$

where ρ is the average density of the particle and ω is the angular velocity of the drum. There exists a critical angular velocity at which F_m equals F_c and this critical value, ω_c, can be found, by equating the expressions for F_m and F_c, to be

$$\omega_c = \left(\frac{3\,\pi\,\nu\,B^2}{\mu_0\,\rho\,\theta\,R^2}\right)^{0.5}$$

The above relationship can be expressed as

$$N_c = 4.99\,\frac{B}{D}\left(\frac{\nu}{\rho\,\theta}\right)^{0.5}$$

where N_c is the critical rotation speed and D the drum diameter.

Since F_m and F_c are both proportional to the particle volume, the particle size does not figure in the above relationship for the critical rotation speed. This means that the dry drum type magnetic separator can be used in the treatment of a feed containing particles with a wide range of sizes.

The expression for N_c highlights several interesting features regarding the standard intensity dry magnetic separator. A large value of N_c is desirable, while a faster speed of rotation allows a greater feed rate while keeping a constant depth of material on the drum. Moreover, the greater the speed at which the drum can be rotated without detachment of high-grade particles, the greater the centrifugal force applied to remove fine particles of gangue attached to the drum and to the magnetic particles. The expression for N_c indicates that it can be increased by: (i) increasing B; (ii) decreasing θ; and (iii) decreasing D. The characteristics of the material of the permanent magnet used limits B. The capacity of the separator is adversely influenced by reducing D. The most attractive way to increase N_c is by decreasing θ. Reducing θ by increasing the number of poles has the added advantage of increasing the degree of agitation applied to the chains of magnetic particles which tend to form between adjacent poles, thus enhancing the probability of the release of trapped gangue particles. However, if is reduced beyond a certain point, there is a significant reduction in B. It is, therefore, necessary to work with an optimum value of which is usually determined by empirical tests.

In the case of a high-intensity wet magnetic separation process, the principal force acting to resist particles from being captured in the matrix is the fluid drag force, F_D, which is given by the expression:

$$F_D = 3\,\pi\,\eta\,d\,V$$

where η is the fluid viscosity, d is the diameter of the particle, and V is the fluid velocity.

The magnetic force, F_M, as calculated for the case of a matrix made up of isolated,uniformly magnetized spheres, is given by the expression:

$$F_M = \frac{1}{3}\pi\,\mu_0\,S\,d^3\,r^{-1}\,M\left(H_0 + \frac{2}{3}M\right)$$

where S is the magnetic susceptibility of the particle, r is the sphere radius (matrix size), M is the magnetization of the sphere (matrix magnetization), and H_0 is the externally applied magnetic field.

It is seen from the two relationships given above that F_M is proportional to d^3 while F_D is proportional to d. This implies that small particles experience more difficulty with regard to collection in the matrix. The smallest particle that can be held by the matrix can be found out by equating F_D and F_M and solving for d. The expression obtained is

$$d = \left[\frac{9\,\eta\,V\,r}{\mu_0\,S\,M\left(H_0 + \frac{2}{3}M\right)}\right]^{0.5}$$

This expression gives clues as to how recovery can be increased (i.e., the minimum size of the recovered particles can be reduced). It can be done by decreasing V, decreasing r, increasing M, or increasing H_0. It is also important to gain an appreciation of the other consequences of changing these variables. Decreasing V leads to a lower capacity and more physical trappings on account of the washing action being less vigorous. Decreasing r brings about the following changes: (i) the collection surface area increases; (ii) the maximum and the average field gradients increase in inverse proportion to r (the magnetic force increases as long as the dimensions of the matrix are larger than those of the particles); (iii) the magnetic permeability is altered; (iv) the permeability to fluid flow comes down; and (v) the matrix becomes more difficult to penetrate with wash water. Increasing H_0 implies increased electric power consumption. Further, M increases as a function of H_0 only until saturation is attained. With a given matrix, therefore, there is a maximum value to which H_0 can be increased; increments beyond this are not economically justifiable since they do not cause M to increase.

2.10
Electrostatic Separation

Every mineral conducts or takes an electric charge on its surface if brought into contact with a source charged to a sufficiently high electrostatic potential. The readiness with which minerals do this varies widely, and it is upon these differences that the technique of electrostatic separation depends. In general, electrostatic separation is applied as a concentration process for only a small number of minerals. However, the process has proved to be highly successful, wherever applied. It is often combined with gravity and magnetic separation processes. Gravity separation is used to remove silica and produce a bulk concentrate; a combination of electrostatic and magnetic methods of separation is then used to separate the valuable minerals contained in it. Table 2.7 shows for a number of minerals the combi-

Table 2.7 Some characteristics of minerals utilized in separation processes.

Nonconductors (pinned)[a]			***Conductors (thrown)***[b]			
Magnetic	***Weakly magnetic***	***Non-magnetic***	***High magnetic***	***Magnetic***	***Weakly magnetic***	***Non-magnetic***
Monazite (4.9–5.4)[c] Xenotime (4.5) Garnet (3.4–3.7) Siderite (3.7–3.9)	Bastnasite (4.9–5.2) Epidote (3.5) Olivine (3.4) Tourmaline (3.0–3.2) Mica (biotite) (2.7–3.3)	Scheelite (5.9–6.1) Zircon (4.6–4.7) Barite (4.5) Corundum (3.9–4.1) Kyanite (3.5) Topaz (3.4) Sillimanite (3.5–3.7) Fluorite (3.2) Mica (muscovite) (2.8–2.9) Beryl (2.6–2.8) Feldspar (2.6) Calcite (2.7) Quartz (2.65) Sulfur (2.0–2.1)	Magnetite (5.5–6.5) Ilmenite (high iron) (4.5–5.0)	Ferberite (6.8) Ilmenite (4.5–5.0) Davidite (4.5)	Wolframite (7.1–7.9) Columbite-tantalite (5.0–8.0) Samarskite (5.5–6.5) Euxenite (5.4–6.0) Hematite (5.0–6.0) Chromite (4.1–5.1)	Gold (12.0–20.0) Copper (8.9) Galena (7.4–7.6) Cassiterite (6.8–7.1) Pyrite (4.9–5.2) Molybdenite (4.7–4.8) Rutile (4.2) Chalcopyrite (4.1–4.3) Limonite (3.6–4.0) Diamond (3.5) Graphite (2.1–2.3)

a) Pinned to electrostatic (high-tension) separator surface.
b) Thrown from electrostatic (high-tension) separator surface.
c) Number in parenthesis under each mineral show the density.

nations of density with conductivity and magnetic properties that can be used to obtain a separation. Starting with a mixture of any of the minerals given in Table 2.7, it may be assessed whether or not they can be separated by electrostatic, magnetic, or gravity methods and whether the use of any single method or of a combination of methods is called for. For example, if the minerals appear in different columns in the table, they may be separated by electrostatic and/or magnetic methods only. On the other hand, if the minerals appear in the same column, they can be separated by gravity concentration if their densities are sufficiently different (usually a difference in specific gravity of nearly 1.0 appears to be adequate for separation by the gravity method).

The electrostatic separation method is the exclusive choice in some specific situations, for example in the cases of rutile and ilmenite deposits. These deposits generally contain minerals of similar specific gravities and similar surface properties so that processes such as flotation are unsuitable for concentration. The major application of electrostatic separation is in the processing of beach sands and alluvial deposits containing titanium minerals. Almost all the beach sand plants in the world use electrostatic separation to separate rutile and ilmenite from zircon and monazite. In this context the flowsheet given later (see Figure 2.35 A) may be referred to. Electrostatic separation is also used with regard to a number of other minerals. Some reported commercial separations include those of cassiterite from scheelite, wolframite from quartz, cassiterite from columbite, feldspar from quartz and mica, and diamond from heavy associated minerals. Electrostatic separation is also used in industrial waste recovery.

It may be added here that electrostatic separation suffers from more or less the same disadvantages as dry magnetic separation in that both require a perfectly dry feed, and both have a relatively small capacity for finely divided material. For most efficient operation, it is necessary that the feed be processed in a layer (one particle deep), but this severely restricts the throughput of the electrostatic separation process.

2.10.1
Electrostatic Separators

In general, all electrostatic separator systems contain at least four components: (i) a charging-discharging mechanism; (ii) an external electric field; (iii) a nonelectrical particle trajectory device; and (iv) feed and product collection systems. Depending primarily on the charging mechanism involved, the electrostatic separator systems are classified into three categories: (i) free fall separators; (ii) high tension separators; and (iii) conduction separators.

Charging by contact electrification is an active mechanism whenever dissimilar particles make and break contact with each other, or whenever they slide over a chute or an electrode. This charging mechanism is most frequently used to charge selectively and obtain an electrostatic separation of two species of dielectric materials as realized in a free fall electrostatic separator.

The high-tension process leads to the separation of a mixture consisting of good and poor electrical conductors. The process is typically used for the separation of rutile and ilmenite (conductors) from zircon and other nonconductors found in beach sands. It is the charging of a corona which operates as the predominant mechanism of charging in a high-tension separator. The essential design features of a high-tension separator are shown in

Figure 2.18. The principle of separation is simple. A mixture of conducting and insulating particles is fed through the feed hopper, H, onto the grounded rotor, C. The grounded rotor provides a continuous surface which introduces the particles to the electric field. All the particles receive a surface charge, σ_s, as they go through an intense corona discharge from the electrode E_1 (the electrode is usually composed of tungsten). The polarity of the electrode used determines the type of corona that is produced. In the event of the electrode being positive, negative ions are accelerated toward the electrode, causing the breakdown of air molecules, with the result that positive ions are repelled outwards from the electrode in the form of a corona glow. In the event of the electrode being negative, positive ions are all accelerated toward the electrode and negatively charged oxygen ions are repelled outwards from the electrode in the form of a corona discharge. The particles, after leaving the corona region, lose their surface charge at a rate which is a function of their electrical resistance, the extent to which they remain in contact with C, and the magnitude of their initial surface charge. The good conductors are quick to share their charge with C and are thrown away from C along a trajectory determined by centrifugal force, gravity, and air resistance. At this point, however, the conductive particles enter the field of influence of the nondischarging electrode, E_2. The electrode tends to attract the falling particles farther away from the rotor C, making possible an accurate control of separation over a wide range of conditions. The story is different for dielectrics or poor conductors. They lose their charge very slowly and are thus held to the surface of C by the electric image force developed as a result of the associated surface charge. Particles composed of good electrical insulators, such as dry quartz, at times remain so strongly adhered to C by the image force that they require to be scraped from the reverse side of C by a fiber brush. In commercial separating machines an A. C. corona discharge electrode A (termed the wiper) is provided on the reverse side of the grounded rotor to partly discharge the adhering particles. This provision reduces the wear of the brush.

Whereas in ion bombardment, using a discharging electrode, charge transfer occurs (high-tension separator), in conductive induction no electric current passes between the electrode and the grounded rotor (conduction separator, Figure 2.19). If a solid particle is placed on a grounded rotor in the presence of an electric field, the particle will develop a surface charge by conductive induction. Conducting particles will quickly assume the ground potential of the rotor, which is opposite to that of the nondischarging electrode. The electro-

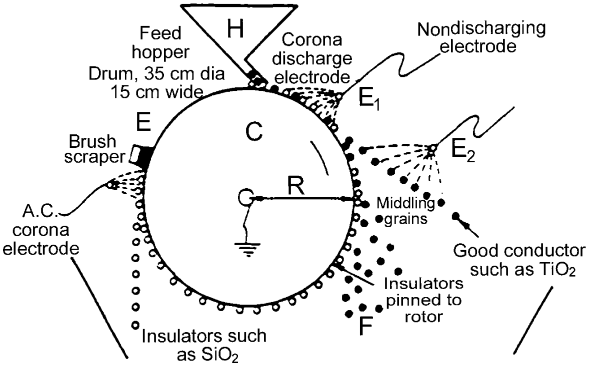


Figure 2.18 Principles of high-tension electrostatic separator.

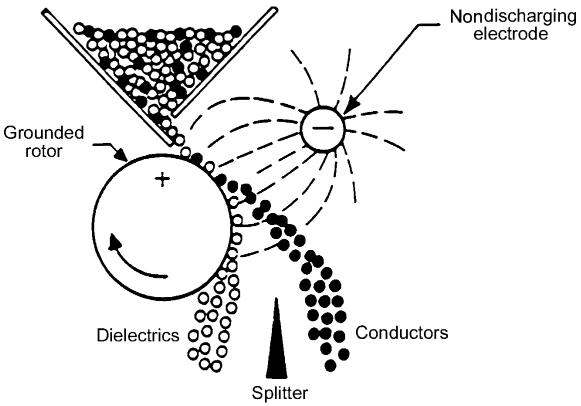


Figure 2.19 Principles of conduction separator.

static forces on these conducting particles will attract them towards the electrode, away from the grounded surface and the particulate flow. Dielectric particles, which are unable to pick up the charge from the rotor, remain polarized and are either attracted to the rotor or pass through the field without being influenced. A suitably placed splitter enables the two process streams, one of the dielectrics and the other of the conductors, to be separated.

2.11
Flotation

An earlier section which dealt with mineral separation included flotation among the category of concentration separation processes. The introduction of flotation was one of the major milestones in the history of mineral processing. There exist variations (natural or artificially created) in the surface properties of mineral particles, and the technique of flotation is based on the utilization of these differences. The actual specific gravity of the mineral particle plays little or no part in the separation.

A simple two-mineral separation, say of galena (specific gravity 7.5) from a siliceous gangue (specific gravity 2.65) can be taken as a good example to illustrate the process. The flotation operation comprises the following successive steps.

1. The raw ore material is ground in water, usually to −48 or −65 mesh.
2. The pulp density is adjusted to a consistency of 15 to 35% solids and the resulting feed is fed to the flotation cell.
3. Addition to the pulp of various reagents which have a number of functions is effected.
4. Aeration, either by agitation or by air injection, that impregnates the pulp thoroughly with bubbles, which are essentially gas-filled holes of macroscopic dimensions in the pulp, is carried out.
5. The attachment of minerals to the bubbles, which is the heart of the flotation process, occurs. Once this occurs, gravity completes the separation readily. In the present example, galena attaches itself to the bubbles and thereby its effective density is drastically reduced. This causes galena to buoy up in spite of the fact that it is, in reality, much heavier than the siliceous gangue.

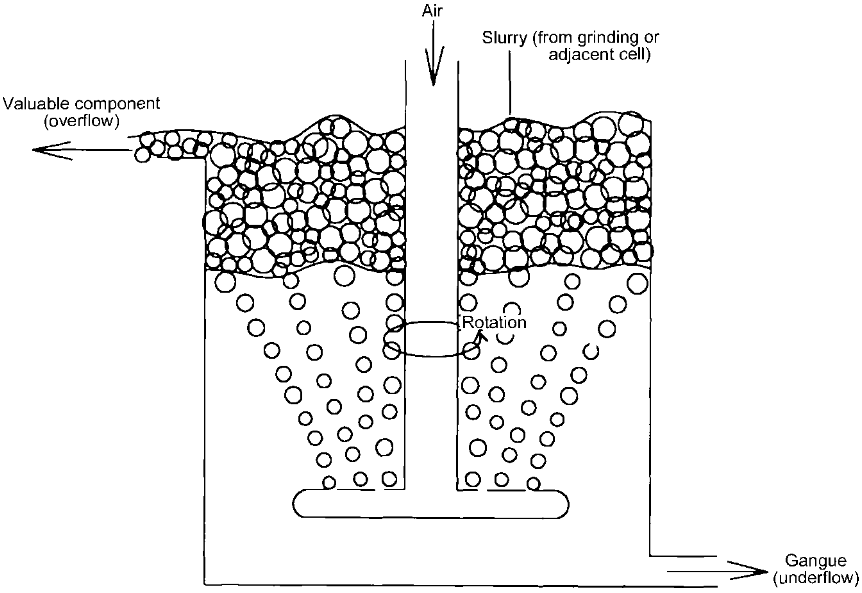


Figure 2.20 A simplified sketch of a flotation cell, showing its basic features.

6. The bubbles are collected as a froth at the surface.
7. The galena-bearing froth is removed from the top and the impoverished tailing is drawn away from the bottom of the cell. A device in which all these processes take place is called a flotation cell (Figure 2.20).

The process of separation of galena from the siliceous gangue, where the float fraction represents the concentrate while the gangue resides in the pulp, is called *direct flotation* (Figure 2.21 B). The process where the opposite happens is called *reverse flotation*. It is necessary that the froth phase is maintained adequately. With a very shallow froth, there is a risk of losing a part of the concentrate into the pulp. As a matter of economics, flotation separation is carried out in as dense a pulp as possible, consistent with good selectivity and pertinent operating conditions. The denser the pulp, the smaller is the volume required in a commercial plant, and also the less is the reagent required, since the effectiveness of most reagents used in flotation depends on their concentrations in solution. Most commercial floats are in pulps of 25 to 40% solids by weight. They can also be as low as 8% and as high as 55%, depending on the situation.

On the basis of the function it performs, the flotation process can be divided into two categories: (i) bulk; and (ii) selective. The process is called bulk or collective flotation when it accomplishes the separation of several valuable components from the gangue minerals. In selective flotation, one valuable component is separated from several others. This selectivity could be accomplished by either using collectors selective with respect to a particular mineral or by differential flotation wherein two or more mineral concentrates are recovered consecutively from the same feed by using modifiers.

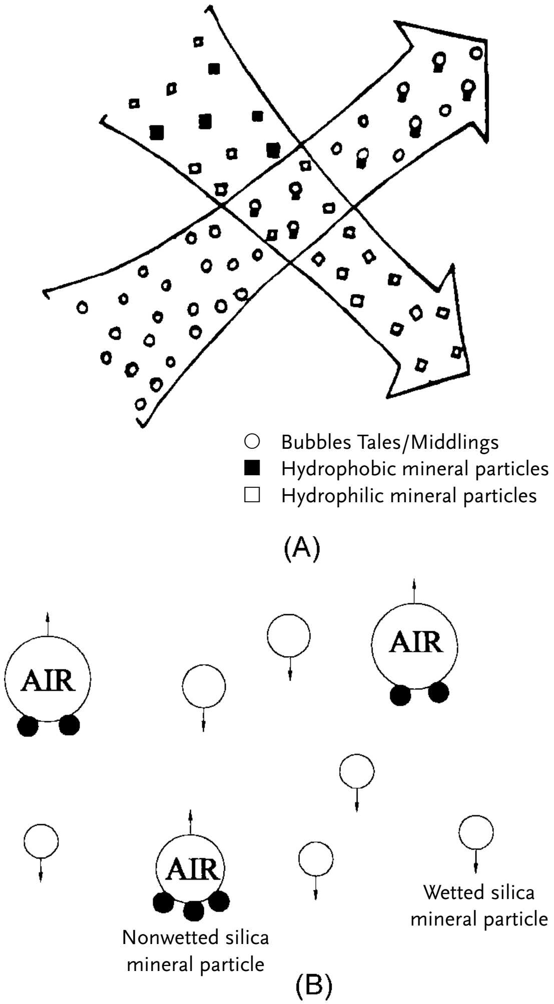


Figure 2.21 (A) Separation of hydrophobic from hydrophilic particles in flotation. Bubbles with some of them attached with hydrophobic mineral particles shown in the rising mode. Hydrophilic mineral particles with minority presence of hydrophobic mineral particles (those lost chance for contact with bubbles) and bubbles attached with hydrophobic mineral particles (those got mechanically driven along with hydrophilic particles) shown in the descending mode. (B) Froth flotation: air bubbles carry nonwetted particles upwards, while wetted mineral particles drown.

2.11.1
Principles

It is considered relevant to begin this presentation on flotation principles by drawing a reference to Figure 2.22 which quite comprehensively presents a summary of general classification of mineral processing separation methods. Present attention is focused on the

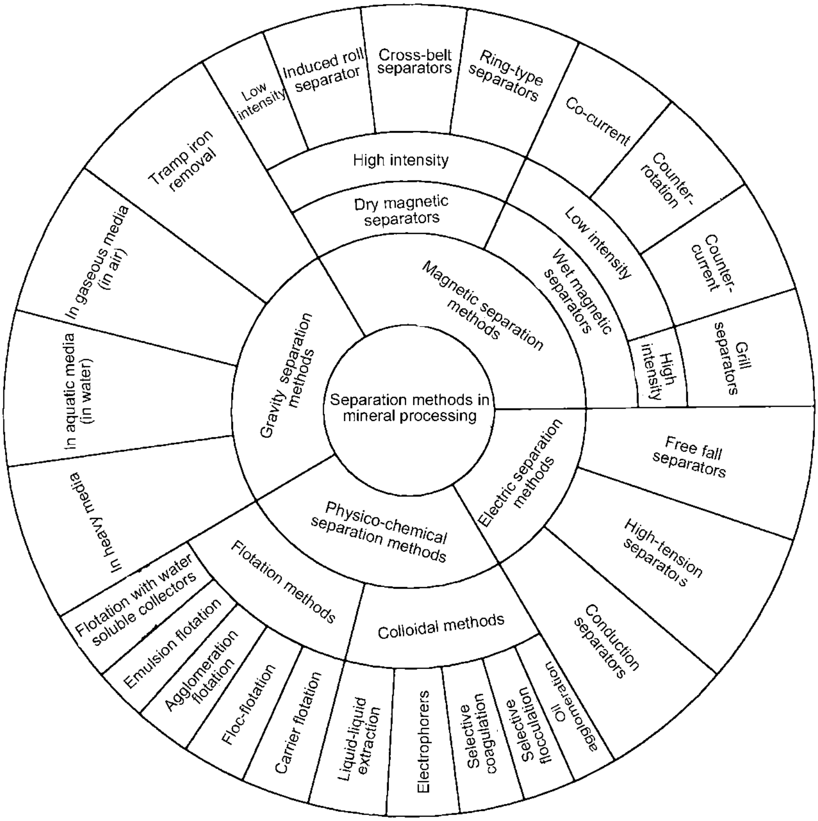


Figure 2.22 Classification of mineral processing separation methods.

classification of the physico-chemical separation methods which can be subdivided into *colloidal* and *flotation* methods. The two methods are based on differences in the surface properties of the minerals separated. In colloidal methods, separation can be achieved by selective aggregation (coagulation, flocculation, agglomeration) of one of the mineral species into aggregates while leaving the other minerals in a dispersed state. The aggregates can then be separated from the dispersed material by sedimentation sieving, or other appropriate techniques.

In flotation it is clear by now that there are three phases: air, mineral, and water. The three are shown in Figure 2.23 (A) to meet at a common boundary. In this condition there will be a balance of interfacial tension forces. These can be resolved so that, for equilibrium at the point of intersection:

$$\gamma_{AM} = \gamma_{MA} \cos \theta_{WA} + \gamma_{WM} \cos \theta_{WM}$$

where γ_{AM}, γ_{WA}, and γ_{WM} are respectively the interfacial tensions between air and mineral, water and air, and water and mineral phases and θ_{WA} and θ_{WM} are the angles shown in Figure 2.23 (A). A special case of this common boundary between the three phases is the contact between the water, the mineral and the air (Figure 2.23 B). In the figure, the phase mineral, has been shown as a plane surface of a solid. In the present situation, θ_{WM} is zero and θ_{WA} is called the contact angle θ. It is the convention that θ is measured in the water phase. The equation above then takes the form as shown below:

$$\gamma AM = \gamma WA \cos\theta + \gamma WM$$

The relationship given above is the familiar Young's equation. If $\theta > 90°$, cos θ is negative and $\gamma_{WM} > \gamma_{AM}$. This implies that attraction of water for mineral is not as strong as the attraction of air for mineral, and the water does not wet the mineral. If $\theta < 90°$, cos θ is positive and $\gamma_{AM} > \gamma_{WM}$. The water has a relatively strong attraction for mineral and the water wets the mineral (Figure 2.23 B). Owing to the difficulty in measuring the actual values of γ_{AM} and γ_{WM} it is the θ which provides the only means of perusing their relative strength. When $\theta = 0°$, the water will spread completely over the mineral surface, and when $\theta = 180°$ there will be no attraction between water and mineral.

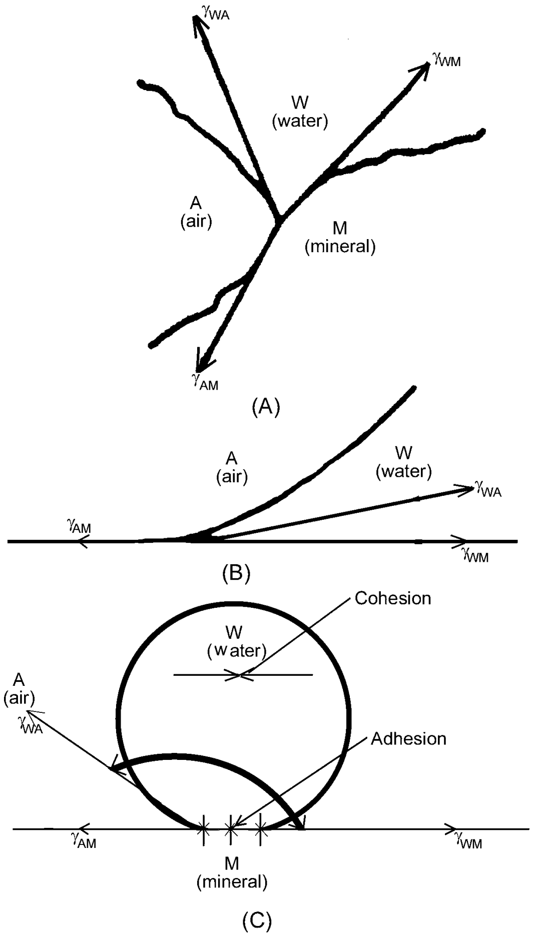


Figure 2.23
(A) Interfacial tensions at the junction between mineral, water and air phases. γ_{WA} stands for the interfacial tension between the phases, water and air, and is drawn along the tangent to the WA phase boundary at the junction. Drawn similarly are γ_{WM} and γ_{AM}.
(B) Contact between air, water and mineral where the mineral phase has a plane surface. θ is the contact angle and the water wets the mineral.
(C) Illustration of the effect of work of cohesion of water and work of adhesion to mineral on the mineral wettability.

The force needed to break the mineral–air interface is called the work of adhesion, W_A, and is equal to the work needed to separate the mineral–air interface and produce in place air–water and mineral–water interfaces. This, in other words, may be represented with interfacial tensions in place as:

$$W_A = \gamma_{WA} + \gamma_{AM} - \gamma_{WM}$$

In the case of air–mineral–water boundary, the Young's equation can be substituted in the above equation and the following relation is obtained:

$$W_A = \gamma_{WA}\,(1 + \cos\theta)$$

when $\theta = 0°$

$$W_A = 2\,\gamma_{WA}$$

and is called the work of cohesion of the water. It may be noticed that if $\theta < 90°$, $W_A > \gamma_{WA}$ and water wets mineral and if $\theta > 90°$, $W_A < \gamma_{WA}$ and the water does not wet the mineral by the given definition of wetting in terms of the contact angle. With complete nonwetting, $\theta = 180°$ and $W_A = 0$.

In summing up, it may be mentioned in a general way that as θ increases from 0° to 180°, the behaviour of mineral particles alters from one extremity of showing complete affinity for water to the other extremity of showing complete repulsion to water. The minerals having affinity for water are called *hydrophilic* and those that are not having such behaviour are called *hydrophobic*. Between the two extremities of the contact angle lie the intermediate values which govern the extent of hydrophobicity or the hydrophilicity of a mineral in any given instance. The scenario involving work of adhesion and of cohesion in a mineral, air, and water system is shown in Figure 2.23 (C).

From the text pertaining to principles of flotation given earlier it is easy to comprehend selectivity in flotation. For selective flotation to occur, there must be an appreciable difference in the degree of wetting and nonwetting of the solid components in the mixture. On this basis, flotation can be described as being one of the more powerful techniques for separating hydrophobic constituent particulates (in a mixture of solid phases) from hydrophilic constituents. From the relationship for γ_{AM} given earlier it can readily be seen that if θ, for instance, is greater than 90° (obtuse angle), $\cos\theta$ is negative and $\gamma_{MW} > \gamma_{AM}$; in this situation the system can lower its energy by lowering the interfacial tension between *A* and *M* in preference to that between *M* and *W*. This is a consideration for having a strong incentive for the mineral not to be wetted by the water. In another instance, where, θ is less than 90° (acute angle), $\cos\theta$ is positive and $\gamma_{AM} > \gamma_{MW}$; in this situation the system can lower its energy by increasing the interfacial tension M and W in preference to that between *A* and *M*. Therefore, unlike the previous case, there is a strong tendency for the water to wet the mineral particle. The value of θ for a mineral relative to that for another must be higher if the first mineral is to be floated in preference to that between *A* and *M*. Therefore, unlike the previous case, there is a strong tendency for the water to wet the mineral particle. The value of θ for a mineral relative to that for another must be higher if the first mineral is to be floated in preference of the second.

Like all processes, the flotation process leads itself easily to thermodynamic analysis. The attachment process implying the attachment of a particle to a bubble occurs only when the free energy change associated with process is negative. A useful form relating to free energy change (ΔG) with the interfacial tension between the water and air (γ_{WA}) and the contact angle is given by the following:

$$\Delta G = \gamma_{WA}\,(\cos\theta - 1)$$

The equation above is called the "thermodynamic criterion of flotation". Its only strict interpretation is that the more negative the value of ΔG, the more is the probability of mineral nonwetting ($\Delta G = 0$ for $\theta = 0°$, and $\Delta G < 0$ for $\theta > 0°$).

Chemical thermodynamics can be used to predict the possibility of a reaction occurring when imposed with a given set of conditions of temperature and pressure. It can also forecast the direction in which the equilibrium of the reaction will be shifted when these parameters are varied. Flotation thermodynamics can prognosticate the likelihood or otherwise of a mineral particle and an air bubble to become attached to each other at the instant of their collision. Clearly, not all particles which collide with bubbles become attached; otherwise, no separation would be possible by flotation. Only those particles that are sufficiently hydrophobic attach themselves to the air bubbles by forming a three-phase contact with a finite contact angle. While flotation thermodynamics can foretell the probability of particle-to-bubble attachment, it begs the question: does it fail to predict the rate of the flotation process? The answer to this question is simply, no. This is easy to comprehend from the fact that the activation energy barrier opposing a particle-to-bubble attachment does not depend on the free energy change accompanying the attachment. However, a deep insight into the mechanism of flotation and a capability to predict the rate of flotation of various minerals in the conditions prevailing in the actual systems would facilitate scale-up and design of industrial flotation plants. Of the different approaches to this problem, the kinetic approach offers an easy and reliable method for realizing this objective.

The study of flotation kinetics relates to a number of mass transfer processes and these are listed in Table 2.8. The term, entrainment which figures in the mass transfer process statements made in Table 2.8 may be elaborated. It is the process by which particles enter the base of a flotation froth and are transferred up and out of the flotation cell suspended in the water between bubbles. Entrainment should be distinguished from true flotation, whereby particles come out of the cell attached to bubble surfaces. True flotation is chemically selective, while the entrainment process recovers both gangue and valuable minerals alike. Entrainment harms the product grade since recovery of the more abundant gangue mineral reduces the quality of the concentrate. This is especially true in the processing of fine ores. Much flotation research has dealt with reducing entrainment in order to improve

Table 2.8 Mass transfer processes.

1. Selective handover of matter from the pulp to the froth by particle–bubble attachment.
2. Nonselective handover of matter from the pulp to the froth by mechanical and hydraulic entrainment.
3. Reversal (both selective and nonselective) of matter from the froth to the pulp through froth subduction, bubble coalescence and liquid drainage.
4. Mechanically or hydraulically induced matter handover from the froth into the concentrate product.

the product grade, and this has been one of the main reasons behind the development of column flotation systems.

The removal rate of particles or the rate of flotation from pulp is essentially governed by: (i) collision between particles and bubbles; (ii) adhesion of particles to bubbles; and (iii) detachment of particles from bubbles. Keeping these factors in mind, one can arrive at the following relationship:

$$P = P_c \cdot P_a \cdot (1 - P_d)$$

where P is the probability collection (it can also be termed as the recovery, R), P_c is the probability of collision between a particle and a bubble, P_a is the probability of adhesion or attachment after collision, and P_d is the probability of detachment.

2.11.2
Flotation Chemistry

The success of flotation depends greatly on the development of the correct chemical conditions in the system in which a given flotation process is to be carried out. An appropriate chemistry is built up by using different chemical reagents. The reagents in use in flotation are broadly divided into two categories: surfactants and regulating or modifying agents. To account for different floatable systems mention may be made of flotation of sulfides, of insoluble oxide and silicate minerals, of semisoluble salts and of soluble salts. Among these sulfide flotation has received most attention and been studied most extensively.

Minerals belonging to the category of insoluble oxide and silicate minerals are many in number. Insoluble oxide minerals include those superficially oxidized and those of oxide type. The former category comprises mainly superficially oxidized sulfide minerals, including metals such as aluminum, tin, manganese, and iron which are won from their oxidic sources. As far as silicate minerals are concerned, there can be a ready reference to several metals such as beryllium, lithium, titanium, zirconium, and niobium which are known for their occurrence as (or are associated with) complex silicates in relatively low-grade deposits.

Those minerals whose solubilities are greater than those of most oxides and silicates, but lower than those of soluble salt minerals, are grouped as “semisoluble salt minerals” (also called salt-type minerals). The list comprising this particular minerals group is calcite, dolomite, magnesite, barite, gypsum, scheelite, carbonate, phosphate, sulfate and some others. These minerals are characterized mainly by their tonic bonding and as has already been pointed out, by their moderate solubility.

Separation of these minerals from oxides and silicates can be readily accomplished as the surface chemical and physical properties of these minerals are very similar. On account of this fact, separation of the metals themselves has proved to be extremely difficult.

Potash minerals represent excellent examples of soluble salt. The components of potash deposits commonly comprise a complex confluence of halides–halite, NaCl; sylvite, KCl; carnallite, $KCl \cdot MgCl_2 \cdot 6\,H_2O$ and/or sulfates–langbeinite, $2\,MgSO_4 \cdot K_2SO_4$; kainite, $MgSO_4 \cdot KCl \cdot 3\,H_2O$ etc. These salts were recovered previously from mixtures comprising natural deposits by a lengthy fractional crystallization procedure. It is by selective flotation in a saturated brine solution that the concentration of the potash minerals is accomplished. The process is, however, preceded by the removal of clay, using hydrocyclones, followed by thickeners and/or inclined hydroseparators. Clays entail an unduly high consumption of all flotation reagents, and this enhances the viscosity of saturated solutions. If desliming is attempted to remove these materials, there substantial losses of potassium chloride (KCl) occur. With ores containing sylvite and carnallite, the separation of clay is followed by selective flotation of either sylvite (using *n*-alkyl amines or sulphonates as collectors) or halite (using *n*-alkyl carboxylates of heavy metals ions and a nonpolar oil addition). The concentrate grade aimed for is about 60% K_2O equivalent. With ores containing other salts as well as sylvite and halite, selective flotation is much more complicated and the grade of the concentrates produced is lower. The sulfate salts of magnesium and potassium can also be separated from sodium sulfates, though less efficiently than chlorides.

This part of the presentation embodies first a general treatment on surfactants followed by the elaboration of frothers, collectors and regulators. The text subsequently involves the area of sulfide flotation, which occupies a premier position in the field of flotation. The section is completed with some important examples of flotation of sulfides. The final section is devoted to natural hydrophobicity which, on its own accord constitutes an important and interesting area in the field of flotation.

2.11.2.1 **Surfactants**

A great many of inorganic and organic reagents are used in flotation for the purpose of controlling the characteristics of interfaces.

Any species (whether organic or inorganic in, nature) which has a disposition to concentrate at one of the five possible interfaces is called a "surface active agent". According to this, an ion is a surface active agent with respect to an oppositely charge surface site. The name surfactants is reserved for surface active amphipatic molecules, R-Z (that is, a molecule of dual character), represented by a polar group Z and a nonpolar group Z. The polar group Z consists of an aggregate of two or more atoms which are covalently bonded but have a permanent dipole moment; the occurrence of this dipole makes the group hydrophilic. In addition to the dipole, the polar group may (but need not) be ionized. The nonpolar group or radical R is commonly represented by a hydrocarbon (but it may be a fluorocarbon or a siloxane). It does not possess a permanent dipole. It stands for the hydrophobic portion of the amphipathic molecule.

As a result of a large number of polar groupings and a still larger variety of nonpolar groups, there exists a vast number of reagents which serve as surfactants. These can be classified either according to the electrical charge associated with their polar group into anionic, cationic, or nonionic, or according to the hydrocarbon structure (alkyl, aryl, phenyl, cyclohexyl, alkylanyl, etc.), or according to the specific type of polar group. The last one in the list is by far the most useful in differentiating the action of surfactants and in specifying their characteristics. An overall subdivision of surfactants into one group representing monopolar species and the other consisting of multipolar ones is also helpful.

Surfactants play a twofold role in flotation:

- by adsorbing at the mineral (solid)–water (liquid) interface, they make the surface of selected minerals hydrophobic in character (the reagents functioning in this way are called collectors);
- they influence the kinetics of bubble–mineral attachment.

The latter surfactants are customarily referred to as frothers, but their frothing abilities are not the most important characteristic.

Since flotation surfactants are, in general, supplied to the interfaces through the aqueous solution phase, it is mainly those reagents that are somewhat water-soluble are used in flotation. The surfactants of particular importance to flotation may be conveniently grouped into: (i) monopolar; and (ii) multipolar. Each group is subdivided into three classes in order to facilitate the discussion of their characteristic behavior in aqueous solutions and during adsorption at interfaces: (i) thio compounds, which act mainly as collectors for metallic sulfides; (ii) non-thio, ionizable compounds, which may act as both collectors and frothers; and (iii) nonionic compounds, some of which act mainly as frothers, while others act as depressants, flocculating agents, and even as activators (collectors).

2.11.2.1.1 **Frothers**

An adequate froth is essential for flotation since it has to bear the mineral and survive until the constituent bubbles pass out of the pulp. Following separation, the froth should not be so persistent as to be resistant to destruction when sprayed. It must possess elasticity for it must not break under the disturbance it controls during its ascent to the surface, otherwise its mineral load would be lost. On reaching the top of the pulp of the cell, a definite thickness of froth has to be maintained to allow cleaning of the floated material to occur. Mechanically entrained gangue particles will tend to escape with the draining liquid. With stiff, rigid, and stable froths an additional spray of water over the top of the froth may facilitate the cleaning action by drainage. Froth becomes stabilized by hydrophobic solids when they adhere to the air–water interface so closely that the draining of the liquid is restricted. If, in addition, extensive flocculation of particles takes place, fairly thick layers of interlocked particles are formed at each of the two air–water interfaces separating the bubbles.

There are requirements for or surfactant to serve as a good flotation frother. The primary purpose of a frother addition is to change drastically the kinetics of particle–bubble attachment. It achieves this feat by ensuring that the thinning of the liquid film between the two colliding particulates, the particle and the bubble, and the rupture of the thinned film (with the necessary establishment of the particle-bubble attachment area) can occur within the collision time. Secondary requirements pertain to ensuring a proper degree of stability of the aggregate particle–bubble aggregate and allowing most (or preferably all) of the mechanically entrapped (and weakly adhering) particles of unwanted minerals to escape with the draining liquid. It may be pointed out that the stability of the particle–bubble aggregate and the stability of the mineralized froth formed during the draining process atop the pulp in the cell are not the same. The former is involved with adhesion and the latter with cohesional behaviours within a mixed liquid–particle film. The mineralized froth should have a restricted degree of stability; it should be stable enough to overflow in cell without losing the attached solid particles, but should break down following entry into the launder.

The frother should not in itself be a strong collector, especially of minerals meant for drowning. It should work in the presence of the other reagents necessary for flotation. The frothers must be soluble in water to some extent; otherwise they would be distributed very unevenly in an aqueous solution, with the result that their surface activity would not be fully effective or exploited. There are three main groups of reagents employed by the mineral industry as frothers (Figure 2.24) these different groups include aliphatic alcohols (me-

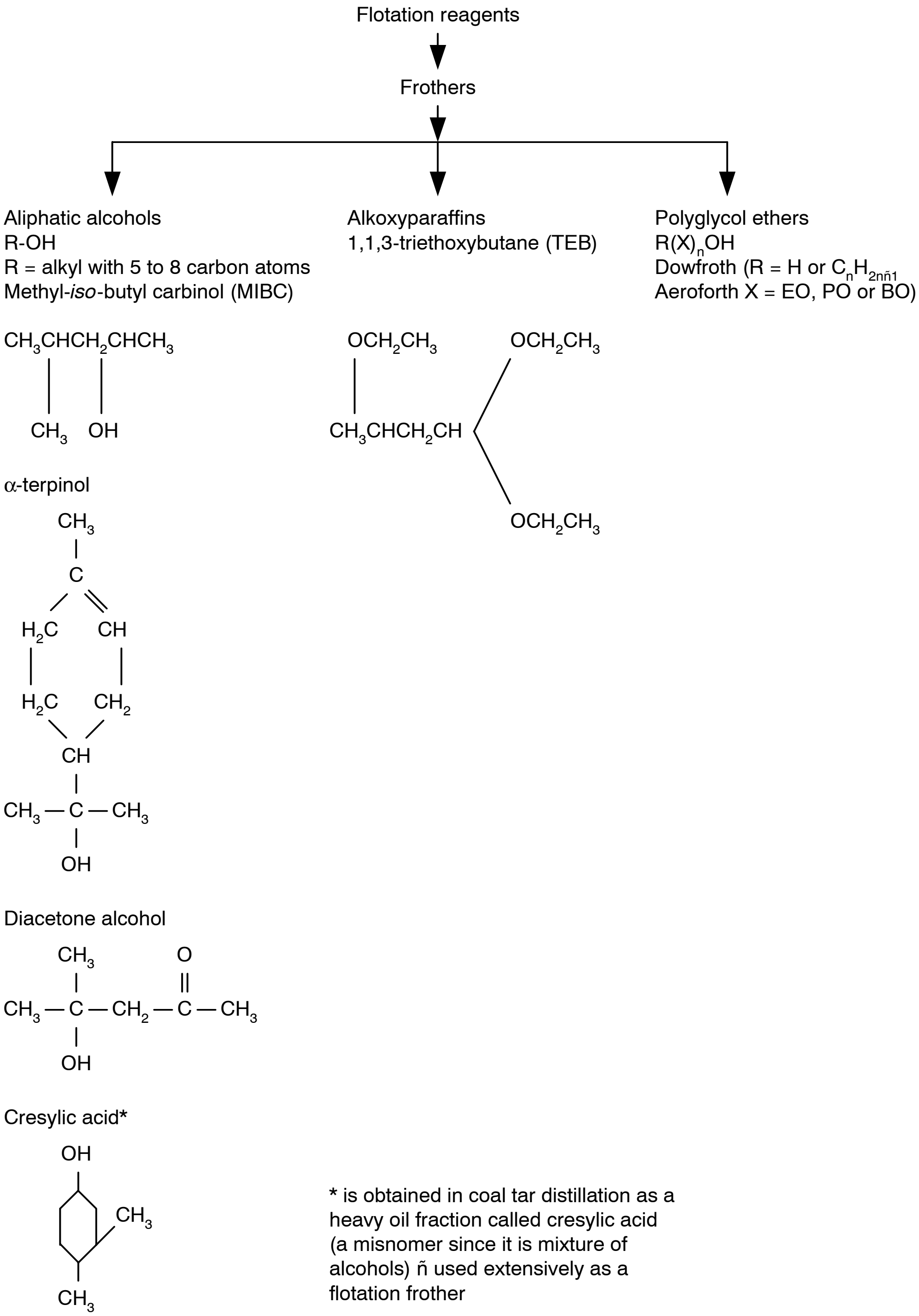


Figure 2.24 Classification of flotation reagents–frothers.

thyl-*iso*-butyl carbinol (MIBC), α-terpinol, diacetone alcohol and creyslic acid), alkoxyparaffins (1,1,3-triethoxybutane), and polyglycol ethers (Dowfroth, Aerofroth). It should be clear by now that frothers are essentially heteropolar reagents comprising polar and nonpolar groups. The adsorption process involves reaction between frother molecules and water wherein the water dipoles join readily with the polar groups and hydrate them. The nonpolar hydrocarbon group, however, remains inert. The process tends to coerce the nonpolar group into the air phase. Thus, the heteropolar structure of the frother molecule leads to its strong adsorption at water–air interface, with the polar group oriented towards the water and the nonpolar groups towards the air. When two bubbles come together, their surface films meet with polar groups facing each other and they tend to repel each other rather than coalesce. This phenomenon provides froth stability.

2.11.2.1.2 **Collectors**

Once the stability of the bubbles has been assured by the use of frothers, it becomes necessary to work on the mineral surfaces. These must be made hydrophobic. Most minerals are ionically or covalently bonded, which explains the fact that they are hydrophilic. Surfactants capable of adsorbing in such a manner that the solid surface is converted from hydrophilic to hydrophobic in character are referred to in flotation systems as "collectors". They are the most critical of the flotation reagents. It may be recalled that if the mineral is to be nonwetted by water, θ must be greater than 90°. Then $\gamma_{AM} < \gamma_{MW}$. To lower γ_{AM}, an extraneous addition adsorbs at the mineral–air interface must be added. This must not lower γ_{WM} and must, therefore, present a surface which has a repelling action on water. Such a substance is the "celebrated collector", this is chemically best described as a heterogeneous (heteropolar) compound that contain a functional inorganic (polar) group coupled with a hydrocarbon chain (nonpolar end). In general, the polar group is the portion of the collector molecule that adsorbs on the mineral surface, while the nonpolar end, being nonionic in nature, provides hydrophobicity to the mineral surface as a result of collector adsorption. In effect, the nonpolar ends of collectors are oriented towards water, and this is responsible for imparting hydrophobicity to the particles. Collectors and frothers bear the similarity that both are heteropolar in nature. The difference between them lies in the fact that the polar groups of collectors have an affinity for the particular mineral of interest, whereas the polar groups of frothers have an affinity for water only. These characteristics have been depicted in Figure 2.25. The collectors are seen to have two functional "ends", one ionic, which is adsorbed at the mineral surface by chemisorption (chemical reaction with the ions of the mineral surface) or by physical adsorption (electrostatic attraction to the mineral surface), and the other an organic chain or group, nonionic in nature, which has provided the hydrophobic surface to the mineral. In a situation where different minerals are present, if the collector can be made to adsorb specifically on one mineral rather than on the others present, this mineral can be rendered nonwettable and can be floated selectively from the other minerals. This represents a selective flotation process. It is important to add that collectors are generally added in small amounts just to provide a monomolecular layer on the substances concerned. Addition of increased amounts, apart from cost, may lead to co-float other substances, a welcoming situation especially when selectivity is desired. It is the experience of practioners of flotation that it is always more difficult to remove a collector that is already adsorbed than to forestall its adsorption.

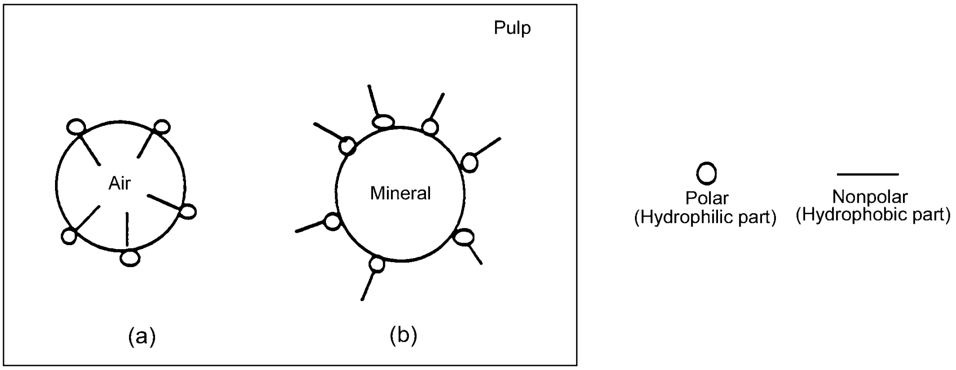


Figure 2.25 Actions of the (a) frother and (b) collector.

There are basically two types of collector molecules: ionizing and nonionizing compounds. The former dissociates into ions in water, while the latter does not. Ionizing collectors are classified in accordance with the type of ion (anion or cation) that causes the water-repellent effect in water.

Anionic collectors may be classified into two types according to the structure of the polar group: oxyhydryl collectors and sulfydryl collectors. The collectors belonging to the category of anionic oxyhydryl collectors are the carboxylates (fatty acids), sulfonates, alkyl sulfates and certain chelating agents. The collectors that belong to the category of sulfydryl anionic collectors are xanthate and a number of other sulfur-bearing surfactants.

The only industrially used cationic collector is amine, which ionizes in aqueous solution by protonation. Based on the number of hydrocarbon radicals bonded to the nitrogen atom, the amines are classified into primary, secondary, tertiary, and quaternary. The amine is termed as a primary amine if only one hydrocarbon group is present with two hydrogen atoms. Correspondingly, amines holding two, three and four hydrocarbon groups are termed secondary, tertiary, and quaternary amines respectively. In addition, there may also be variations present in the configuration of the hydrocarbon chain of the amine. The amines can be alkyl, aryl, and alkylaryl. Primary, secondary, and tertiary amines are weak bases, but quaternary amines are strong bases. Quaternary amines, then, are fully ionized at all values of pH, while the ionization of primary, secondary and tertiary amines is pH-dependent. It may in general be pointed out the affinity of forces for adsorption of cationic collectors on mineral surfaces is not as strong or irreversible as the chemical characteristic as cationic collectors. The cationic collectors, therefore, tend to be weak in their collecting power, and while they are most effective in slightly acidic solutions, they are inactive in strongly alkaline and acidic solutions. Those collectors which are nonionizing compounds once adsorbed, render the mineral hydrophobic in same manner as heteropolar collectors. The classification of collectors as described herein is shown in Figure 2.26 (A).

An important aspect of collector is shown in Figure 2.26 (B). It is seen that, when tested separately as pure particles, each of the three different X, Y and Z may require a different threshold collector concentration ($C_x < C_y < C_z$) for, say, 95% recovery. Theoretically, it would thus appear that starting with the lowest level of threshold collector concentration, such as

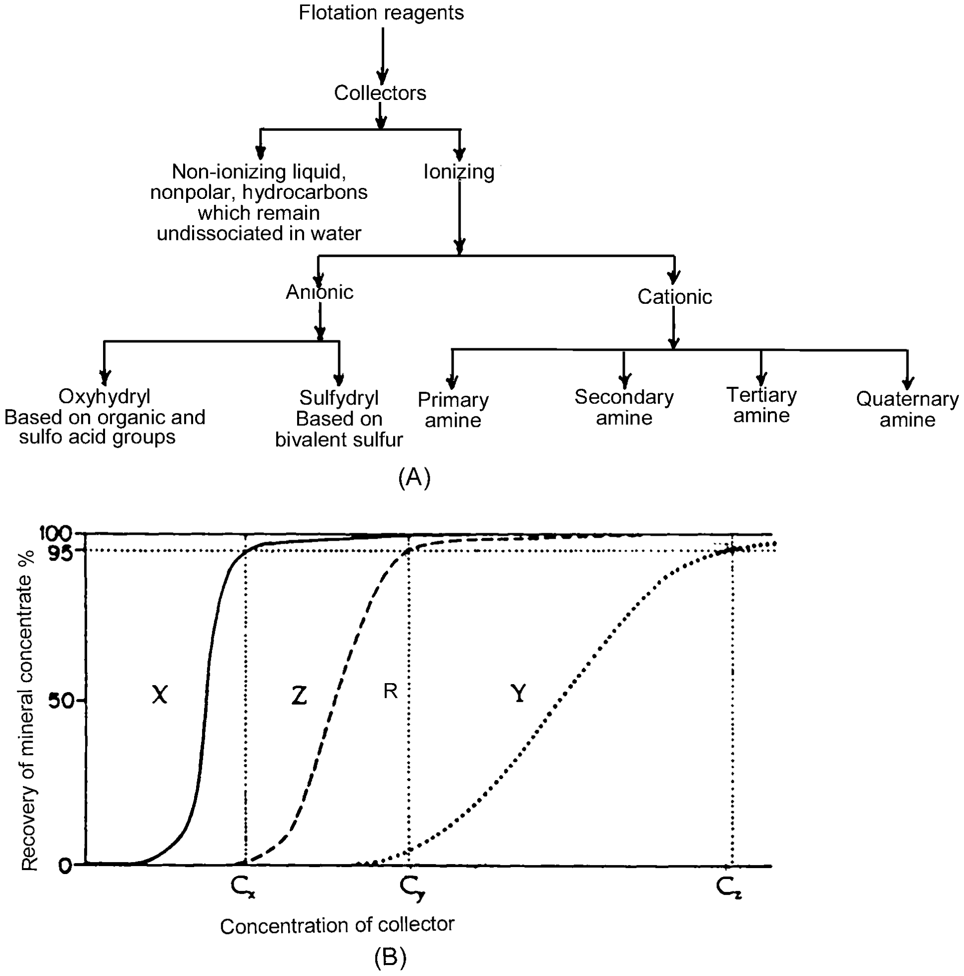


Figure 2.26 (A) Classification of flotation reagents-collectors; (B) threshold concentration of collector (see text for description).

C_x, a selective separation of mineral x could be attained first without any appreciable quantity of mineral y and z being floated. An increase of the concentration to C_z (Figure 2.26 B) should then allow mineral z to be floated next, leaving mineral y to be floated last, after the concentration of collector is raised above C_y. It may, however, be pointed out that as soon as the three minerals are mixed together, they often begin to interact, mutually altering their individual surface characteristics. In consequence, the theoretically possible selectivity based on the use of an appropriate collector concentration alone is not commonly attained. The effects of mutual alteration of surface characteristics may be ameliorated by the control of pH and by additions of modifying agents. Thus, the selectivity in practice is achieved not so much through different concentrations of collector alone but through a combined effect of activating and depressing agents together with the collector species.

2.11.2.1.3 Regulators

In the flotation process, the function of the regulators or modifiers is to modify the action of the collector, either by enhancing or by reducing its hydrophobic effect on the mineral surface. They thus make the collector action more selective towards certain minerals. Regulators are classified into three groups of reagents, which are known as activators, depressants, and pH modifiers, as shown in Figure 2.27. The purpose of regulators is to prepare the surfaces of the various solids for the subsequent selective adsorption of the surfactant(s) in such manner that only the desired particles are made hydrophobic.

Activators are those reagents which act in a manner converse to the action of depressants, i.e., they render those minerals floatable which either have been temporarily depressed or would not float without their assistance. They are generally soluble salts which ionize in the aqueous medium. The ions then react with the mineral surface, providing a monomolecular coating and thereby making the mineral surface favourably disposed to the collectors. Sphalerite (ZnS) is essentially not floatable with common collectors. The addition of Cu^{2+} to the solution, however, alters the mineral surface to CuS, which can adsorb collector. This feature is described elaborately in a later section.

A strict control of the pH of the pulp is usually the first important requirement for a successful selective separation by flotation. All surfactants that can act as collectors do so only within a certain narrow range of the pH scale. When such surfactant species adsorb as collectors within this pH range on several solid phases, specific inorganic or organic ions (or nonionized multipolar species) known as “depressants” must be added to suppress those phases whose separation with the chosen solid is not required. The depressants act in an opposite manner to the activators and counteract the collectors. A naturally occurring depressant is slime. Slimes present in a comminuted mineral coat the particles, and this has a retarding action on the adsorption of collectors on them. Among the chemicals used as depressants, mention may be made of sodium cyanide which depresses pyrite (FeS_2) while floating galena (PbS), sphalerite (ZnS), or copper sulfide (CuS); zinc sulfate which depresses sphalerite while floating galena; sodium ferrocyanide which depresses copper sulfides while floating molybdenite (MoS_2); lime to depress pyrite; sodium silicate to depress quartz; and dextrins to depress graphite and talc during sulfide flotation. Nokes reagent and anamol-D are also important depressants. Nokes reagent is a reaction product of phosphorus pentasulfide and sodium hydroxide. The anamol-D reagent is prepared by dissolving 20% by weight of arsenic oxide in a concentrated solution of sodium sulfide. The depressing action of both these reagents ensues from sodium sulfide. The section on sulfide flotation (see later) describes the chemical aspects of the depressing action of sodium sulfide.

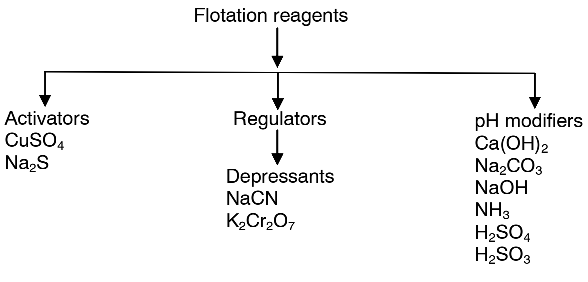


Figure 2.27 Classification of flotation reagents–regulators.

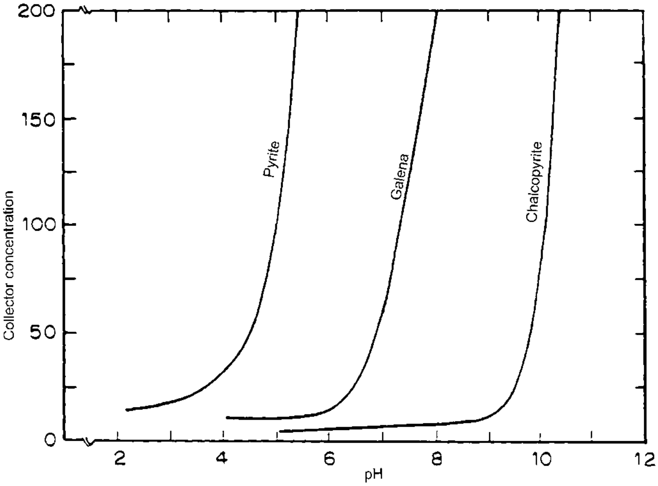


Figure 2.28 Critical pH curves for flotation with sodium dithiophosphate as collector for some sulfidic minerals.

Chemicals identified as pH modifiers, which are also referred to in the literature by terms such as "conditioners" and "alkalinity regulators", can play an important role in the flotation process. The control of pH is important not only in determining the efficiency at which a particular mineral may be floated but also in discriminating between minerals having similar surface properties. For example, it can be seen from Figure 2.28 that by using a collector concentration of 25 mg L^{-1} of sodium diethyl dithiophosphate and a pH value lying between 6.5 and 9.5, it is possible to obtain separation of galena and pyrite from chalcopyrite since under these conditions of the pulp, chalcopyrite will float but galena and pyrite will not do so. On reducing the pH value to 6, the galena can be floated, from the pyrite. Flotation, wherever possible, is implemented in an alkaline condition; this is because most collectors are stable under alkaline conditions. These conditions also minimize corrosion problems pertaining to cells, pipework, etc. The control of alkalinity is effected by adding appropriate quantities of lime, soda ash (sodium carbonate) and, to a lesser extent, caustic soda (sodium hydroxide) or ammonia. In cases where a decrease in pH is required, sulfuric or sulfurous acid is used. Lime, used in the form of milk of lime, is usually the preferred reagent to regulate the pulp alkalinity. The pH control agent has to carry out certain additional functions which include: (i) precipitation of heavy metal ions such as Cu^{2+}, Pb^{2+}, etc., which might cause accidental activation or depression or reaction with the collector; (ii) prevention of hydrolysis of the collector which may take place at low pH values; and (iii) inhibition of corrosion by acid mine waters. The reagent for pH control is, therefore, often added at the earliest point in the grinding operation preceding flotation.

2.11.2.2 **Sulfide Flotation**

Flotation of sulfide minerals is a popular topic in the literature dealing with flotation. It displays well the application of the different flotation reagents such as frothers, collectors, depressants, and activators.

2.11.2.2.1 **Principles**

The adsorption of collectors on sulfide mineral occurs by two separate mechanisms: chemical and electrochemical. The former results in the presence of chemisorbed metal xanthate (or other thiol collector ion) onto the mineral surface. The latter yields an oxidation product (dixanthogen if collector added is xanthate) that is the hydrophobic species adsorbed onto the mineral surface. The chemisorption mechanism is reported to occur with galena, chalcocite and sphalerite minerals, whereas electrochemical oxidation is reportedly the primary mechanism for pyrite, arsenopyrite, and pyrrhotite minerals. The mineral, chalcopyrite, is an example where both the mechanisms are known to be operative. Besides these mechanisms, the adsorption of collectors can be explained from the point of interfacial energies involved between air, mineral, and solution.

Chemisorption phenomena

The chemisorption mechanism can be well explained with the mineral, galena. The collector ion used is xanthate ion (C^-). The mechanism of its adsorption occurs in the following steps:

- The dissolved oxygen in the pulp oxidizes the sulfide surface to sulfate according to the following reaction:

  $$PbS(s) + 2\ O_2\ (g) \rightleftharpoons PbSO_4\ (s)$$

- In aerated pulps, carbonate ions are present; these partake in the replacement reaction as shown below:

  $$PbSO_4\ (s) + CO_3^{2-}\ (g) \rightleftharpoons PbSO_3\ (s) + SO_4^{2-}$$

  The feasibility of the above reaction ensues from the data on the solubility products of lead sulfate and lead carbonate salts. Evidence abounds that both sulfate and carbonate ions are present.

- This step is characterized by the replacement reactions between the xanthate ion (C^-) and the carbonate and sulfate ions (and hydroxyl ion, depending on pH) as represented by the following:

  $$PbCO_3\ (s) + 2\ C^-\ (g) \rightleftharpoons PbC_2\ (s) + CO_3^{2-}$$

  $$PbSO_4\ (s) + 2\ C^-\ (g) \rightleftharpoons PbC_2\ (s) + SO_4^{2-}$$

  $$Pb(OH)_2\ (s) + 2\ C^- \rightleftharpoons PbC_2\ (s) + 2\ OH^-$$

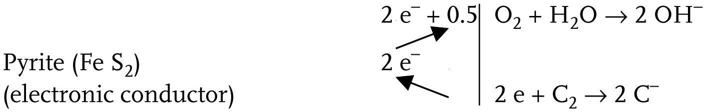
- This step is characterized by bulk precipitation of lead xanthate on the mineral surface.

Electrochemical phenomena

The electrochemical mechanism can be well explained with the mineral pyrite. The collector ion is xanthate ion (C^-), a member in the anodic sulfydryl collectors group. Two electrochemical reactions occur on the surface of the pyrite. There is the formation of dixanthogen (C_2) by anodic oxidation of xanthate ion (C^-) on the surface of pyrite coupled with cathodic reduction of adsorbed oxygen. These reactions are shown below:

Anodic reaction: $2\ C^- \rightleftharpoons C_2 + 2\ e^-$
Cathodic reaction: $0.5\ O_2\ (ads) + H_2O + 2\ e^- \rightleftharpoons 2\ OH^-$

Since sulfides are electronic conductors, electron transfer occurs through the solid sulfide. Schematically,



The overall reaction is:

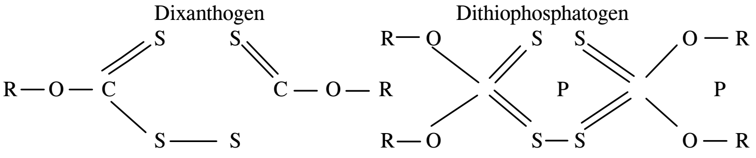
$$2\ C^- + 0.5\ O_2\ (ads) + H_2O \rightleftharpoons C_2 + 2\ OH^-$$

A semi-conducting mineral, such as a galena, when in an aqueous solution develops a potential called the “rest potential”. This parameter governs the sensitivity of sulfide minerals to oxygen, and in turn the oxide and cathode reactions to take place on them. If the rest potential for the mineral-solution system is greater than the reversible potential for the xanthate oxidation, as it is with pyrite, there will be formation of dixanthogen. If, on the other hand, the rest potential is less than the reversible potential for xanthate oxidation, there will not be any formation of dixanthogen. In that case, only metal xanthate will form. Another reagent has been shown to perform in a manner similar to sulfydryl collectors in the pyrite system, and this is dithiophosphate. This reagent is more difficult to oxidize to its dimer, dithiophosphatogen, however, than xanthate is to oxidize to dixanthogen. That is,

$$C_2 + 2\ e^- \rightleftharpoons 2\ C^-; \qquad E^0 = -0.06\ V$$

$$(DTP)_2 + 2\ e^- \rightleftharpoons 2\ DTP^-; \qquad E^0 = -0.25\ V$$

where C^- and DTP^- stand for xanthate and dithiophosphate ions, respectively. The structural formulas of dixanthogen, C_2, and dithiophosphatogen, $(DTP)_2$, are presented below:



where *R* stands for the hydrocarbon chain.

Interfacial energy

Separation of galena from its associated gangue mineral silica by flotation as depicted in Figure 2.21 (B) as an example of direct flotation encountered here as a model to describe the role of interfacial energy. This separation is accomplished by using a collector, namely, sodium ethyl xanthate. Normally, water will wet both galena and silica, but in the presence of a small quantity of the collector, the contact angle is raised from near zero to 60° on the galena, whereas the contact angle on silica remains close to zero. The reagent meant to function as collector incorporated in the aqueous medium dissociates into xanthate anions

($-S \cdot CS \cdot O \cdot C_2H_5$) and sodium cations ($Na^+$). The xanthate anion thus is seen to be heteropolar; hydrocarbon nonpolar radical connected with its polar group. The polar group ending in a negatively charged sulfur atom, is attracted to the lead ions (Pb^{2+}) in galena. Thus, insoluble lead xanthate can be considered to exist on the galena particles. The nonpolar ethyl group, C_2H_5, faces outwards and is attracted to the water molecules to a smaller degree than was the galena. The value of the mineral–water interfacial energy (γ_{MW}) is thus raised and since the air-xanthate attraction is greater than the water–xanthate attraction, the mineral–air interfacial energy (γ_{MA}) is lowered and θ increases. There appears to be no comparable adsorption on the silica particles, which remains wetted by water and drown to be disposed of as tailings, while galena floats off as a concentrate. The structure of the collector and the adsorption phenomenon as described are illustrated in Figure 2.29 (A, B). From the description provided, it is clear that cation (sodium) plays no part to impart hydrophobicity to the mineral. The value of the water–air interfacial energy (γ_{WA}) is a significant parameter. If γ_{WA} is reduced very much by excessive frother additions, then the action of the collector (xanthate) will be adversely influenced simply because the contact angle θ will come down to outweigh the increase in γ_{WA}. There is definitely an optimum level of frother addition beyond which the collector action tends to be destroyed. If too much collector is added, this may lead to a situation where the mineral particle is unable to penetrate the air–water interface and consequently will not float. If the stretch of the carbon chain in the xanthate ion is increased, θ increases – apparently due to diminishing water –

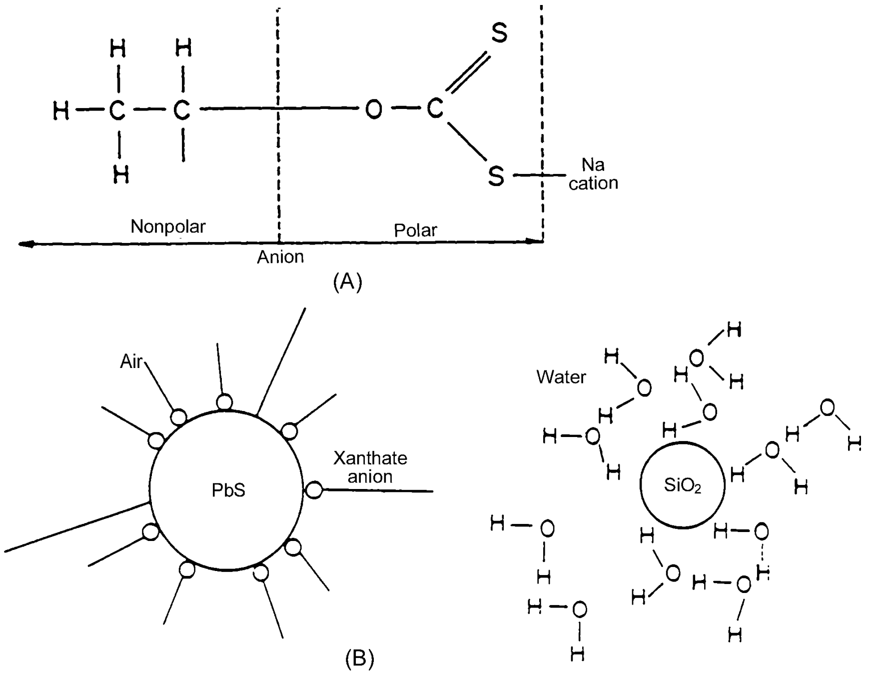


Figure 2.29 (A) Structure of sodium ethyl xanthate; (B) galena particles with xanthate anions adsorbed on the surface influencing it for attachment to an air bubble. The silica is wetted by the polar water molecules.

xanthate affinity. Thus, for amyl xanthate anions, –S · CS · O · C_5H_{11}, θ is 90° compared with 60° for ethyl xanthate.

2.11.2.2.2 Examples

Some specific examples in the field of sulfide flotation will now be described.

An example involving the separation of galena (PbS) from chalcocite (Cu_2S) is first considered here (to illustrate the role of depressants e.g., sodium cyanide, which is quite extensively used in sulfide flotation). In this case, copper ions at the surface of Cu_2S form a stable complex $Cu(CN)_2$. A similar complex with lead is unstable. The addition of the collector, xanthate, results in its adsorption on the surface of galena but not on the altered surface of the copper-containing mineral. As a consequence of these chemical effects, galena is separated by froth flotation while chalcocite remains in the slurry. Curves depicting the feasibility of the flotation of various sulfidic minerals and their separation under specified conditions of the chemistry of the pulp are shown in Figure 2.30. It can be seen that chalcopyrite is floatable from pyrite at a pH of 7.5 with 40 mg L^{-1} of sodium cyanide. Since, of the copper mineral, chalcopyrite lies closest to pyrite relative to the influence of alkali and cyanide, all the copper minerals will float with chalcopyrite. Thus by choosing carefully pH and cyanide concentration, to obtain acceptable separations. This is, of course, theoretical; in practice, the separation is more difficult because of other variables. Adsorption of xanthate by galena is not influenced by cyanide, the alkali alone serving as a depressant.

The flotation of sphalerite, the sulfidic mineral source of zinc, is next considered as an example to illustrate the role of activators. This mineral is not satisfactorily floated solely by the addition of the xanthate collector. This is due to the fact that the collector products formed, such as zinc xanthate, are soluble in water, and so do not furnish a hydrophobic film around the mineral particles. It is necessary to add copper sulfate which acts as an

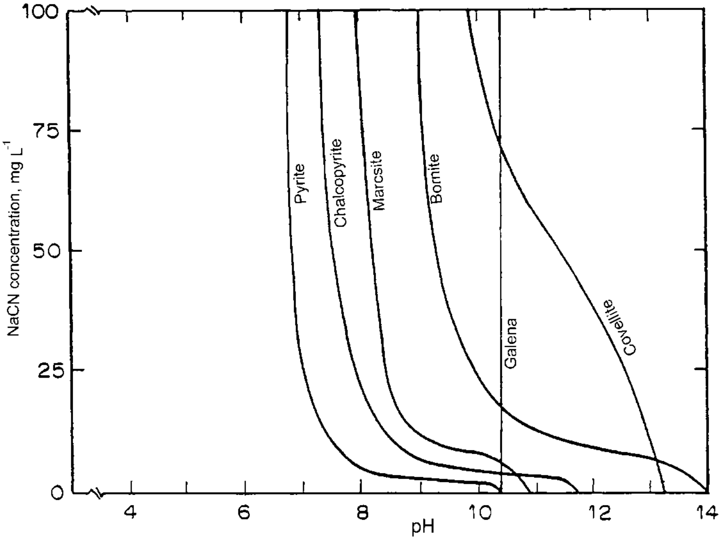


Figure 2.30 Critical pH for flotation with potassium ethyl xanthate in presence of sodium cyanide.

activator. Copper sulfate dissolves quickly and dissociates to yield copper ions, which form copper sulfide molecules at the mineral surface according to the reaction:

$$\mathrm{ZnS + Cu^{2+} \rightleftharpoons CuS + Zn^{2+}}$$

The copper sulfide formed on the surface of the sphalerite mineral reacts readily with the xanthate, and forms insoluble copper xanthate, which makes the sphalerite surface hydrophobic. Such a reaction for activating sphalerite occurs whenever the activating ions are present in the solution. It is thus necessary to deactivate sphalerite (to prevent the occurrence of natural activation) in the case of some ores. With lead–zinc ores, for example, natural activation occurs due to Pb^{2+} in solution

$$\mathrm{ZnS + Pb^{2+} \rightleftharpoons PbS + Zn^{2+}}$$

The mineral, sphalerite, on account of its resistance to oxidation, contributes very little of Zn^{2+} through dissolution. In this case, zinc sulfate is added and the reaction, which is shown in the parenthesis, is pressed into proceeding from right to left (i.e., $\mathrm{PhS + Zn^{2+} \rightarrow ZnS + Pb^{2+}}$). This is equivalent to saying deactivation of sphalerite. Besides Pb^{2+}, Cu^{2+} is also known to give rise to activation. In this case, cyanide ions are introduced into the system. The stability of $\mathrm{Cu(CN)_2^-}$, relative to $\mathrm{Zn(CN)_4^{2-}}$ results in ratios of dissolved Cu to Zn such that activation cannot occur.

In the molybdenum flotation circuit, the use of sodium sulfide as a depressant is quite important in order to depress sulfides of copper which are invariably associated. In solution, sodium sulfide hydrolyzes and then dissociates:

$$\mathrm{Na_2S + 2\ H_2O \rightleftharpoons 2\ NaOH + H_2S}$$

$$\mathrm{NaOH \rightleftharpoons Na^+ + OH^-}$$

$$\mathrm{H_2S \rightleftharpoons H^+ + HS^-}$$

$$\mathrm{HS^- \rightleftharpoons H^+ + S^{2-}}$$

The products of hydrolysis and dissociation depend on the pH. In an acid medium, hydrogen sulfide, which has no depressing action, evolves. It is, therefore, necessary to use alkaline circuits in which HS, predominates. These sulfide ions are adsorbed on the copper sulfide mineral surface and react with the surface previously coated with cuprous xanthate. The reaction causes desorption of the collector, and as a result of this desorption the copper sulfide minerals generally become hydrophilic. There is, however, no action of the sulfide ions on molybdenite, and so molybdenite retains its hydrophobic character.

2.11.2.3 Natural Hydrophobicity

Most minerals are hydrophilic; in other words, they show affinity for water. This also implies that the contact angle is very much less than 90°. As the contact angle assumes values beyond 90° up to 180°, the hydrophobicity of the mineral concerned in the given system progressively attains 100%.

Among solids, teflon exhibits the largest hydrophobicity ($\theta = 108°$). Solids of teflon type, with their high contact angles, are called "naturally hydrophobic" and float without the assistance of chemical reagents. Artificial hydrophobicity to which the collector contributes is really not required to float solids or minerals characterized by natural hydrophobicity.

Some of the best known examples among natural floaters are molybdenite, stibnite, talc, graphite, native sulfur, coal, and some types of hydrocarbons, such as asphalt. Their natural hydrophobicity ensures high flotation rates with almost any type of collector, and even with natural frothers, such as pine oil and cresylic acid. It has been postulated that native floatability results when at least some fracture or cleavage surfaces form without rupture of interatomic bonds other than residual bonds. The case for the mineral, molybdenite, can be taken as a representative example for elaboration on the various aspects of flotation of naturally floatable minerals. Studies on the structure of molybdenite crystals have provided an explanation as to why the mineral is endowed with natural floatability. Molybdenite has a layered structure. There are basically two types of bonds: intralayer, and interlayer bonds. The former are covalent bonds between sulfur and molybdenum atoms (S-Mo-S), while the latter are weak Van der Waals–London bonds between sulfur atoms in adjacent layers. As a consequence of this special structural feature of molybdenite, when it is comminuted, two different types of site are found on the surface of molybdenite particles: (i) nonpolar sites created by the rupture of Van der Waals–London bonds (termed “faces”) and (ii) polar sites created by the rupture of the covalent bonds (termed “edges”). The “face” surfaces have an electrically neutral character and a low surface energy and the contact angle for them is about 80°. Because of these characteristics, the “face” surfaces exhibit little attraction for molecules with a high surface energy, such as water. The “edge” surfaces, on the other hand, are ionic and chemically active. The contact angle for these surfaces is about 30°. These features are responsible for the hydrophilic nature of the “edge” surfaces. The extent of water repellency or hydrophobicity of molybdenite seems to depend on the ratio of the surfaces of these two types. The planes along which molybdenite fractures by cleaving are the “faces” and represent the predominant part of mineral exposure upon comminution. This explains why molybdenite is a hydrophobic mineral. The natural floaters listed earlier as examples are generally found in porphyry copper ores. While their separation from copper has not been a problem, their separation from molybdenite is, at times, quite difficult. Talc normally floats faster than molybdenite, and to obtain a separation between the two, molybdenite is depressed and talc floated. Graphite is structurally very similar to molybdenite, and because of this flotation cannot accomplish a separation between the two. Fortunately, it appears that they do not occur together. Particle sizing of molybdenite has a bearing on its floatability. Larger molybdenite particles have a higher “faces” to “edges” ratio and thus they are more floatable. Smaller particles have a greater “edges” to “faces” ratio with a correspondingly reduced contact angle and represent a reduced floatability situation. This explains why the recovery of molybdenite particles in their finely divided state (extensively ground material) is seriously hampered by their enhanced tendency for wetting.

Although the selected surfaces of the naturally hydrophobic minerals have a net hydrophobic character, two additional factors must be considered. First, whereas the overall behaviour of the surface is classified as possessing a net hydrophobic character, the fact is that there may be a significant number of hydrophilic sites on the surface. As a result hydrophobic solids may still show a surface charge and may have an adsorption potential. A second factor worthy of consideration is the fact that crystal planes other than those showing a net hydrophobic character become exposed during size reduction. As a result particles that might be thought to show native floatability may, truly, possess a significant portion of their surface composing of other cleavage planes which do not show hydrophobicity. The case for molybdenite described above finely illustrates the present point on the likely consequences of communition on the naturally floatable feature of the crystalline solids.

Drawing reference to the flotation practice of molybdenite, it may in the first instance be pointed out that production of molybdenite by flotation results from the processing of primary molybdenum ores and copper porphyry ores in which molybdenite is recovered as a byproduct. This by-product accounts for about one-third of the total molybdenum production in the western world.

Primary molybdenum ores at a relatively coarse grind go through an initial stage of flotation. At Climax Molybdenum, for example, the first separation is made at 35% + 100 mesh. The flotation system uses vapour oil as a promoter and pine oil as frother. A sulfonated coconut oil (syntax) is added to the system to emulsify the oil.

The processing of copper–molybdenum concentrates yielded from copper porphyry ores by flotation involves conferring either molybdenite or the copper sulfide mineral's hydrophilicity. Typical bulk copper–moly concentrates assay with 25% copper and 1% molybdenum. Generally, the copper sulfides are rendered hydrophilic by subjecting the bulk copper-moly concentrate to conditioning with specific copper sulfide depressants. The sulfide depression of copper sulfide is chosen in preference to the depression molybdenite because, in so doing, the minor constituent, MoS_2, is floated with a resultant lower chance of contamination on account of mechanical transport of unwanted material to the froth. A variety of reagents can be deployed in order to depress copper sulfide minerals from bulk copper–moly concentrates: (i) alkali sulfides and polysulfides; (ii) Noke's-type reagents; (iii) oxidants (both thermal and chemical treatments); and (iv) cyanide, ferrocyanide, ferricyanide. In the industrial practice, a combination of the listed depressants is used. Examples, however, exist in which molybdenite is depressed by dextrin, and the copper sulfides are floated.

2.11.3
Flotation Systems

Flotation, like all other separation processes, is imperfect in that simply by applying this process only once, very little separation may be achieved. For example, the underflow from a flotation unit may have many hydrophobic particles that have failed to encounter an air bubble, or the overflow may have hydrophilic particles that have simply been caught in the wake of an air bubble or in a collection of hydrophobic particles secured to a bubble. It is, therefore, common practice to operate many cells in complicated series – parallel arrangements, perhaps with adjustment of chemistry at some point. This is necessary because only a limited separation is usually attainable in a single device, and as such there is a need for roughing, cleaning, and scavenging components in a circuit. Generally speaking, roughing is the primary operation, which utilizes a moderate separating force to remove the fully liberated valuables. Scavenging utilizes strong chemistry conditions to recover as much of the remaining valuables as possible. Finally, cleaning utilizes a low separating force which upgrades the rougher concentrate by removing misplaced waste material. A simple arrangement of using these elements is shown in Figure 2.31. A series of rougher cells (with the underflow passing from one cell to the next) makes a rough separation of the slurry obtained after grinding into two streams. The mineral-rich stream then passes to a second series of cleaner cells whose objective is to remove as much residual gangue as possible,

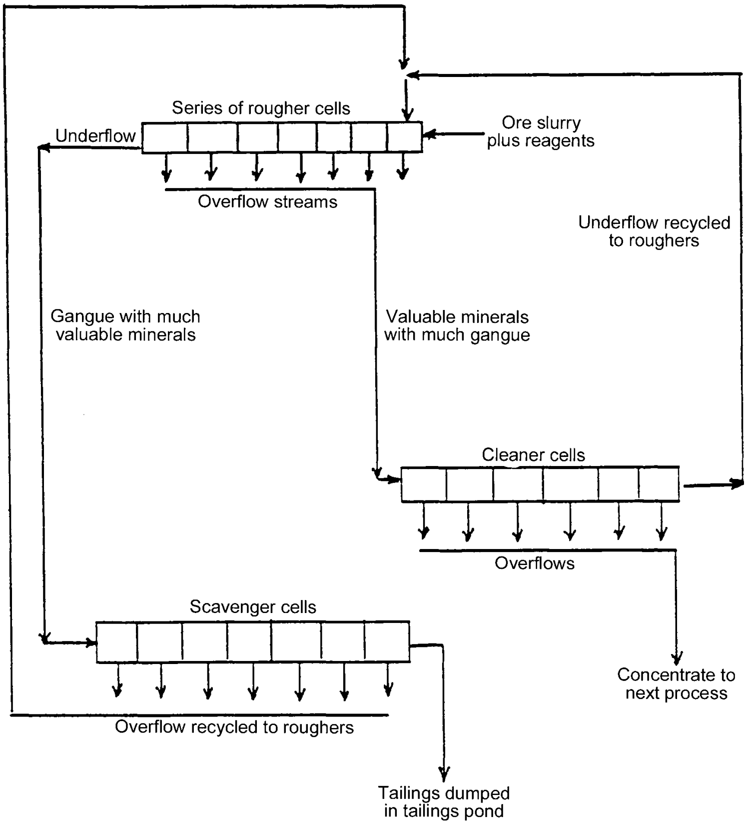


Figure 2.31 One way in which a number of flotation cells can be arranged into a flotation system.

and yields a slurry of concentrate particles or heads that has much of the valuable mineral in the ore, and a second stream that is recycled to the rougher cells. The other stream from the rougher cells, having less of the valuable mineral (but not so minor as to be discarded), goes on to the scavenger cells where as much as possible of the valuable mineral is recovered from the tailings stream departing to the waste pond. This scavenged valuable mineral is put back to the rougher cells.

2.11.4
Flotation Machinery

A flotation machine must satisfy certain requirements which are listed in Table 2.9. All told, the components of a flotation system are the following:

- A cell (a container with an impeller or an aeration device, capable of keeping the solids in suspension and providing aeration for frequent air bubble–particle collisions).

Table 2.9 Requirements of flotation machine.

1. All particles must be maintained in suspension. This requires that upward pulp velocities exceed the settling velocity of all particles present.
2. All particles ordering the machine must have the opportunity to be floated.
3. Dead space is undesirable, since it means reduction in effective volume of the machine.
4. Aeration should be correct in order to disperse fine air bubbles throughout the pulp. The extent of aeration needed depends upon the particular mineral system and quantity being floated.
5. Promote particle–bubble collision in order that bubbles collect mineral particles as they go, and assemble as a froth on top.
6. Provide an undisturbed pulp region immediately below the froth. This is to minimize entrapment of pulp in the froth and turbulent disruption of the froth layer.
7. Provide sufficient depth of froth to allow drainage of entrained particles to take place.

- A feed (a mixture of solids to be separated, suspended in water at usually about 1 : 3 solids to water ratio, by weight; referred to as flotation pulp).
- Regulating or modifying agents (ions such as H^+ and OH^- for controlling the pH, dissolved oxygen or oxidizing species like HS^-, HCO_3^-, CN^-, and metals ions derived from the partial dissolution of some solids or intentionally added to serve as depressants and activators; also, specifically added organic compounds for depressing or activating action).
- Surfactants (a minimum of two are usually needed – collector and frother).
- Air (drawn in by the suction of the impeller and/or injected under pressure into the pulp).

A flotation cell essentially consists of a rectangular tank, equipped with suitable mechanisms for agitation and aeration. While these features are common in any type of flotation cell (including laboratory flotation cells) industrial flotation cells have additional features such as arrangements for entry of the feed slurry and exit of the products. The mineral-laden froth is removed by rotating froth paddles and the tailings by overflow through a height-controllable weir arrangement. There are two basic types of flotation machines, pneumatic and mechanical. Pneumatic cells, which today are confined to special applications, have no mechanical components in the cell. Agitation is produced by the inflow of air and/or slurry, and gas bubbles are introduced by an injector, a change of pressure, or electrolysis. Mechanical cells usually consist of long troughs with a series of mechanisms. While the design details of the mechanisms vary, an extremely short and precisely worded description may be provided for all as to be consisting of an impeller that revolves within baffles. Air is drawn or pumped down a central shaft and is dispersed by the impeller.

It may be added that continuous developments are taking place in flotation cell design. A reader wishing to have a detailed information concerning a particular type of cell is better served by brochures published by the manufacturer than by a book.

2.12
Dewatering

The dewatering process is carried out to fulfill different purposes. Thus while dewatering in one instance may be applied to yield dry concentrate for shipment, at some other instance the calling may be different in that it is required to be carried out in order to prepare the feed for the subsequent processes. Dewatering methods are: (i) sedimentation; (ii) filtration; and (iii) thermal drying. Usually a combination of these methods is used in mineral processing. The major portion of water is removed by sedimentation, or thickening, which yields a thickened pulp containing about 55–65% solids by weight. This stage is capable of separating up to 80% of the water. Filtration of the thick pulp gives rise to a moist filter cake of between 80 to 90% solids, but this may need thermal drying to yield a suitable end product of about 95% solids by weight.

2.12.1
Sedimentation

The removal of suspended solid particles from a liquid mainly by making use of gravitational settling is called “sedimentation”. Sedimentation is at its best when there exists a large difference in density between solid and liquid. This is invariably the case in mineral processing where water is the carrier liquid. Sedimentation cannot always be used in hydrometallurgy. This is because in some cases the carrier liquid maybe a high-grade leach liquor having a density approaching that of the solids. In such instances, filtration may be necessary. In general, two principal steps are involved in sedimentation, thickening and clarification. The two are governed by similar principles, but they have different objectives. Thickening is the term used if the objective is to increase the solids concentration, whereas clarification is the removal of solids to obtain a liquid substantially free of solids. Separations basing on clarification involve sedimentation which is not characterized by a clearly defined interface between the clear liquid and the sediment. As a consequence, the capacity is limited by the amount of solid that can be accepted in the overflow. Operations basing on thickening, on the other hand, are characterized by a clearly defined interface between the clear liquid and the sediment. As a consequence, the capacity is limited by the underflow conditions. A difference between clarification and thickening is that in the latter process all solids are allowed to settle.

In the present context of solid–liquid separation, it may additionally be pointed out that apart from the gravitational force, nongravitational forces may also be used and the methods which involve these are cycloning and centrifuging. In centrifuging, the forces are generated through a rotating basket, whereas in cycloning the shell is stationary and only the liquid spins.

The sedimentation process is concerned essentially with the settling of particles and, therefore, bears a relationship with the particle size. Very fine particles settle very slowly and in these situations, in order to speed up the sedimentation process, it becomes necessary to agglomerate the particles into large lumps which settle more rapidly.

2.12.1.1 Coagulation and Flocculation

Coagulation and flocculation have an important bearing on the sedimentation process. In the process of coagulation, extremely fine colloidal particles come together and adhere directly to each other. They do so because of forces of mutual attraction among the particles. Adhesion due to these attractive forces is opposed by the presence, around each particle, of an electrically charged atmosphere, which produces repulsive forces between particles approaching each other. In any system there is, therefore, a balance between the attractive forces and the electrical repulsive forces operating at the solid–liquid interface. In a given system the electrical charges on the particle surfaces are of the same sign. For aqueous suspensions with pH values of 4 and above, the electrical charges on the particle surfaces are generally negative. Positively charged surfaces occur mainly in strongly acidic solutions. The repulsion forces, apart from inhibiting coagulation, also retard settlement of the particles by keeping them in constant motion. The smaller the particle the more pronounced is this effect. Depending on the surface charge of the particles, salts containing charged cations such as Al^{3+}, Fe^{3+}, and Ca^{2+} as well as lime and sulfuric acid are some of the agents that are added to promote the coagulation of particles. These additives, termed "coagulants", essentially have a charge opposite to that on the particles. They thus cause charge neutralization when dispersed in the system and permit the particles to come into contact and mutually adhere to form agglomerates under the influence of the attractive forces.

The process of flocculation involves the formation of agglomerates which are much more open than those occurring in coagulation. The process relies upon molecules of a suitable reagent acting as bridges between separate suspended particles. The reagents used to form such bridges are long-chain organic polymers. Earlier, natural materials, such as starch, glue, gelatine, and guar gum, were used for this purpose, but these are now being increasingly substituted by synthetic materials. Among these synthetic materials the polyacramides are the most extensively used as flocculants. To illustrate their mode of action, reference may be drawn to an anionic polyacramide. Its action depends on a segment of this very long molecule being adsorbed on the surface of a particle, leaving a large portion of the molecule free to be adsorbed on another particle, thus developing a bridge between the particles. In practice, many such interparticle bridges are formed, linking a number of particles together. The factors that influence the degree of flocculation are: (i) the strength of polymer adsorption on the particle surface, (ii) the degree of agitation during flocculation, and (iii) the degree of agitation following flocculation. Flocculants are normally made up to stock solutions of 0.5–1%, which are diluted to about 0.01% before being added to the slurry. The diluted solution is added at a number of points in the stream to ensure its availability in every portion of the system. It is necessary to have a mild agitation at the points of addition, and shortly thereafter, to aid dispersion of the flocculent in the process stream. Once flocs have formed, severe agitation must be avoided.

Flotation is certainly the major separation method based on the surface chemistry of mineral particles. It is, however, not the only method. Selective flocculation and agglomeration may be mentioned as other methods used commercially to a limited extent. The former is for hematite, while the latter is for coal and finely divided metallic oxide minerals. Both processes use the same principles as described for flotation to obtain selectivity. In selective flocculation, polymeric flocculants are used. The flocculants selectively adsorb on the hematite, and the hematite flocs form and settle readily. Thereby separation from the siliceous gangue can be obtained. In selective agglomeration, one mineral is made hydrophobic so that it can adsorb fuel oil, which is an often-used hydrocarbon for this duty. High shear conditions are then used by which fuel oil-coated mineral particles can come into physical contact and agglomerate. The size of the agglomerate increases to the point at which separation based on size difference becomes possible.

Flocs possess two important settling features. The first is their complicated structure. The aggregates are lax, the interparticle bond in them is weak, and they hold a large amount of water in their structures, which is retained with the flocs when they settle. The second feature of the flocculated pulp is the complexity of its settling mechanism.

2.12.1.2 Thickener Machinery

The sedimentation process is carried out on a large scale in equipment called thickeners. The thickening process is defined as the removal of a portion of the liquid from a slurry or a suspension, thereby concentrating the solid particles in the remainder. Thickeners exploit the gravitational forces for the separation of solids from liquids and are widely used in the industry. Their operating cost is low, maintenance problems are minimal, and performance quite reliable. Although thickeners come in various shapes and types, the most common type is the cylindrical continuous thickener wherein feed enters through a central feed well at the surface, and eventually settles into a thickened sludge blanket in a conical base, where a slowly rotating mechanism rakes it to a central discharge. Clear liquid overflows into a launder around the periphery of the tank.

2.12.2
Filtration

Filtration is a process of separating solids from a liquid by means of a porous medium which holds back the solids and permits the liquid to clear. Industrial filtrations range from simple straining to highly complex separations. The fluid may be a liquid or gas; the solid particles may be coarse or fine, stiffer or pliant, elongated or round, separate individuals or aggregates. The feed suspension may carry a heavy load of solids or almost none. It may be hot or cold, or under vacuum or pressure. Other matters also apply in filtration. The relative values of the components involved must be considered, as sometimes the fluid is the valuable component, sometimes the solid, and sometimes both. In some situations the separation of components needs to be virtually complete; in others only a partial partition is desired. The conditions under which filtration is carried out are many and varied, and the choice of the most suitable type of equipment depends on many factors. A multitude of filters has therefore been developed. Whichever type of equipment is used, a filter cake gradually develops on the porous filter medium and the resistance to flow progressively increases throughout the filtration operation. The factors influencing the rate of filtration are (i) the pressure drop from the feed to the far side of the filter medium; (ii) the filtering surface area; (iii) the filtrate viscosity; (iv) the resistance offered by the filter cake; and (v) the resistance of the filter medium.

In many mineral processing procedures, filtration follows thickening. The thickened pulp may be fed to storage agitators from where it is drawn off at a uniform rate to the filters. In order to aid filtration flocculants are sometimes added to the agitators. Filtration is adversely affected by slimes, since they tend to choke the filter medium. This is reduced by flocculation and lower molecular weight flocculants are preferred over those with high molecular weights. This is because the flocs formed with the latter are relatively large, and entrain water within their structure. This, in effect, increases the moisture content of the filter cake.

The choice of the filter medium is often the most important consideration to ensure efficient operation of a filter. Its function is generally to act as a support for the filter cake, while the initial layers of cake provide the actual filter. The filter medium should be selected primarily on the basis of its ability to retain solids without binding. It should be mechanically strong and corrosion resistant, and should offer as little resistance as possible to the flow of the filtrate. The media are made from widely different materials such as cotton, wool, linen, nylon, jute, silk, glass fiber, porous carbon, metals, rayon and other synthetics, and miscellaneous materials like porous rubber. Cotton fabrics are most commonly used because they are available in a wide variety of weaves, and are cheap.

Liquid-solid filters may be classified into four categories, depending on the service they perform: strainers, clarifiers, cake filters, and filter thickeners. A *strainer* is commonly little more than a metal screen placed across a flow channel for removal of dirts or rusts from a moving fluid. When the screen becomes clogged in service, it is easily replaced. *Clarifiers* also remove small quantities of solids, commonly to yield sparking clear liquids, as beverages or printing inks. The separated solids are most often rejected. The filter medium in a clarifier is a septum of cloth or a cartridge of metal disks. *Cake filters* remove large quantities of solids from a liquid as a cake or sludge. *Filter thickeners* result in the partial removal of a thin slurry, passing some clear liquid and a thickened but still flowable suspension of solids.

From the definition of filtration it should go without saying that the function of filtration equipment is to filter a slurry, so as to separate the solid more or less completely from the liquid. Depending on the nature of the slurry, the driving force required for separation may be grouped into four categories, namely, gravity, vacuum, pressure, and centrifugal. There may be several ways by which filtration grouping can be carried out, the most important ones being the operating cycle, vacuum or pressure, batch or continuous driving force, and operating mode. These details are mostly covered by expressing that filtration equipment can be of either the continuous or batch type, and either constant pressure (vacuum) or constant rate. In the constant pressure type the rate of filtration falls gradually as the cake builds up. In contrast, in the constant rate type the pressure is enhanced gradually in order to maintain the filtration rate as the resistance of the cake progressively increases. The device size is based on the filter surface area required.

Continuous vacuum filters are mostly of the constant pressure type and are mainly used in dewatering concentrated slurries such as concentrates. These filters are classified into disk, drum, and horizontal filters. The drum and the disk filters are the mainstay for most final detwatering, the drum filters being used to a lesser extent than the disk filters. These two groups of filters remove most fine particles from a process stream.

The drum filter consists of a 1 to 5 m diameter cylindrical drum that rotates while remaining partially submerged in an open-feed slurry tank. The drum surface is wrapped around tightly with the filter medium. The drum shell is divided into compartments, and drain lines are connected to the central valve system that permits either vacuum or pressure as governed by the cycle, which normally consists of filtration, draining, and discharge by air blast or mechanical means. Coke washing and filter cloth cleaning can also form a part of a cycle.

In operational terms, the disk filter is similar to the drum filter, but filtration is conducted by using a series of large-diameter filter disks that carry the filter medium on both sides of the disk. They are connected to the main horizontal shaft and partly immersed in the feed slurry. The central shaft is connected by a set of valves which serve to provide vacuum and air, as in drum filters. As the disk sections are immersed during rotation, a vacuum is applied to form a cake on both sides of the disk. The cycle of operation is similar to that in a drum filter. This system is used extensively in the iron ore industry for dewatering magnetite concentrates.

The processes involving filtration, washing and drying all occur on a travelling belt filter cloth which is provided with suction boxes underneath, and in continuous vacuum filters which are also called belt filters. A number of variations are available, and the belt can be either linear or circular. Slurry is placed on the belt at the beginning, and filtration occurs by both suction and gravity. The filter cake is discharged from the belt using scrapers prior to belt reversing. Excellent washability and relatively low capital and operating costs are some advantages of belt filters, but they need a high dosage of flocculant and more floor area for a given filter area.

Pressure filters or *filter presses* are commonly of the batch type, and are characterized by smaller floor area, high filtration rates, and lower capital cost. Dryer cakes are produced. The chemical industry uses these filters more widely than mineral processing industries, mainly because of its batch operation. The most common types of pressure filters used are the plate and frame presses. These comprise a series of vertical, alternating parallel frames and plates, with the filter cloth being held against the plate and the formation of cake occurring in the hollow frame.

In situations where conventional dewatering methods are inapplicable because of very low settling rates (as in the case of clays), or low moisture content is needed prior to the next operation, then devices called *centrifuges* are used. As the name implies, these devices use centrifugal force is used to enhance solid–liquid separation. These units involve high capital cost and high maintenance but they can perform many duties, for example as classifiers, thickeners, clarifiers, and filters. The hydrocyclones are an example of centrifugal devices used for classification or thickening that are simple and not expensive. However, they do not produce a very high solids concentration in the underflow, and their efficiency falls rapidly at fine size ranges. Hydrocyclones are still valuable for initial dewatering prior to thickening. For primary dewatering, many other classifiers can also be used.

The solid bowl centrifuge is one type of centrifuge. It consists of a horizontal bowl which revolves at a high speed. Slurry enters at the center of one end of the bowl, and the liquid emerges from the other end by means of a revolving scroll. The incorporation of a washing stage can be made at this stage. The extent of dewatering needed and the application determine the bowl size. These systems are particularly suited for processes clarification.

The perforated basket centrifuge is an other type of centrifuges. The material transport occurs through vertical vibrations in the basket. These vibrations cause loosening of the bed of particles, assisting drainage, and making it possible to run the device at lower speeds than are required for solid bowl centrifuges. On account of the perforations in the basket these types of centrifuge are not suitable for use with feeds that contain significant amounts of fines. Rather they are commonly used in dewatering coal.

2.12.3
Thermal Drying

The last stage of dewatering is thermal drying, which normally follows the thickening and filtration of concentrates. However, unlike thickening and filtering which are mechanical methods of water elimination, drying is a thermal process wherein all or part of the residual moisture in the filter cake is removed by the application, direct or indirect, of some form of heat. It is an expensive method because energy is wasted in heating the solids, but is necessary in many instances because mechanical dewatering is incapable of reducing the moisture content below a certain limit. The extent of reduction in moisture by thermal drying is governed by economics and specifications needed for the mineral product in terms of flow properties of particles, dust prevention, and some other specifics. Thermal drying aims at reduction of the moisture content to about 5% by weight. A still smaller moisture content (or for that matter complete drying) is often not necessary, and may also create dust problems. In general, drying a solid means implies the removal of relatively small amounts of water or other liquid from the solid material, to reduce the content of residual liquid to an acceptable low value. In general, drying a solid means implies the removal of relatively small amounts of water or other liquid from the solid material, to reduce the content of residual liquid to an acceptable low value. Drying is usually the final step in a series of operations. Water may be present either as free water or as combined water. Free water consists of physically attached liquid water which wets the solid particle surfaces; this free water exerts the same vapour pressure as pure water. Combined water is that which is chemically combined with the solid matrix; it exerts an equilibrium vapour pressure less than that of pure water. The removal of combined water will not be considered here because its removal results in chemical changes in the solid and, therefore, it is more appropriate at this point to consider this phenomenon of calcination. It should be borne in mind that it is generally cheaper to reduce the moisture content mechanically by press or centrifuges than thermally, and hence it is advisable to reduce moisture content as much as is practicable before feeding the material to a heated dryer.

The process of drying involves heat transfer and diffusion, and can accordingly be divided into two stages. During the first stage, in which the material is wet, the rate of evaporation is constant. This is known as constant rate period. In the next stage, as the surface is dry the water must be forced to the surface by diffusion, which is slower than evaporation. This is, therefore, known as the falling rate period. The whole process therefore involves heat transfer as well as material transfer. Heat transfer can be achieved either by direct contact between the heating medium and the material, or by indirect contact in which the material and the medium are separated by a wall. Heat transfer and diffusion can be facilitated if the material is agitated or sprayed or the moisture extracted during the process of drying. Although evaporation is the main operation in drying of materials, in certain cases it is equally essential that the physical appearance and properties of dried product be preserved. A critical choice of processing conditions and the method of heat transfer is necessary in such cases.

The principal reasons for drying of concentrates are usually one or more of the following: (i) to make them easier to handle and to provide them with free-flowing properties, both for ease of shipment and for convenient use by the procurer; (ii) to reduce the transportation cost of shipment to the user's premises; and (iii) to preserve the physical and chemical characteristics or the condition of the concentrate during shipping and any storage before actual use.

There are many types of drying equipment used for moisture reduction in mineral concentrates, and most of these are designed for continuous operation. All concentrate dryers usually operate at atmospheric pressure only, and the heating may be affected in a number of ways. Generally, it is carried out by direct passage of air or hot gases through or over the material, or by indirect heating. Indirect heating involves the isolation of the material to be dried from the hot gases or hot fluid, with heat transfer to the solids being brought about by contact with the heated surfaces, by air heated by contact with the heated surfaces or by air heated by contact with the heated parts of the dryer. Direct firing is commonly employed by the minerals industry. The indirect mode of firing is adopted in cases where the material is not to be allowed to come into contact with the hot gases.

A large number of dryers have been designed for each group of materials, with different arrangements and methods of heating, as well as heating mediums. Dryers may be classified as to whether the material is a rigid or granular solid, a semisolid paste, or a liquid solution or slurry; as to whether or not the matter is agitated during drying; or as to whether the operation is batch or continuous. Still another division is according to method of heat transfer, direct or indirect, or according to heating medium, air, hot water, fuel oil, natural gas electricity, waste heat or steam, and, in extreme instances solar energy. The common types of dryers employed for mineral concentrates are: (i) rotary dryers; (ii) stationary hearth dryers; (iii) rotary tray dryers; (iv) fluid bed dryers; (v) spray dryers; and (vi) spiral flight dryers. When hot gases are in use for moisture removal, the gas flow is either co-current or counter-current to the flow of solids. Among the different types of dryers, the rotary dryer is still the most common type of mechanical dryer in use, but does not usually have a high thermal efficiency. Flash dryers are very rapid in operation because the solids are exposed only briefly to the hot gases. Fluidized bed dryers which employ hot gases to suspend the solids, are efficient and rapid but need elaborate dust collection systems. The field of application of fluidized bed principally pertains to working with fines. Dryers incorporated with indirect firing are used for combustible solids.

2.12.4
Evaporation

A special case involving heat transfer to a boiling liquid occurs so often that it is considered separately as an individual operation. It is called evaporation. The aim of this process is to concentrate a solution made of a nonvolatile solute and a volatile solvent. In the overwhelming majority of evaporations the solvent is water. The process of evaporation is carried out by vapourizing a part of the solvent to yield a concentrated solution or thick liquor. Evaporation differs from drying in that the residue is a liquid – sometimes a highly viscous one – rather than a solid. Evaporation differs from distillation in that the vapour normally is a single component, and even when the vapour is a mixture, no effort is spent in separating it fractions. Evaporation differs from crystallization in that accent is placed on concentrating a solution rather than forming and growing crystals. In specific situations, as for example, in the evaporation of brine for the production of common salt, evaporation does not differs sharply from crystallization. Evaporation sometimes yields a slurry of crystals in a saturated mother liquor.

Usually in evaporation the thick liquor is the valuable product and the vapour is condensed and discarded. There are, however, specific situations where the opposite is true. In this context, mention may be made of the fact that mineral-containing water is often evaporated to yield a solid-free product for boiler feed, for special process requirements, or for human consumption. This technique is often called water distillation, but technically it is evaporation.

Most evaporators are heated by steam condensing on metal tubes, and the material to be heated flows inside the tubes. When a single evaporation is used, the vapour from the boiling liquid is condensed and discarded. This method is called single-effect evaporation, and although it is simple, it uses steam ineffectively. If the vapour from one evaporator is fed into the steam chart of a second evaporator, and the vapour from the second is then sent to a condenser, the operation becomes double-effect. The heat contained in the original per unit of steam introduced into the first effect is roughly doubled. The general method of enhancing the evaporation per unit of steam by employing series of evaporators between the steam supply, and the condenser is called multiple-effect evaporation. The main types of steam-heated tubular evaporators are: short-tube evaporators; long-tube vertical evaporators (forced-circulation, upward-flow; and downward-flow types); and agitated-film evaporators.

2.13
Mineral Processing Flowsheets

This section on flowsheets basically aims to provide some illustrative examples of the use of the various mineral processing unit operations that have been described. A general flowsheet involving almost all the unit operations pertinent to mineral processing is shown in Figure 2.32. The others refer specifically to beach sands, lead–zinc concentration, molybdenum, and the rare earths.

Processing of beach sands provides a good example of the response of minerals to magnetic and electrostatic fields. A generalized flowsheet for separating the mineral constituents of beach sands is shown in Figure 2.33 (A). It will be seen that the separation is essentially based on the differences in the magnetic properties and in the electrical conductivity of the various minerals present in the beach sands. The behaviour of some typical beach sand minerals, as for instance magnetite, ilmenite, garnet, monazite, rutile, zircon, and quartz, in respect of their responses towards magnetic and electrostatic separators is indicated in Table 2.7. A reference is also drawn to Figure 2.33 (B) which exclusively shows flotation playing the centrally important role in lead–zinc concentration.

A schematic flowsheet for molybdenum recovery from porphyry coppers is shown in Figure 2.34. Here the important role is played by flotation. The first stage involves collective flotation of copper and molybdenum. The floated product is upgraded through two or three cleaning flotations. Finally, molybdenum is recovered by depressing copper values. In order to depress a mineral, some kind of oxidation should be implied on its surface, or re-

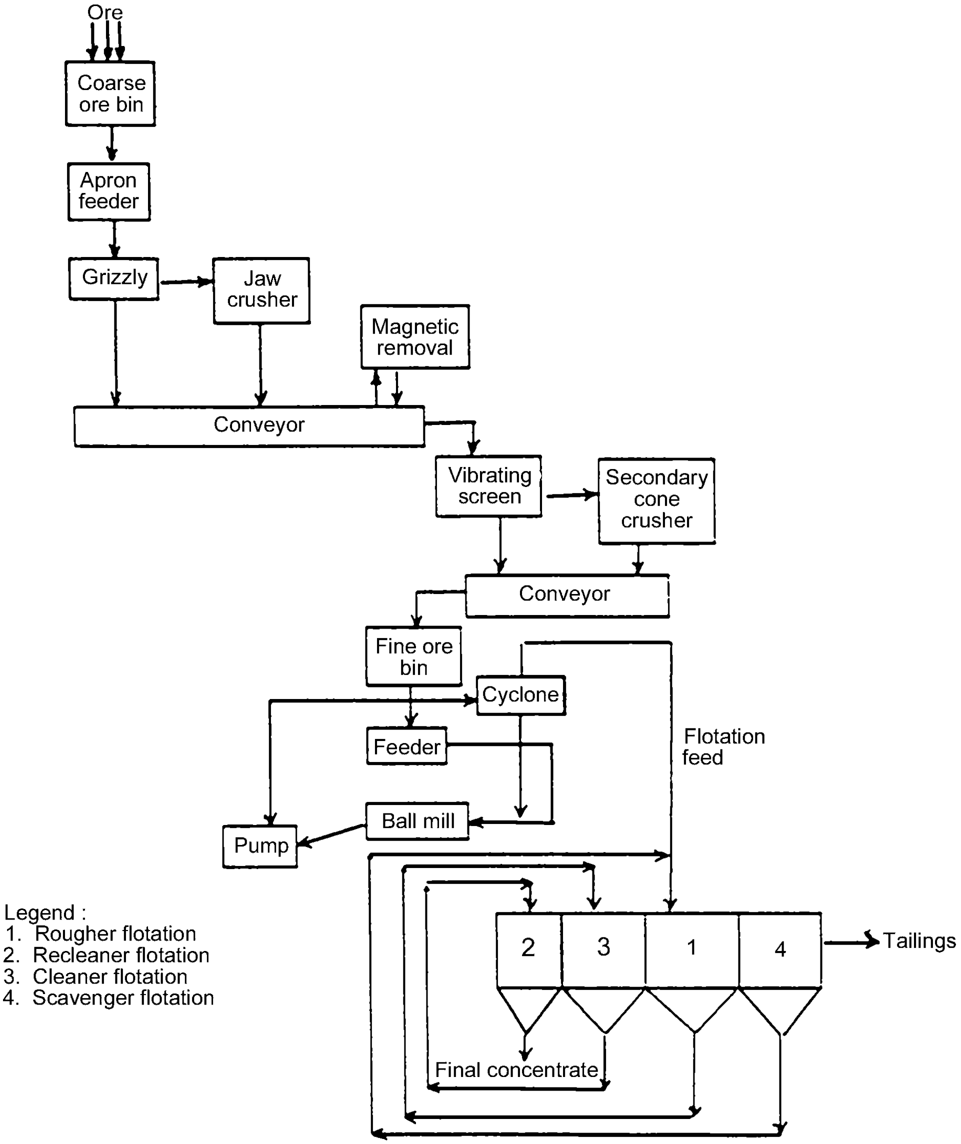


Figure 2.32 A general mineral processing flowsheet.

sidual flotation reagents are completely destroyed. The removal of residual flotation reagents can be accomplished either by heat (steam treatment or roasting), or by chemical means (oxidizing reagents). Molybdenum remains essentially inert to these treatments, unlike copper minerals. The rougher flotation which follows thermal/chemical oxidation step yields molyconcentrate and depresses copper values to join as tails.

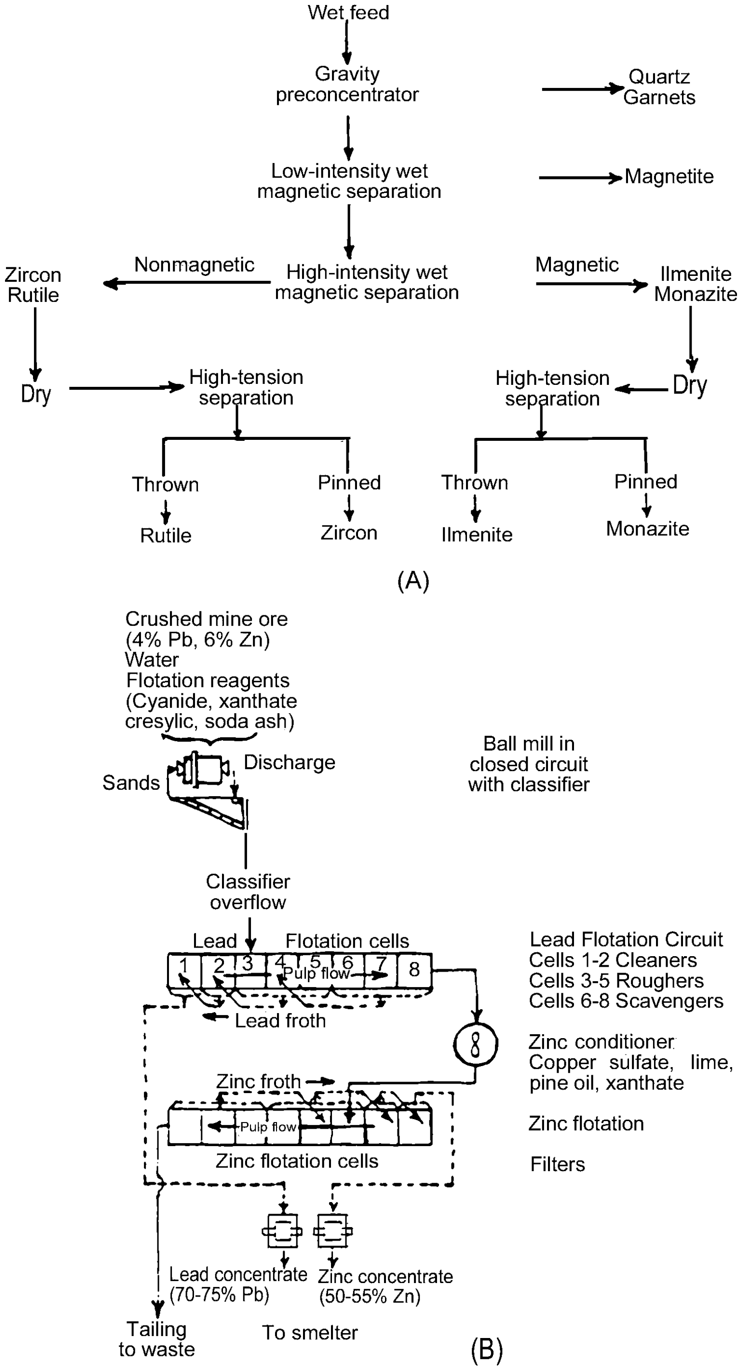


Figure 2.33 (A) A simplified flowsheet of beach sand processing; (B) lead-zinc concentration and their separation.

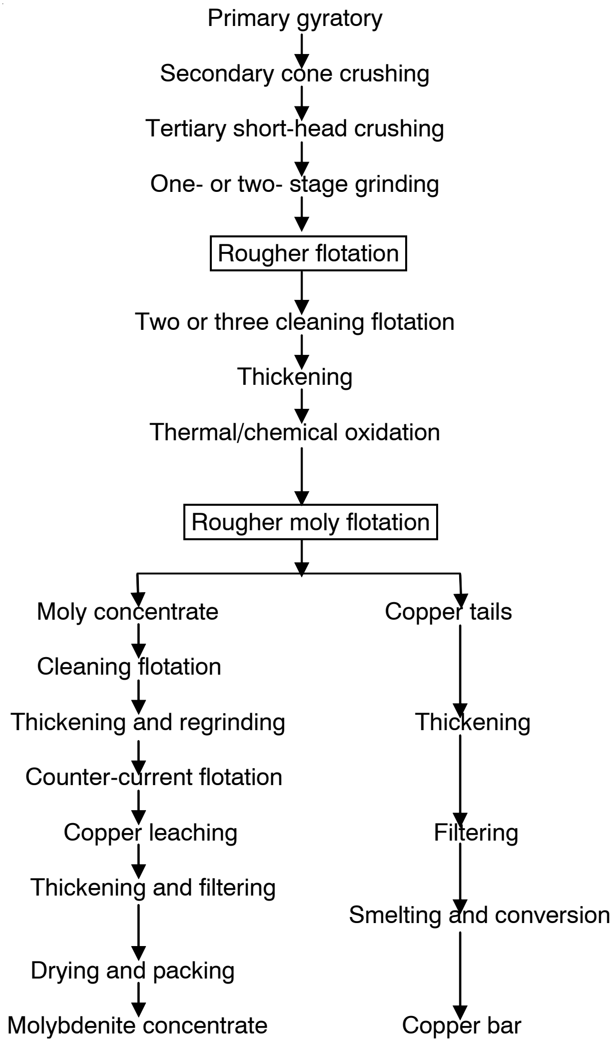


Figure 2.34 A schematic flowsheet for molybdenum recovery from porphyry coppers.

The current rare earths resources are the base minerals, monazite, xenotime, and bastnasite. The processing flowsheet of the mineral-bearing beach sand in Thailand is shown in Figure 2.35 (A). The flowsheet for processing bastnasite mined from Mountain Pass in California is shown in Figure 2.35 (B), and that proposed for concentrating rare earths in the beneficiation plant of Baotou in China is shown in Figure 2.35 (C). It is seen that flotation prominently figures in the two flowsheets Figure 2.35 (B) and (C).

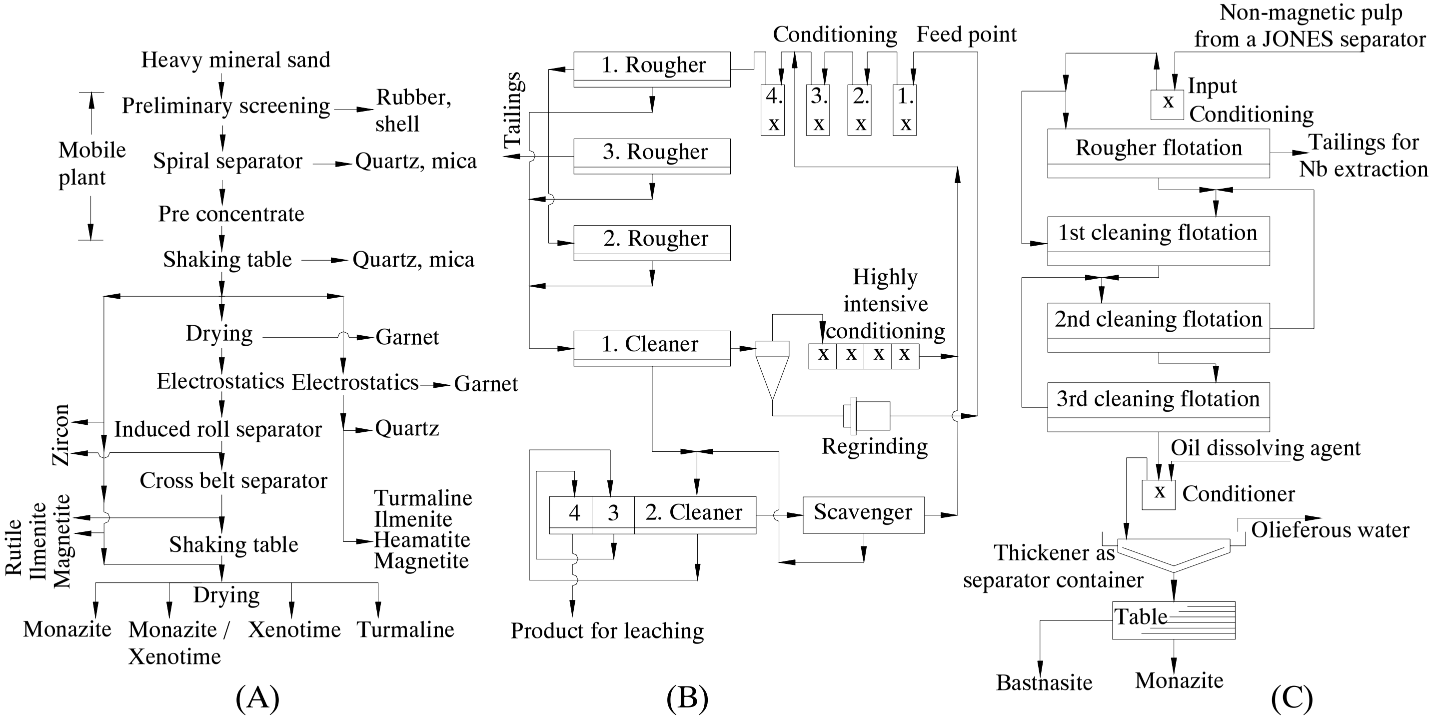


Figure 2.35 (A) Flowsheet for heavy mineral processing in Thailand. (B) Flowsheet for processing bastnasite from mountain pass, California. (C) Proposed flowsheet for concentration of rare earths in the beneficiation plant of Baotou, China.

2.14
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3
Thermodynamics and Kinetics

3.1
Introduction (Thermodynamics)

This chapter is concerned with two subjects, namely thermodynamics and kinetics.

Thermodynamics is an impressive branch of physical science which deals with the relationships between all forms of energy such as heat, chemical energy, mechanical or electrical work, and the macroscopic properties of material systems. Because thermodynamics deals with the general laws governing the transformations of macroscopic systems, without taking into account the microscopic mechanisms (at the atomic or molecular levels), the results are widely applicable and are independent of the microscopic explanations. Thermodynamics is relevant to physics, chemistry, and biology as well as to geology, the applied sciences and engineering including, of course, chemical metallurgy. There is barely any need to make elaboration on thermodynamics as applied to chemical metallurgy. It remains, in fact, amply illustrated and in-built in some of the chapters that follow.

The present text on thermodynamics is quite concise, and it is hoped that it will prepare readers well both for using thermodynamic methods and for delving more deeply into the subject with the supporting aid of a good deal of standard reference texts (some of which) are listed at the end of the chapter). The text presented here introduces some of the common concepts and definitions in vogue in thermodynamics, and a familiarity with them is considered the first useful step in the study of thermodynamics.

In thermodynamics, the term “system” means a portion of the physical universe, large or small, enclosed by a real or an imaginary boundary and thus separated from the rest of the universe, which constitutes the “surroundings”. The system can be either homogeneous or heterogeneous. There are three types of systems: (a) closed systems (or nonflow systems); (b) open systems (or flow systems), and (c) isolated systems. A closed system is a system of fixed mass. No mass transfer occurs across the system boundary. However, there can be energy transfer into or out of the system. A certain quantity of fluid in a cylindrical container, bound by a piston, constitutes a closed system. An open system is one in which matter (or mass) can cross the boundary of the system. In addition, there can also be energy transfer. In an isolated system is there is no interaction between the system and the surroundings. It is of fixed mass and energy, and there is no mass or energy transfer across the system boundary. Two types of open systems exist: (1) steady-state, and (2) unsteady state. If the properties of any part of the system are constant, regardless of the duration of an

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operation or a process, the so-called open system is the steady-state flow system. When the properties of any part of a system undergo fluctuation and variation, the open system is then termed as an unsteady state flow system.

The state (or behaviour) of a system is described by variables or properties which may be classified as: (a) extensive properties such as mass, volume, kinetic energy; and (b) intensive properties which are independent of system size, e.g., pressure, temperature, concentration. An extensive property can be treated like an intensive property by specifying that it refers to a unit amount of the substance concerned. Thus, mass and volume are extensive properties, but density, which is mass per unit volume, and specific volume, which is volume per unit mass, are intensive properties. In a similar way, specific heat is an intensive property, whereas heat capacity is an extensive property.

The variables whose values determine the thermodynamic state of a system are called its thermodynamic coordinates or its state variables. Pressure and temperature are examples of state variables. When the thermodynamic coordinates of a system change, the system is said to undergo a process. There are two types of processes: reversible and irreversible. An appreciation of these processes can readily be obtained by drawing reference to any two thermodynamic states of a system. Let a particular path between the two states be considered. If this path is such that in a process all the changes that take place in any part of the system or its surroundings are exactly reversed when the process is carried out in the reverse direction, then the process is said to be reversible. In a reversible path, when a given process has been carried out and then reversed, both the system and its surroundings come back exactly to their original states and no net change occurs in any part of the system or the surroundings. On the other hand, a process which involves the spontaneous transition of a system from a nonequilibrium state to an equilibrium state is called an irreversible process. An irreversible process is also called a spontaneous or a natural process. Such processes always leave a net change in the system and the surroundings after the system has been taken from one state to another and then brought back to the original state. The mixing of gases, the passage of heat from a hot body to a cold one etc. are examples of spontaneous processes. A system is said to be in equilibrium when it does not undergo a spontaneous process with time. The equilibrium state is essentially the result of a spontaneous process from a certain nonequilibrium state. The determination of the equilibrium state is of key importance in thermodynamics, since a knowledge of this state permits the determination of the direction in which any spontaneous chemical reaction will proceed from any given starting point.

Besides the reversible and irreversible processes, there are other processes. Changes implemented at constant pressure are called isobaric process, while those occurring at constant temperature are known as isothermal processes. When a process is carried out under such conditions that heat can neither leave the system nor enter it, one has what is called an adiabatic process. A vacuum flask provides an excellent example a practical adiabatic wall. When a system, after going through a number of changes, reverts to its initial state, it is said to have passed through a cyclic process.

Very closely interrelated concepts in thermodynamics are those of energy, work and heat. Energy is generally perceived as the capacity to do work. Mechanical work is performed whenever the point of application of a force is displaced in the direction of the applied force. Heat is a form of energy. Heat and work are interconvertible. The interconversion of heat and work is one of the prime concerns of thermodynamics.

The subject of thermodynamics embodies the principles of energy conversion in macroscopic systems. The general restrictions which experience has shown to apply to all such conversions are known as the *laws of thermodynamics*. These laws are fundamental in the sense that they cannot be derived from anything more basic. They do not require to be proven, but their acceptance is based on the fact that the conclusions derived from them are consistent with the results of all known experiments.

3.2
Zeroeth Law

The zeroeth law of thermodynamics was stated at a later point of time than the first, the second, and the third laws of thermodynamics. Since it was not thought to be reasonable to encroach on the longstanding, traditional enumeration of the basic principles contained in the three laws, their nomenclature was left unchanged and the new law was termed the zeroeth law of thermodynamics. It is this law which establishes the fact that temperature bears as important a relation to thermodynamics as force does to statics or velocity does to dynamics. It is by using the concept of temperature that the terms hot and cold are distinguished. The zeroeth law of thermodynamics states that when a substance A is in thermal equilibrium with a substance B, and also separately with a substance C, then B and C will be in thermal equilibrium with each other. According to this law, A, B and C are said to be equally hot or at the same temperature.

Thus the zeroeth law introduced a concept of temperature and provided a method for measuring it. If a small system is placed in contact with a large one so that a thermal equilibrium is established between them, the two will have the same hotness. Some easily observable property of the small system, such as its volume at constant pressure or its pressure at constant volume, which is related to the degree or its hotness, can be measured. By adopting a suitable scale, relationship between hotness of the small system and the selected property can be interpreted as temperature. Such a system then becomes a thermometer, an indicator of temperature while the large system which suffers only a slight change in temperature in attaining the equilibrium state is called a thermostat.

3.3
First Law

The first law of thermodynamics has been stated in various ways. A few selected statements are: (i) energy can neither be created nor destroyed though it may be converted from one form to another; (ii) whenever a quantity of one form of energy disappears, its equivalent in another form makes its appearance; (iii) for a system in contact with its surroundings the sum of the energies of the system and its surroundings remains constant howsoever differently it may be shared between the two; and (iv) it is impossible to make a perpetual machine which would produce work without consuming energy. This law introduced the concept of conservation of energy. The system and its surroundings together constitute an isolated system and, according to the first law, the total energy of an isolated system is constant. The total energy is also called the internal energy and it represents the sum total of all types of energy contained within the system boundaries. It should be mentioned here that it is not possible to assign an absolute value to the internal energy of a system; however, changes in internal energy can be measured. The first law is also stated in terms of such changes, and for this purpose a closed system is considered.

A closed system undergoing a change of state or a process is considered. Although mass transfer is prohibited across the boundaries of a closed system, energy transfer is permitted. This energy transfer can occur as work and heat transfer, both of these being only different forms of energy. If q is the amount of heat transferred to the system and w is the amount of work transferred from the system, then the change, ΔU, in the internal energy, U, of the closed system can be expressed as

$$\Delta U = q - w$$

Here, q is considered to be the heat absorbed by the system from the surroundings and w, the work done by the system on the surroundings. The terms q and w are written with lower-case letters to indicate that they are not functions of the state of system. The net energy transfer $(q - w)$ is stored in the system in the present example. Energy in storage is neither heat nor work, but is called internal energy or simply energy of the system. The first law is most often stated in the form of the given equation, which brings out not only the fact that heat and work are different forms of energy but also the criterion that the total energy of the system and the surroundings is conserved in the process. In a similar way, if an infinitesimal change in the state of the system is considered, the first law is often written in the form of the following equation:

$$\mathrm{d}U = \delta q - \delta w$$

the symbols remind that δq and δw are not derivatives of system state functions. The internal energy changes by the same amount between the initial and the final states of the system during the process, irrespective of the manner in which the process is carried out. To indicate that the value of U depends only on the state of the system and on nothing else, U is called a state function and changes in U, i.e., $\mathrm{d}U$ or ΔU, are said to be path independent. The values of the corresponding heat and work changes between the two states of the system do not have such a property. These values depend on the manner in which the process is carried out. In other words, the amount of heat or work transferred in the process depends on the path that the system traverses in going from one state to the next. The quantities δq and δw are, therefore, path dependent. While differential changes in state functions such as U, V, T are indicated as $\mathrm{d}U$, $\mathrm{d}V$, $\mathrm{d}T$, similar changes in path-dependent quantities like heat and work are represented as δq and δw. In mathematical parlance, $\mathrm{d}U$ is a perfect differential, while δq and δw are not. When the path is specified, the changes in q and w become definite and differential changes in these quantities can be represented as $\mathrm{d}q$ and $\mathrm{d}w$. The first law may then by expressed as

$$\mathrm{d}U = \mathrm{d}q - \mathrm{d}w$$

When a process is carried out at a constant pressure, P, the work done by the system can be represented as

$$dw = P\,dV$$

and the first law expression is

$$dU = dq - P\,dV$$

It is clear from the entire matter described above that in chemical systems conservation of energy is usually handled in terms of three quantities: (i) work done by the system on the surroundings which is taken as plus (+) w or the work done by the surroundings on the system which is taken as (–) w; (ii) heat gained by the system ($+q$) and heat lost by the system ($-q$); and (iii) the increase ($+\Delta U$) or decrease ($-\Delta U$) in the internal energy of the system as a result of the process carried through.

3.4
Thermochemistry

The specific application of the first law of thermodynamics to study chemical reactions is referred to as thermochemistry. Thermochemistry is concerned with the measurement or calculation of the heat absorbed or given out in chemical reactions. Precisely therefore, thermochemistry is the part of thermodynamics dealing with "enthalpy (i.e., heat content) changes" accompanying chemical reactions. In this context, it will be useful to refer to some of the important terms associated with thermal effects.

The heat capacity, C, of a system is defined as the heat introduced or withdrawn to raise or lower the temperature of the system by one degree celsius. Thus,

$$C = \frac{\delta q}{\delta T}$$

The concept of heat capacity is used only when the introduction of heat to, or the removal of heat from, the system brings about a corresponding change in temperature. The concept is not used in certain situations such as those involving phase changes. For example, if the system is a mixture of solid iron and liquid iron under one atmosphere pressure and at 1535 °C (melting point of iron), then the addition of heat simply melts some of the iron and no temperature change results. In such a situation the heat capacity, as the definition goes, would be infinite.

The expression for heat capacity brings out the fact that it is an indefinite quantity even when mass is specified, since δq is so. This is no longer the case when certain conditions, particularly constant volume or constant pressure conditions, are specified. The heat capacity then becomes a definite quantity as a consequence of δq becoming a definite quantity.

It is usual to encounter in studies of energy changes associated with reactions of chemical interest, a great variety of chemical materials and transformations. There are many ways by which transformations are implemented but it is convenient to consider two conditions that are special and occur frequently: (i) the volume of the system is kept constant; and (ii) the pressure on the system is held constant. The second scenario, for example, is that occurring for reactions or other processes carried out in containers that are open to atmosphere.

Let us first consider the constant volume condition. The heat capacity at constant volume (C_v) is given by the following expression:

$$C_v = \frac{\delta q_v}{dT}$$

When the volume is held constant, $dV = 0$, the equation expressing the first law becomes

$$dU = dq_v$$

The expression for the heat capacity at constant volume, C_v, may thus be written as

$$C_v = \left(\frac{dU}{dT}\right)_v$$

and

$$dU = C_v\, dT$$

Now let the constant pressure condition be considered. The heat capacity at constant pressure, C_p, is represented by

$$C_p = \frac{\delta q_p}{dT}$$

For a finite process in which the system changes from state 1 to state 2, the work done at constant pressure is

$$\int_1^2 dw = P\int_1^2 dV$$

The first law expression may now be written as

$$\int_1^2 dU = \int_1^2 dq_p - P\int_1^2 dV$$

so that

$$U_2 - U_1 = (q_2 - q_1) - P\,(V_2 - V_1)$$

On rearrangement,

$$q_p = (U_2 + P\,V_2) - (U_1 + P\,V_1)$$

where $q_p = q - q_1$ is the heat absorbed by the system at constant pressure in going from state 1 to state 2.

A thermodynamic function called enthalpy or heat content, represented by H, is now defined as follows

$$H = U + P\,V$$

Using this function in the earlier expression for heat absorbed at constant pressure,

$$q_p = H_2 - H_1 = \Delta H$$

For an infinitesimal change

$$C_p = \left(\frac{dq}{dT}\right)_p = \left(\frac{dH}{dT}\right)_p$$

and

$$dH = C_p \, dT$$

It is thus seen that heat capacity at constant volume is the rate of change of internal energy with temperature, while heat capacity at constant pressure is the rate of change of enthalpy with temperature. Like internal energy, enthalpy and heat capacity are also extensive properties. The heat capacity values of substances are usually expressed per unit mass or mole. For instance, the specific heat which is the heat capacity per gram of the substance or the molar heat, which is the heat capacity per mole of the substance, are generally considered. The heat capacity of a substance increases with increase in temperature. This variation is usually represented by an empirical relationship such as

$$C_p = a + b\,T + C\,T^{-2}$$

where a, b, and c are constants (for a given substance) and T is the temperature in degrees Kelvin. The unit of C_p is calories per degree per mole or joules per degree per mole.

The term specific "heat" is an unfortunate historical legacy, as only for very special conditions are these derivatives related to energy transfer in the form of heat. The term "heat capacity" is also a misnomer, as it implies incorrectly that heat is a "storable" entity.

It is now be pertinent to move on to chemical reactions which, as mentioned earlier, are central to the subject of thermochemistry. Metallurgical processes are mostly carried out at constant pressure and, therefore, enthalpy assumes the role of a very important thermodynamic parameter in metallurgical thermochemistry.

The heat absorbed in a process at constant pressure is equal to ΔH, the increase in the enthalpy of the system. It can thus be said that the heat change accompanying a chemical reaction is equal to the difference between the total heat content of the products and that of the reactants, at constant pressure and temperature conditions. This quantity is called the heat of reaction, ΔH, and can be expressed as follows

$$\Delta H = \sum H \text{ (products)} - \sum H \text{ (reactants)}$$

where all the enthalpy values refer to the specified temperature and a pressure of one atmosphere.

Two types of situation may generally arise in respect of this equation. In the first, the enthalpy of the products exceeds that of the reactants (ΔH is positive), while in the second the converse happens (ΔH is negative). A reaction that conforms to the former situation is called an *exothermic reaction* and a reaction that corresponds to the latter situation is called an *endothermic reaction*. An exothermic reaction is accompanied by evolution of heat. An endothermic reaction, in contrast, occurs with absorption of heat. Enthalpy changes are associated with different types of reactions in forms such as the heat of formation of a compound, the heat of combustion of a substance, the heat of transformation, and the heat of solution. In defining these enthalpy changes one clearly stipulates the amounts of the reacting substances. The heat of formation of a compound is the change in enthalpy that results when one mole of the compound is formed from its constituent elements. Since the absolute value of the heat content of a substance is not known, the convention in thermochemistry is to take the heat contents of elements in their standard states, i.e., in their stable forms under one atmosphere pressure-to be zero, at 25 °C (298 K). On this basis

- The heat of formation of one mole of a compound at 25 °C, as defined above, turns out to be the same as the heat content of one mole of the compound at 25 °C.
- The heat of combustion of a substance is the enthalpy change that occurs when one mole of the substance (an element or a compound) is completely burnt in oxygen.
- The heat of transformation is defined as the change in enthalpy that results when one mole of a substance undergoes a specific change of state such as melting, evaporation, or allotropic modification.
- The heat of solution is the enthalpy change that occurs when one mole of the solute is added to form a solution of a particular concentration.

There are two important relationships in thermochemistry which are very useful in the calculation of enthalpies of reactions. These are known as Hess's law and Kirchoff's equation.

Hess's law states that the overall change in enthalpy in a reaction is the same whether the reaction takes place in one step or through a number of intermediate steps. This law can also be regarded as a consequence of the fact that enthalpy is a state function so that the enthalpy difference between the final state (products) and the initial state (reactants) is the same, irrespective of the reaction path (sequence in which the reaction takes place). As an example, let the following reaction be considered,

$$C + O_2 = CO_2$$

For this reaction the standard heat of reaction at 298 K, ΔH^0_{298}, equals –393510 J. Now let the following two reactions, which also finally result in the formation of CO_2, be considered

$$C + 0.5\ O_2 = CO \qquad (\Delta H^0_{298} = -110530\ J)$$

$$CO + 0.5\ O_2 = CO_2 \qquad (\Delta H^0_{298} = -282980\ J)$$

Adding,

$$C + O_2 = CO_2 \qquad (\Delta H^0_{298} = -110530\ J - 282980\ J = -393510\ J)$$

The overall enthalpy change is the same as that indicated earlier. An useful consequence of Hess's law is that thermochemical equations can be added and subtracted just like algebraic equations. This facilitates the calculation of enthalpy changes for reactions which cannot be studied experimentally.

In general, the heat capacity of any substance changes with change in temperature. Thus in a reaction, the heat capacities of reactants and products change with variation in temperature and this change results in change of ΔH values for reactions as the temperature varies. For example, in the generalized typical reaction shown below,

$$\begin{tikzcd}
\text{Reactants } (R) \text{ at } T_1 \arrow[r, "\Delta H_{\mathrm{T}_1}"] \arrow[d, "C_{\mathrm{p}}^{\mathrm{R}}(T_2 - T_1)"'] & \text{Products } (P) \text{ at } T_1 \arrow[d, "C_{\mathrm{p}}^{\mathrm{P}}(T_2 - T_1)"'] \\
\text{Reactants } (R) \text{ at } T_2 \arrow[r, "\Delta H_{\mathrm{T}_2}"] & \text{Products } (P) \text{ at } T_2
\end{tikzcd}$$

Starting from reactants at temperature, T_1, products at temperature, T_2, are obtained. This is accomplished in two ways.

In the first way, the reaction is conducted at temperature, T_1 (heat of reaction = ΔH_{T_1}) and product is also obtained at temperature, T_1. The products at T_1 are then heated to temperature, T_2 (heat involved = $C_{\mathrm{p}}^{\mathrm{P}}(T_2 - T_1)$) to obtain products at temperature, T_2. In this way, the heat required to obtain products at T_2 starting from reactants at T_1 is $\Delta H_{\mathrm{T}_1} + C_{\mathrm{p}}^{\mathrm{P}}(T_2 - T_1)$.

In the second way, reactants at temperature, T_1 are heated to the temperature, T_2 (heat involved = $C_{\mathrm{p}}^{\mathrm{R}}(T_2 - T_1)$ to obtain reactants at temperature, T_2. Reaction is then conducted to convert reactants at T_2 to products at T_2 (heat of reaction = ΔH_{T_2}). In this way, the heat required to obtain products at T_2 starting from reactants at T_1 is $C_{\mathrm{p}}^{\mathrm{R}}(T_2 - T_1) + \Delta H_{\mathrm{T}_2}$.

Pursuing either of the two ways described, reactants from a given initial state ultimately reach the same final state. Then, according to Hess's law, the heat required in both the ways should be the same. In other words,

$$\Delta H_{\mathrm{T}_1} + C_{\mathrm{P}}^{\mathrm{p}}(T_2 - T_1) = \Delta H_{\mathrm{T}_2} + C_{\mathrm{p}}^{\mathrm{R}}(T_2 - T_1)$$

or

$$\Delta H_{\mathrm{T}_2} - \Delta H_{\mathrm{T}_2} = (C_{\mathrm{P}}^{\mathrm{p}} - C_{\mathrm{p}}^{\mathrm{R}})(T_2 - T_1)$$

The C_{p} values used here, of course, refer to the mean values of C_{p} in the temperature interval $T_1 - T_2$. The above expression may be rewritten as:

$$\frac{\mathrm{d}(\Delta H)}{\mathrm{d}T} = \Delta C_{\mathrm{p}}$$

where ΔC_{p} refers to the difference in the specific heat between the products and reactants (i.e., $\Delta C_{\mathrm{p}} = C_{\mathrm{p}}^{\mathrm{P}} - C_{\mathrm{p}}^{\mathrm{R}}$).

This equation is the well-known *Kirchoff's equation* that is more often used in the integrated form, which is

$$\int_{T_1}^{T_2} \mathrm{d}(\Delta H) = \Delta H_{\mathrm{T}_2} - \Delta H_{\mathrm{T}_1} = \int_{T_1}^{T_2} \Delta C_{\mathrm{p}}\, \mathrm{d}T$$

or

$$\Delta H_{\mathrm{T}_2} = \Delta H_{\mathrm{T}_1} + \int_{T_1}^{T_2} \Delta C_{\mathrm{p}}\, \mathrm{d}T$$

To calculate the heat of reaction at any temperature T_2, when the heat of reaction at a given temperature T_1 is known it is necessary to have information on the dependency of heat capacity on temperature for all the reactants and products. This information, as has been described earlier, is available in the form of equations such as:

$$C_p = a + b\,T + c\,T^{-2} + \ldots$$

where a, b, c are constants for a given substance and T is the temperature.

Usually, the temperature T_1 is taken as 298 K. Including also the standard conditions, the equation becomes

$$\Delta H^0_T = \Delta H^0_{298} + \int_{298}^{T} \Delta C_p \, dT \pm \Delta H^t$$

The last term in the above equation, ΔH^t, refers to the enthalpies of transformation that the reactants and/or products may undergo in the temperature interval 298 to T. Enthalpies of transformations are added (the sign is "+") if products transform and subtracted (the sign is "–") if reactants transform. Molar heat capacities of reactants and products do vary with change in temperature. If the variation is not appreciable, the C_p may be assumed to be constant, with respect to temperature and the equation becomes

$$\Delta H_T = \Delta H^0_{298} + \Delta C_p\,(T_2 - T_1)$$

and

$$\Delta C_p = \sum C_p^P - \sum C_p^R$$

For example, if the general reaction

$$a\,A + b\,B = c\,C + d\,D$$

is considered, then

$$\Delta C_p = (c\,C_{p_C} + d\,C_{p_D}) - (a\,C_{p_A} - b\,C_{p_B})$$

If the value of ΔH_T is to be calculated very accurately, the variation of C_p with temperature must be taken into account and this is done using the following expression for ΔC_p:

$$\Delta C_p = \Delta a + \Delta b\,T + \Delta c\,T^{-2} + \ldots$$

and if there is phase transformation in the temperature range considered, C_p values for each of the phases should be taken into account and accordingly different expressions for ΔC_p will have to be calculated in different temperature ranges. Thus,

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_t} \Delta C_p \, dT + \Delta H_t + \int_{T_1}^{T_2} \Delta C_p \, dT$$

where, for example, the product undergoes an endothermic phase transformation at T_t and its enthalpy of transformation is ΔH_t.

3.5
Second Law

The first law of thermodynamics enunciates that heat and work are mutually convertible, but the law does not concern itself with the extent of this convertibility. In other words, if one were to be guided by the first law alone, then every process involving the conversion of energy should be feasible, provided that energy is neither created nor destroyed. Thus according to this law, in every cyclic process work may be completely converted into heat or heat may be completely converted into work; heat may flow from a hot to a cold or from a cold to a hot body; a gas may expand from high pressure to low pressure or contract from low pressure to high pressure. It is known from our experience that not all of this is true. In natural processes, work is not completely converted into heat; heat flows from a hot to a cold body, but the reverse flow is not possible; a high-pressure gas expands to low pressure, but the opposite process does not occur. It is true that these spontaneous processes can be reversed, but not on their own. Some external agency is required to make the reverse process occur. A piece of ice when kept in the atmosphere absorbs heat and melts but it will not solidify and give back heat without any work being performed on it.

The examples cited above demonstrate that the first law has some limitations, and it cannot predict whether the system will spontaneously undergo a change, i.e., whether a certain process is possible or not. Experience shows that a spontaneous process can proceed in a particular direction only. The first law does not specify this direction. Neither does it provide any information regarding the conditions under which no net process can take place at all, i.e., when a system is in equilibrium. The first law merely states that work transfer during a cycle is equal to the heat transfer and does not impose any restriction on the direction of heat and the work transfer. It is the second law of thermodynamics which provides answers to the questions that have been raised. Like the first law, the second law is also a generalization of experience and is essentially a statement of the fact that certain processes which are wholly consistent with the first law nevertheless do not occur. Although the second law can be stated in a number of ways, all statements can be shown to generalize the knowledge that natural processes tend to go to a state of equilibrium. The second law totals our experiences with equilibria, just as the first law did for our experience with energy. The general enumerations of the second law, like the conservation-of-energy enumeration of the first law, are not immediately applicable to chemical problems. The following presentation of general statements of the law, will show that the law can be expressed in a practically useful form.

Two classically important statements have been provided. The first statement, due to Lord Kelvin, is that it is not possible by a cyclic process to take heat from a reservoir and convert it into work without at the same time transferring heat from a hot to a cold reservoir. This statement of the second law is related to equilibria when it is realized that work can be obtained from a system only when the system is not already at equilibrium. The statement recognizes that the spontaneous process is the flow of heat from a higher to a lower temperature and that only from such a spontaneous process can the work be acquired. The second important classic statement, due to Clausius, is that it is not possible to transfer heat from a cold to a hot reservoir without at the same time converting a certain amount of work into heat. The operation of a refrigerator readily illustrates this statement of the second law. Neither the statement from Kelvin nor the one from Clausius follows from the first law of thermodynamics. No conflict with the first law of thermodynamics would be confronted if the heat were completely transformed into work or if heat were to flow from a lower to a higher temperature. The second law of thermodynamics is a different generalization about heat and work from that given by the first law of thermodynamics.

The following question can now be posed: can one find a criterion that decides, given an initial state, the possible final state of the system as a result of the occurrence of a certain process under a given set of conditions? This question could be answered if there exists some property of the system, that is, some function of the state of the system, which has different values at the start and at the conclusion of a possible process. This function cannot be internal energy which, as has been mentioned earlier, is constant in an isolated system. A function possessing the desired property could be found, however. It was first defined by Clausius and is called the "entropy" of the system. Like the internal energy, it is a function of the state of the system only and it either increases or remains constant in any possible process taking place in an isolated system. In terms of entropy, the second law may be stated as: in every process occurring in an isolated system, the entropy of the system either increases or remains constant. It increases in an irreversible process and remains constant when the process is reversible. Like the first law, the second law of thermodynamics can also be stated in several other ways. However, for the development of thermodynamics with regard to its metallurgical and chemical applications the presently stated form is perhaps the most explicit.

It has been seen thus far that the first law, when applied to thermodynamic processes, identifies the existence of a property called the internal energy. It may in other words be stated that analysis of the first law leads to the definition of a derived property known as internal energy. Similarly, the second law, when applied to such processes, leads to the definition of a new property, known as the entropy. Here again it may in other words be said that analysis of the second law leads to the definition of another derived property, the entropy. If the first law is said to be the law of internal energy, then the second law may be called the law of entropy. The three Es, namely energy, equilibrium and entropy, are centrally important in the study of thermodynamics. It is sometimes stated that classical thermodynamics is dominated by the second law.

3.5.1
Entropy

Entropy can be described by considering a closed system undergoing a reversible process. The entropy change, dS, of the system is defined by the relationship

$$dS = \frac{dq_{\mathrm{rev}}}{T}$$

where dq_{rev} is the heat absorbed by the system isothermally at constant pressure and T is the temperature of the system at which the heat absorption takes place. Elaborating on the above expression, when a certain amount of heat, q, is applied to a system at temperature, T, its disorder or entropy increase. Entropy is often visualized in terms of the disorder of the system; the greater the disorder the larger is the entropy. The magnitude of the entropy change is related to the heat q and the temperature T as given below:

$$\Delta S \propto q$$

and

$$\Delta S \propto \frac{1}{T}$$

The first expression clarifies that entropy of the system increases when it takes up heat. Absorption of heat results in rise of temperature. Increase in entropy per degree rise in temperature is not the same at all temperatures: it is more at low temperatures and relatively less at high temperatures. This is shown by the inverse relationship between the entropy change and temperature. The combined expression for the variation of entropy change with quantity of heat and temperature, therefore becomes,

$$\Delta S \propto \frac{q}{T}$$

The proportionality constant is 1 for reversible thermodynamic processes and

$$\Delta S = \frac{q_{\mathrm{rev}}}{T}$$

This equation was originally arrived at by the French Engineer Sadi Carnot in 1824 during his investigation on the efficiency of heat engines. In terms of the heat and the entropy changes in the system, the second law may be expressed as follows:

$$\mathrm{d}S \geq \frac{\delta q}{T}$$

The equality applies when heat is transferred reversibly and the inequality refers to irreversible or natural or spontaneous transfer of heat. Thus,

$$\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T}$$

$$\mathrm{d}S > \frac{\mathrm{d}q_{\mathrm{irrev}}}{T}$$

With the entropy term introduced, it is possible to make a combined statement of the first and the second laws. To do this, one may consider an infinitesimal change of state of a closed system. For this, the first law gives

$$\mathrm{d}U = \mathrm{d}q - P\,\mathrm{d}V$$

and if this change occurs reversibly, the second law gives

$$dS = \frac{dq}{T}$$

or

$$dq = T\,dS$$

Combining the above equations

$$dU = T\,dS - P\,dV$$

There are some restrictions on the applicability of this equation and these include: (i) that the system is closed, and (ii) that the work associated with volume change is the only type of work performed by the system. Many useful relationships can be obtained by combining the first and second law expressions; these have been summarized in Table 3.1.

At this stage, it would be worthwhile to consider some processes and the entropy changes associated with them.

In a system undergoing a reversible adiabatic process, there is no change in its entropy. This is so because by definition, no heat is absorbed in such a process. A reversible adiabatic process, therefore, proceeds at constant entropy and may be described as isentropic. The entropy, however, is not constant in an irreversible adiabatic process.

The simplest process involving a change in entropy is a reversible process occurring at a constant temperature, T. For such a process, the change in entropy, ΔS, can be expressed as

$$\Delta S = \frac{\Delta q_{\mathrm{T}}}{T}$$

The change in entropy of a system in such an isothermal reversible process thus equals the heat absorbed by the system divided by the absolute temperature of the system. A common example of a reversible isothermal process is a phase change under constant pressure during which the temperature also remains constant. To implement the change reversibly, the system is brought into contact with a heat reservoir at a temperature infinitesimally higher than the equilibrium temperature at the given pressure. The phase change then

Table 3.1 Thermodynamics equations as obtained from the first and the second laws of thermodynamics.

Thermodynamic equations	***Remarks***
$\delta q = dU + \delta W$	This holds good for any process undergone by a closed system.
$dq = dU + P\,dV$	This holds good for a closed system when only PdV work is present.
$dq = T\,dS$	This is true only for a reversible process.
$T\,dS = dU + P\,dV$	This holds good for any process reversible or irreversible, undergone by a closed system, since it is a relationship among properties which are not dependent on path.
$T\,dS = dH - V\,dP$	This equation relates only the properties of closed system. There is no path function term in the equation, and therefore it holds good for any process.

proceeds very slowly, and at all stages of the process the system is essentially at the equilibrium temperature T. The heat q_T taken up by the system equals the heat of transformation, ΔH_{tr}, and the change in entropy, ΔS, can then be written as

$$\Delta S = \frac{\Delta H_{tr}}{T}$$

In most processes, a reversible absorption of heat is accompanied by a change in temperature, and a calculation of the corresponding entropy change requires an evaluation of the integral of $\delta q/T$. The term q is related to the heat capacity of the system which is usually expressed as a function of temperature. In a constant volume process, for example, the entropy change is

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_v}{T}\,dT$$

and in a constant pressure process, it is given by

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_p}{T}\,dT$$

The processes that occur at a finite rate, with finite differences of temperature and pressure between parts of a system or between a system and its surroundings, are irreversible processes. It has been shown that the entropy of an isolated system increases in every natural (i.e., irreversible) process. It may be noted that this statement is restricted to isolated systems and that entropy in this case refers to the total entropy of the system. When natural processes occur in an isolated system, the entropy of some portions of the system may decrease and that of other portions may increase. The total increment, however, is always greater than the total decrement. The entropy of a nonisolated system may either increase or decrease, depending on whether heat is added to it or removed from it and whether irreversible processes occur within it. Considered all in all, it is necessary to define clearly the system under consideration when increases and decreases in entropy are discussed.

3.5.2
Free Energy

In thermodynamics, entropy enjoys the status as an infallible criterion of spontaneity. The concept of entropy could be used to determine whether or not a given process would take place spontaneously. It has been found that in a natural or spontaneous process there would be an increase in the entropy of the system. This is the most general criterion of spontaneity that thermodynamics offers; however, to use this concept one must consider the entropy change in a process under the condition of constant volume and internal energy. Though infallible, entropy is thus not a very convenient criterion. There have, therefore, been attempts to find more suitable thermodynamic functions that would be of greater practical convenience and utility. This has led to the introduction of two other functions, which incorporate the entropy but are more convenient to use in many cases. These two functions are known as *Helmholtz free energy* (also known as work function) and *Gibbs free energy*. They lend themselves to the treatment of equilibrium state toward which process moves. In studies of processes (say of chemical reactions) which are usually performed in the laboratory at a constant temperature in a thermostat and in either open reactors when P is constant or in closed reactors when V is constant, the concepts of the two terms as defined below are helpful.

Helmholtz free energy, represented by the symbol A, is defined as:

$$A = U - T\,S$$

In this expression U is the internal energy, T is the absolute temperature and S is the entropy.

Gibbs free energy, represented by the symbol G (the symbol F is also sometimes used in place of symbol G), is defined as:

$$G = U - T\,S + P\,V$$

where P and V refer, as usual, to the pressure and the volume of the system. This definition may be expressed in two alternative forms. First, by using the relationship, $A = U - T\,S$

$$G = A + P\,V,$$

and second, by using the relationship $H = U + PV$,

$$G = H - T\,S$$

Before proceeding to describe the utility of Gibbs free energy in discussing equilibria, it is worthwhile presenting expressions relating the changes in G to changes in the other thermodynamic parameters of a system.

Keeping in view the expression for G, one obtains, in the differential form,

$$\mathrm{d}G = \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T + V\,\mathrm{d}P + P\,\mathrm{d}V$$

It has been seen earlier that by combining the first and the second laws, the following relationship can be arrived at:

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V$$

Using this relationship, one could write

$$\mathrm{d}G = V\,\mathrm{d}P - S\,\mathrm{d}T$$

At constant pressure ($\mathrm{d}P = 0$), this can be expressed as

$$\mathrm{d}G_\mathrm{P} = -\,(S\,\mathrm{d}T)_\mathrm{P}$$

or

$$\left(\frac{\delta G}{\delta T}\right)_\mathrm{P} = -S$$

Similarly, at constant temperature ($dT = 0$),

$$dG_T = (V\,dP)_T$$

or

$$\left(\frac{\delta G}{\delta P}\right)_T = V$$

These relationships interrelate the parameters pressure, volume and temperature with the Gibbs free energy of a system. It may be pointed out that the results embodied in these equations are applicable to closed systems only.

The free energy change in a chemical reaction is expressed in the same way as the enthalpy of the reaction is expressed. For example, the free energy change in the reaction

$$a\,A + b\,B = c\,C + d\,D$$

is

$$\Delta G = c\,G_C + d\,G_D - a\,G_A - b\,G_B$$

or

$$\Delta G = \sum G\ \text{(products)} - \sum G\ \text{(reactants)}$$

In the case of a system undergoing a simple process that takes it from state A to state B,

$$\Delta G = G_B - G_A$$

For such a system undergoing a finite change from state A to state B, one has

$$\Delta S = S_B - S_A = -\left[\left(\frac{\delta G_B}{\delta T}\right)_P - \left(\frac{\delta G_A}{\delta T}\right)_P\right]$$

or

$$\Delta S = -\left[\frac{\delta(G_B - G_A)}{\delta T}\right]_P = -\left(\frac{\delta \Delta G}{\delta \mathrm{T}}\right)_P$$

so that,

$$\left(\frac{\delta \Delta G}{\delta T}\right)_P = -\Delta S$$

Similarly,

$$\left(\frac{\delta \Delta G}{\delta P}\right)_T = \Delta V$$

From the relationship between the free energy change and the entropy change given above, it follows that the slope of a plot of ΔG against T, i.e., of free energy change against temperature, gives the negative of the entropy change for the process.

For a finite process occurring at constant temperature T and pressure P, the free energy change can be expressed as

$$\Delta G = \Delta H - T\,\Delta S$$

The above equation is especially valuable in highlighting the importance of change in free energy as an explicit criterion for the spontaneity of a chemical reaction. The occurrence of a chemical reaction is indicated only when there is an overall decrease in the energy of the system. This was originally identified with only the enthalpy of the system, and the exothermicity of a reaction was taken to indicate that it would occur spontaneously. Inadequacy of enthalpy change as the sole arbiter of the actual energy change in the system was brought by the existence of spontaneous endothermic reactions. Similarly, reactions in which the entropy change is negative but spontaneous were also identified. It thus became imperative that the real indicator of the overall decrease in the energy of the system should combine both the enthalpy and entropy changes. The free energy change incorporates the changes in enthalpy and entropy in such a way as to express the combined effect to indicate the direction of the chemical reaction. Spontaneous reactions may thus be endothermic or may occur with negative entropy change but cannot occur with a positive free energy change. In other words, in a spontaneous reaction the combination of endothermicity attended with a negative entropy change is prohibited.

Substituting for ΔS in the equation given above,

$$\Delta G = \Delta H + T\left(\frac{\delta \Delta G}{\delta T}\right)_{\mathrm{P}}$$

The above equation is known as the Gibbs–Helmholtz equation. It enables the evaluation of the ΔH of a reaction from a knowledge of the free energy change (ΔG) and of its temperature coefficient $[(\delta \Delta G)/(\delta T)]_{\mathrm{P}}$.

An alternative form of the Gibbs–Helmholtz equation can be obtained as follows.

At constant pressure,

$$\Delta G\,\mathrm{d}T = \Delta H\,\mathrm{d}T + T\,\mathrm{d}(\Delta G)$$

Dividing both sides of this equation by T^2 and rearranging the terms, one obtains

$$\frac{T\,\mathrm{d}(\Delta G) - \Delta G\,\mathrm{d}T}{T^2} = -\frac{\Delta H\,\mathrm{d}T}{T^2}$$

Since the left-hand side of this equation is of the form $\mathrm{d}(x/y) = (y\,\mathrm{d}x - x\,\mathrm{d}y)/y^2$, one has

$$\frac{\mathrm{d}(\Delta G/T)}{\mathrm{d}T} = -\frac{\Delta H}{T^2}$$

Expressed in this form, the Gibbs–Helmholtz equation is widely used in experimental thermodynamics to determine ΔH, the enthalpy of a reaction, from the experimentally determined variation of ΔG with temperature. The Gibbs–Helmholtz equation may also be written as

$$\frac{\mathrm{d}(\Delta G/T)}{\mathrm{d}\left(\frac{1}{\mathrm{T}}\right)} = -\Delta H$$

The Gibbs–Helmholtz equation is applicable to closed systems of fixed composition undergoing isobaric (constant pressure) processes.

An important use of the free energy function is to obtain a simple criterion for the occurrence of spontaneous processes and for thermodynamic equilibrium. According to the second law of thermodynamics,

$$\mathrm{d}S \geq \frac{\delta q}{T}$$

where the "greater than" sign refers to an irreversible process, and the "equal to" sign to a reversible process. Using the statement of the first law of thermodynamics, the term q may be replaced and one may write the following:

$$\mathrm{d}S \geq \frac{\mathrm{d}U + \delta w}{T}$$

If in any process $\mathrm{d}U$ and δw both are zero, then one obtains

$$\mathrm{d}S \geq 0$$

Now for δw to be zero, the process has to be a constant volume process and in that case

$$\mathrm{d}S_{\mathrm{U,V}} \geq 0$$

where the subscripts U and V denote constancy of internal energy and of volume. In other words, when the internal energy and the volume are maintained constant, the entropy of a system increases in a spontaneous (irreversible) process, but remains unaltered when the system undergoes a reversible process, i.e., when it is in a state of thermodynamic equilibrium. Since the entropy can either increase or remain constant in a process, one can conclude that the entropy of a system at equilibrium is a maximum at constant internal energy and volume.

Substituting $\mathrm{d}w = P\,\mathrm{d}V$,

$$\mathrm{d}S \geq \frac{\mathrm{d}U + P\,\mathrm{d}V}{T}$$

or

$$T\,\mathrm{d}S \geq \mathrm{d}U + P\,\mathrm{d}V$$

or

$$\mathrm{d}U - T\,\mathrm{d}S + P\,\mathrm{d}V \leq 0$$

At constant temperature and pressure, $dG = dU - T\,dS + P\,dV$, and so for any process,

$$dG_{T,P} \leq 0$$

where the "less than" sign refers to a spontaneous process and the "equal to" sign to an equilibrium process. Since most reactions are performed under constant pressure and temperature conditions (i.e., isobaric and isothermal conditions), this relationship is very useful to stipulate the conditions for the occurrence of a spontaneous process or an equilibrium (i.e., reversible) process. Since $dG_{T,P}$ is either less than or equal to zero, depending on whether the system undergoes a spontaneous change or is in an equilibrium state, it follows that for a system in equilibrium, at a given temperature and pressure, the free energy must be a minimum. All the spontaneous processes occurring at constant temperature and pressure are accompanied by a decrease in the free energy. This result is of fundamental importance for it gives a simple and convenient criterion for assessing whether a given process is possible or not. For a finite process, implemented under constant pressure and temperature conditions, this criterion may be expressed as:

$$\Delta G_{T,P} \leq 0$$

The above form of the thermodynamic representation of the condition for the occurrence of a spontaneous process or of equilibrium is frequently used.

3.6
Third Law

The second law of thermodynamics has introduced entropy, and this function has been shown to be important when directions of spontaneous changes are investigated. The second law, moreover, shows how differences in entropy of two states of a system can be determined. The third law gives a method for assigning a value to the entropy of a system. The third law of thermodynamics also, like the first and the second laws, is an expression of our experience with nature. It has evolved from Nernst's observations that at very low temperatures the enthalpy and the free energy of a reaction approach each other asymptotically, that the asymptote is parallel to the temperature axis and just above absolute zero they virtually cease to vary with temperature. This behaviour is shown schematically in Figure 3.1 (A). Mathematically, the changes in the free energy and the enthalpy of a reaction in the vicinity of absolute zero are expressed as:

$$\lim_{T\to 0} \frac{d\Delta G}{dT} = 0$$

and

$$\lim_{T\to 0} \frac{d\Delta H}{dT} = 0$$

As $(\delta \Delta G/\delta T)_p = -\Delta S$, and $(\delta \Delta H/\delta T)_p = -\Delta C_p$, it follows:

$$\lim_{T\to 0} \Delta S = 0 \quad \text{and} \quad \lim_{T\to 0} \Delta C_p = 0$$

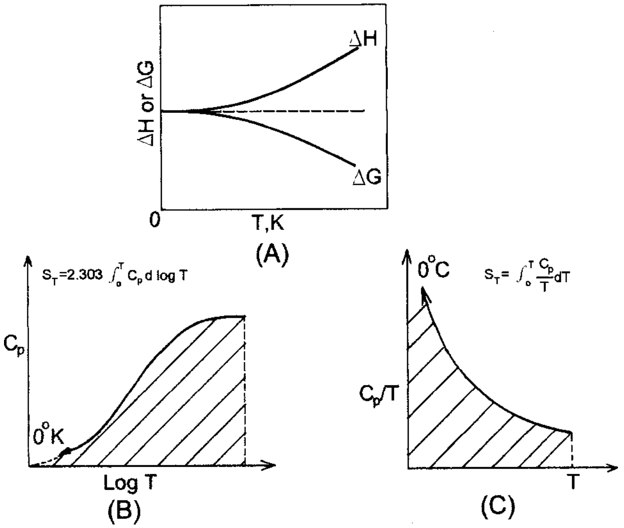


Figure 3.1 (A) Plots for the change in enthalpy and free energy of a reaction as a function of temperature; (B) plot between C_p and log T; (C) plot between C_p/T.

This is an expression of Nernst's postulate which may be stated as: the entropy change in a reaction at absolute zero is zero. The above relationships were established on the basis of measurements on reactions involving completely ordered crystalline substances only. Extending Nernst's result, Planck stated that the entropy, S_0, of any perfectly ordered crystalline substance at absolute zero should be zero. This is the statement of the third law of thermodynamics. The third law, therefore, provides a means of calculating the absolute value of the entropy of a substance at any temperature. The statement of the third law is confined to pure crystalline solids simply because it has been observed that entropies of solutions and supercooled liquids do not approach a value of zero on being cooled.

At a constant pressure, the entropy of any pure substance can be calculated for any temperature through the use of the procedure that is herein being described. The entropy change taking place during an isothermal reversible process, it may be recalled, is equal to the heat change involved divided by the absolute temperature:

$$\mathrm{d}S = \frac{\mathrm{d}q}{T} = \frac{C_\mathrm{p}\,\mathrm{d}T}{T}\,; \quad \int_0^T \mathrm{d}S = \int_0^T \frac{C_\mathrm{p}\,\mathrm{d}T}{T}$$

$$S_\mathrm{T} - S_0 = \int_0^T C_\mathrm{p}\,\mathrm{d}\ln T = 2.303\int_0^T C_\mathrm{p}\,\mathrm{d}\log T$$

According to the third law $S_0 = 0$. Therefore,

$$S_\mathrm{T} = 2.303\int_0^T C_\mathrm{p}\,\mathrm{d}\log T$$

S_T is the absolute entropy of the substance at T K. For the evaluation of S_T a graph is plotted either between C_p and log T as shown in Figure 3.1 (B) or between C_p/T and T as shown in Figure 3.1 (C) and for the evaluation of the integral in equation,

$$S_T = 2.303 \int_0^T C_p \, d\log T$$

the area below the curves is measured. If in going to the temperature T K from 0 K at a pressure of 1 atm a solid substance undergoes changes such as fusion and vapourization, the entropy of the substance in the gaseous form in the final state of T K and one atmosphere can be computed from comprehensive equation presented below:

$$S_T = \int_0^{T_f} C_{p(s)} \, d\ln T + \frac{L_f}{T_f} + \int_{T_f}^{T_v} C_{p(l)} \, d\ln T + \frac{L_v}{T_v} + \int_{T_v}^{T} C_{p(G)} \, d\ln T$$

where T_f = temperature of fusion, L_f = latent heat of fusion, T_v = temperature of vapourization, L_v = latent heat of vapourization and $C_{P(s)}$, $C_{p(l)}$ and $C_{p(G)}$ are the specific heats over the relevant temperature range (Figure 3.2).

It may be noted that the entropy at 298 K S_{298} is taken as the standard reference. Accordingly, the entropy of the substance at a temperature higher than 298 K will be

$$S_T = S_{298} + \int_{298}^{T} C_p \, d\ln T$$

In general case, where the substance undergoes a variety of transformations as shown in the Figure 3.2, the entropy of the temperature, T, S_T, becomes that given by the following equation:

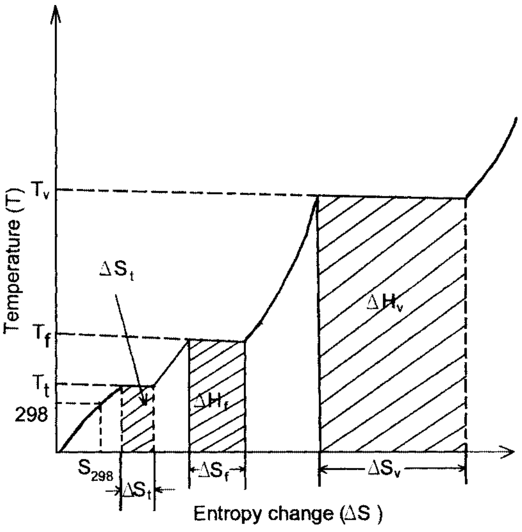


Figure 3.2 Change of entropy of a substance with temperature – the substance has undergone an allotropic change (t), fusion or melting (f) and vapourization (v) over the entire temperature range.

$$S_T = S_{298} + \int_{298}^{T_t} C_{p(s_1)}\, d\ln T + \Delta S_t + \int_{T_t}^{T_f} C_{p(s_2)}\, d\ln T + \Delta S_f$$
$$+ \int_{T_f}^{T} C_{p(l)}\, d\ln T + \Delta S_v + \int_{T_v}^{T} C_{p(g)}\, d\ln T$$

The shaded areas represent the values of the different enthalpies of transformation.

3.7
Chemical Equilibrium

Customarily chemical equilibrium has very instructively been introduced by describing the underlying meaning of reversible and irreversible reactions.

In many cases, it has been proved that the products of a reaction themselves react forming the original reactants once more. A general reaction of the type in which reactants R_1 and R_2 from products P_1 and P_2 at a given temperature is considered. This is expressed as a forward reaction by:

$$R_1 + R_2 \rightarrow P_1 + P_2$$

Again, P_1 and P_2 react to regenerate R_1 and R_2. This is expressed as a reverse reaction by:

$$P_1 + P_2 \rightarrow R_1 + R_2$$

These two oppositely directed reactions are represented by a single equation as:

$$R_1 + R_2 \rightleftharpoons P_1 + P_2$$

Here, the sign of equality (=) has been replaced by the double oppositely directed arrows ($\rightleftharpoons$) called a sign of reversibility. Such a reaction is called a reversible reaction. The reversibility of reactions can be detected when both the forward and the reverse reactions occur to a noticeable extent. Generally, such reactions are described as reversible reactions. The most important criterion of a reaction of this type is that none of the reactants will become exhausted. When the reaction is allowed to take place in a closed system from where none of the substances involved in the reaction can escape, one obtains a mixture of the reactants and the products in the reaction vessel. Every reversible reaction, depending on its nature, will after some time reach a stage when the reactants and the products coexist in a state of balance, and their amounts will remain unaltered for unlimited time. Such a state of a chemical reaction is called *chemical equilibrium*, and the point of such an equilibrium varies only with temperature.

Theoretically, all chemical reactions are reversible. There are, however, many reactions in which the extent of the reverse reaction (i.e., combination of the products to produce the reactants) is very small as to be considered negligible. Such reactions which are ordinarily found to proceed to completion in one direction are said to be irreversible reactions. The decomposition of potassium chlorate

$$2\ KClO_3 \rightarrow 2\ KCl + 3\ O_2$$

of ammonium nitrite

$$NH_4NO_3 \rightarrow N_2 + 2\ H_2O$$

and the precipitation of silver chloride

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

are examples of some familiar irreversible reactions. In fact it should be appreciated that these and other similar reactions are also reversible in character, and a truly irreversible reaction does not exist. It has been well founded that all the so-called irreversible reactions can be made to proceed in the reverse way, if the correct experimental conditions are set up. A specific example may be taken in this context. When a mixture of two parts of hydrogen and one part of oxygen is exploded at ordinary temperature under the influence of an electric spark, it is turned completely into water. There is no detectable residue of the participants of the reaction in the reaction vessel. It has, however, been found that at temperatures above about 1500 °C, water vapour is decomposed to an appreciable extent into hydrogen and oxygen. The reverse reaction that takes place at high temperatures must occur even at a very negligible extent under ordinary conditions. So, although the combination of hydrogen and oxygen leading to the formation of water is regarded as an irreversible reaction under ordinary conditions of temperature and pressure, it is in fact also a reversible reaction.

There are two different approaches, namely, kinetic and thermodynamic, which are useful for describing chemical changes and chemical equilibria. The law of mass action is the basis for the kinetic approach. According to the kinetic approach, the equilibrium state results from a dynamic balance between opposing reactions. The thermodynamic approach defines the equilibrium state as one of maximum stability, i.e., one of minimum free energy. Both kinetic and thermodynamic approaches lead to identical descriptions of the chemical compositions corresponding to the equilibrium state. At equilibrium, further changes in the chemical composition of the system cannot occur. The kinetic approach is useful for gaining an understanding of chemical reactions and of the mechanisms of their approach to equilibrium. The thermodynamic approach is useful for assessing the effects of factors such as temperature, pressure, volume, and composition on chemical equilibrium.

In the kinetic approach, the classical test for equilibrium as regards any given reaction is to allow the reaction to proceed in a closed system in the forward direction (left to right as written) until no net change is observable in the composition of the system with time. The reaction is then allowed to proceed in the backward direction (right to left) until again no net change is observable in the composition with time. If chemical equilibrium has been attained, the composition of the system would have reached the same value from either direction. As an example, let the reversible reaction, $H_2 + I_2 \rightleftharpoons 2\ HI$, be considered. When hydrogen and iodine are reacted in a closed vessel, initially the reaction proceeds entirely from the left to the right. However, when some hydrogen iodide molecules are formed, the reaction from the right to the left also starts to take place. For some time the speed of the former (forward reaction) would be greater than that of the latter (backward or reverse reaction). But the speed of the backward reaction would gradually increase as more and more hydrogen iodide molecules are formed. Eventually, a stage would be reached when the speeds of the two reactions would be equal. At this point the reaction would have reached equilibrium. This state of equilibrium can be made to continue indefinitely if all the experimental conditions are kept unchanged. In the equilibrium state, the numbers of hydrogen, iodine and hydrogen iodide molecules do not change. However, the equilibrium is not a static but a dynamic one. Hydrogen and iodine molecules would be reacting to yield hydrogen iodide but the associated loss in their concentrations would be made up since hydrogen iodide would also decompose to give back hydrogen and iodine. Thus, although the concentrations of the reactants and of the product would remain unaltered at equilibrium, actually the associated chemical equilibrium would be dynamic in nature. The double arrow symbol in the equation $H_2 + I_2 \rightleftharpoons 2\,HI$ is indicative not only of the reversibility of the reaction but also of the fact that dynamic equilibrium prevails. The term dynamic equilibrium can also be looked at in terms of a hydraulic equivalent of the equilibrium state, by which it is meant to be like water maintaining its level in a vessel in which some water is flowing in and an equal amount is flowing out. It is not like having a steady level of water in the vessel when the inlet and the outlet are plugged, in which case it is called a static equilibrium. This is the other recognized term of the hydraulic equivalent of an equilibrium state.

3.7.1
Law of Mass Action

Quantitative observations on the influence of the concentrations of the reactants and of the products participating in a reversible chemical reaction in equilibrium were generalized by Guldberg and Waage, and this led to the formulation of what is known as the law of mass action. This law states that the rate at which a reaction occurs at a given temperature is directly proportional to the active mass of each of the reacting substances. The term active mass in a homogeneous system refers to the molar concentration, that is, the number of gram-molecules of the substance in unit volume. If x grams of a substance A of molecular weight M be present in V liters, then x/M gram-moles of A are present in V liters. The active mass of A is $x/(M \cdot V)$. Therefore, the law of mass action may be stated alternatively as: at constant temperature, the rate of a chemical reaction varies directly as the molar concentration of the reacting substances. Molar concentration is generally expressed by enclosing the symbols or the formula of the substances involved in the reaction in square brackets. In general, if molecular concentrations are employed to represent the active masses of components, the law of mass action cannot be applied without modification to reactions occurring in solution. This is due to the fact that in such cases the numerical value of the equilibrium constant shows considerable variation. With the object of obtaining agreement with the law of mass action it is conventional to substitute the molecular concentrations the so-called "activities" of the various components. The relationship of activity and molecular concentration is shown by $a = cf$, where a = activity, c = molecular concentration, and f = activity coefficient. The activity coefficient f is the factor by which the molecular concentration must be multiplied if the law of mass action is to be obeyed.

Let the case of a simple reversible reaction, occurring under isothermal and isobaric conditions, be considered:

$$A + B \rightleftharpoons C + D$$

and let [A], [B], [C], and [D] denote the molar concentrations of the species A, B, C, and D respectively at equilibrium. Then the rate of formation of C and D would be proportional to the product of [A] and [B]. The forward velocity of the reaction can, therefore, be expressed as $k_f \cdot [A] \cdot [B]$, where k_f is known as the forward velocity constant and represents the rate of the reaction when both [A] and [B] equal unity. Likewise, the rate of formation of A and B would be expressed as $k_r \cdot [C] \cdot [D]$, where k_r is the reverse velocity constant. At the equilibrium point, the forward velocity of the reaction would equal its reverse velocity:

$$k_f [A] [B] = k_r [C] [D]$$

or

$$\frac{[C] \cdot [D]}{[A] \cdot [B]} = \frac{k_f}{k_r} = K$$

where K is called the equilibrium constant.

It maybe noted that the reaction, $2\,A + B \rightleftharpoons C + 2\,D$ may be written as $A + A + B \rightleftharpoons C + D + D$ and at equilibrium one would have:

$$K = \frac{[C]\,[D]\,[D]}{[A]\,[A]\,[B]} = \frac{[C]\,[D]^2}{[A]^2\,[B]}$$

It was shown by Guldberg and Waage that when solids are present in a system, their active masses may be taken as constant and included in the equilibrium constant, K. For example, in the reaction:

$$K_2CO_3\ (aq) + BaSO_4 \rightleftharpoons K_2SO_4\ (aq) + BaCO_3$$

$BaSO_4$ and $BaCO_3$ are pure solids and their active masses may be taken as constant and included in the equilibrium constant, K, which now simplifies to:

$$K = \frac{[K_2SO_4]}{[K_2SO_3]}$$

It thus follows that in the general equation, $A + B \rightleftharpoons C + D$, if, for example, B and D are pure solids, the equilibrium constant can be expressed as:

$$K = \frac{[C]}{[A]}$$

Proceeding further with the general solution in which no reactant or product is a pure solid, for the following reversible reaction, occurring at constant temperature and pressure,

$$\nu_A\,A + \nu_B\,B = \nu_C\,C + \nu_D\,D$$

where the νs are the stoichiometric coefficients of the reactants A, B and the products C, D, respectively, the rate of the forward reaction, r_f is given by

$$r_f = k_f\,[A]^{\nu_A}\,[B]^{\nu_B}$$

and the rate of the reverse reaction, r_r can be expressed as

$$r_r = k_r\,[\mathrm{C}]^{\nu_C}\,[\mathrm{D}]^{\nu_D}$$

where k_f and k_r are the rate coefficients in the forward and the reverse directions respectively and [A], [B], [C], and [D] are the pertinent active masses. Since equilibrium has been described as the condition of dynamic balance between the forward and the reverse reactions, at equilibrium r_f must equal r_r, so that

$$k_f\,[\mathrm{A}]^{\nu_A}\,[\mathrm{B}]^{\nu_B} = r_f = k_r\,[\mathrm{C}]^{\nu_C}\,[\mathrm{D}]^{\nu_D} = r_r$$

It, therefore, follows, that the equilibrium constant for the reaction considered is given by

$$K = \frac{k_f}{k_r} = \left(\frac{[\mathrm{C}]^{\nu_C}\,[\mathrm{D}]^{\nu_D}}{[\mathrm{A}]^{\nu_A}\,[\mathrm{B}]^{\nu_B}}\right)_{\mathrm{equil}}$$

It has been seen that at equilibrium, the relations, $r_f = r_r$ and $K = k_f/k_r$ hold. The ratio r_f/r_r is of interest for any composition even if it is not the equilibrium composition. By dividing the expression for r_f by that for r_r one obtains

$$\frac{r_f}{r_r} = \frac{k_f}{k_r} = \left(\frac{[\mathrm{A}]^{\nu_A}\,[\mathrm{B}]^{\nu_B}}{[\mathrm{C}]^{\nu_C}\,[\mathrm{D}]^{\nu_D}}\right)$$

The ratio

$$\frac{[\mathrm{C}]^{\nu_C}\,[\mathrm{D}]^{\nu_D}}{[\mathrm{A}]^{\nu_A}\,[\mathrm{B}]^{\nu_B}}$$

at any composition of the reaction system is termed the reaction quotient, Q. It could be seen that Q has a form similar to that of K, the equilibrium constant, but does not necessarily correspond to the condition of equilibrium. It follows that

$$\frac{r_f}{r_r} = \frac{k_f}{k_r} \cdot \frac{1}{Q} = \frac{K}{Q}$$

When $K = Q$, $r_f = r_r$ and there is equilibrium. When $K > Q$, $r_f > r_r$ and the net reaction proceeds from left to right (i.e., in the forward direction). When $K < Q$, $r_f < r_r$ and the net reaction proceeds in the reverse direction. The term K/Q will be encountered again later in this chapter, in the context of the Van't Hoff isotherm.

The value of the equilibrium constant, K, for any reaction is independent of (i) the actual quantities of the substances involved, (ii) the direction from which the equilibrium is attained, (iii) the presence of inert substances, and (iv) the presence of a catalyst. However, it depends upon certain factors as indicated in the following:

- Change of temperature: The rate of a reaction is generally enhanced on increasing the temperature; the extent of enhancement depends on the activation energy of the reaction under consideration. Since the activation energies may be different for the forward and the backward reactions, the value of K changes with changing temperature.
- The method of representing the equilibrium state: The value of the equilibrium constant changes if the reversible reaction is considered to proceed in the reverse direction. For example, the reaction $A + B \rightleftharpoons C + D$ can also be written as $C + D \rightleftharpoons A + B$ so that $[A] \cdot [B]/[C] \cdot [D] = k_r/k_f = K'$. In this case the value of the equilibrium constant for the reverse reaction is given by $K' = 1/K$. To avoid such confusion while applying the law of mass action, the concentrations of the products are always placed in the numerator and those of the reactants in the denominator.
- The choice of stoichiometric equations: If a reversible reaction can be represented in terms of two different stoichiometric equations, the values of K obtained in the two cases will be different. For example, the formation of carbon monoxide can be represented as

  (a) $2\,C + O_2 \rightleftharpoons 2\,CO$ or (b) $C + 0.5\,O_2 \rightleftharpoons CO$

In the case of (a)

$$K_1 = \frac{[CO]^2}{[C]^2[O_2]}$$

and in the case of (b)

$$K_2 = \frac{[CO]}{[C]\,[O_2]^{0.5}}$$

so that, $K_1 = K_2^2$.

It will be of interest to illustrate some applications of the law of mass action to homogeneous gaseous equilibria. Two types of reaction would be considered: (i) those in which no change in the total number of molecules occurs consequent to the reaction; and (ii) those involving changes in the total number of molecules. A reaction of the first type can be generally presented as:

$$2\,AB\,(g) \rightleftharpoons A_2\,(g) + B_2\,(g)$$

When the species are reacted, let it be assumed that starting with m_1 gram molecules of A_2 and m_2 gram molecules of B_2, the amount of A_2 left in the reactor at equilibrium is $(m_1 - x)$ gram molecules. Since 2 molecules of AB are formed with 1 molecule of A_2 and 1 molecule of B_2, x molecules of A_2 must have reacted with x molecules of B_2 to give $2\,x$ molecules of AB. The amount of B_2 at equilibrium will then be $(m_2 - x)$ gram molecules and that of AB will be $2\,x$ gram molecules. If V is the total volume at equilibrium, the following relationships would hold:

$$[A_2] = \frac{m_1 - x}{V}; \quad [B_2] = \frac{m_2 - x}{V}; \quad [AB] = \frac{2\,x}{V}$$

Applying the law of mass action to this reaction, one has

$$K = \frac{[A_2]\,[B_2]}{[AB]^2}$$

Substituting for $[A_2]$, $[B_2]$ and [AB], the final expression for K is obtained as

$$K = \frac{(m_1 - x)\,(m_2 - x)}{4\,x^2}$$

Alternatively, by making use of the partial pressures of the species involved instead of their concentrations, the expression for the equilibrium constant may be obtained as

$$K_p = \frac{p_{A_2} \cdot p_{B_2}}{p_{AB}^2}$$

The expression for K involving the concentrations of the species involved is found to be independent of volume. This implies that any change of pressure is not going to change the final state of equilibrium. The same result can be obtained by taking into consideration the alternative expression involving the partial pressures. If the pressure on the system is increased to n times its original value then all the partial pressures will be increased in the same proportion. This obviously implies that the equilibrium is independent of the pressure. The effect of some other factors on this reaction may now be considered. One such factor can be the addition of substances. For example, on addition of more A_2, the partial pressure of A_2 in the reactor would increase momentarily from p_{A_2} to some value, p'_{A_2}. It has already been seen that

$$K_p = \frac{p_{A_2} \cdot p_{B_2}}{p_{AB}^2}$$

and on change of the partial as a result of the addition one would have

$$K'_p = \frac{p'_{A_2} \cdot p_{B_2}}{p_{AB}^2}$$

In order that the value of the equilibrium constant does not change, K'_p should equal K_p; for this to happen p_{B_2} must decrease and/or p_{AB} must increase, i.e., more of B_2 and A_2 will react to yield AB. A similar consequence would follow on the addition of the component B_2 at equilibrium. Another factor can be the addition of an inert gas. This can be done at constant volume. In this case, since there is no change in the total volume, the concentrations of A_2, B_2 and AB will have the same individual values as before the addition of the inert gas and as such there will be no change in the reaction or in the value of the equilibrium constant. An alternative way of adding the inert gas is to do so at constant pressure. In this case, the addition will cause an increase in the number of moles in the gas mixture and this will merely lead to an increase in the total volume at constant temperature, without altering the initial quantities of A_2 or B_2. Since the mass law equation for this type of reaction mixture does not contain the volume factor, there would be no change in the equilibrium constant. Thus for the type of equilibrium considered, the addition of an inert gas has no effect on the sate of equilibrium whether it is implemented at constant volume or at constant pressure.

A reaction of the second type can generally be represented as

$$AB\ (g) \rightleftharpoons A\ (g) + B\ (g)$$

Let m moles of the gaseous substance AB be heated in a closed reactor of volume V. A state of equilibrium is reached by the time x moles of AB are dissociated into the constituents. Since 1 mole of AB dissociates into 1 mole of A and 1 mole of B, x moles of AB will yield x moles of A and x moles of B. Thus at equilibrium,

$$[AB] = \frac{m - x}{V}; \quad [A] = \frac{x}{V}; \quad [B] = \frac{x}{V}$$

Application of the law of mass action gives

$$\frac{[A]\,[B]}{[AB]} = \frac{\frac{x}{V} \cdot \frac{x}{V}}{\frac{m - x}{V}} = \frac{x^2}{V\,(m - x)} = K$$

This expression for the equilibrium constant is found to contain the term V in the denominator. Since K must remain constant, an increase in V would cause x also to increase. Stated in an another form, the dissociation of AB is favoured by a reduction in the pressure. A pressure increase would bring down V, and to maintain the constant value of K, x must decrease. Thus, a pressure increase would tend to inhibit the dissociation of AB. As in the previous case, it will be of interest in this case also to examine the effects of some other factors on the equilibrium. It is left to the readers as an exercise to establish for this case the following results: (i) the effect of the addition of either A or B is to suppress the degree of dissociation of AB; (ii) the addition of an inert gas at constant volume does not alter the degree of dissociation of AB; and (iii) the addition of an inert gas at constant pressure increases the degree of dissociation of AB.

Certain characteristics of chemical equilibria may be explicitly stated:

- *Permanency:* at a given temperature, when the system has attained a state of equilibrium, it does not change further with time. In other words, the composition of the equilibrium mixture remains unchanged forever.
- *Approachability from both sides:* at a given temperature a reaction typically representable by $A + B \rightleftharpoons C + D$ attains exactly the same state of equilibrium irrespective of whether it is started with the reactants, A and B or the products, C and D.
- *Incompleteness of the reaction:* this is the chief criterion of chemical equilibria. A reversible reaction is never complete in any direction provided none of the products is allowed to escape from the system. Stated differently, in the equilibrium condition, the reactants and the products are all present simultaneously in the reaction vessel. If any of the substances were to vanish, its concentration would become zero and the value of the equilib-

rium constant, K, would than be either zero or infinity. In such a situation, K loses its significance.

Consideration thus far has been on only balanced reactions which occur in one phase, that is, homogeneous reactions. There are, of course, a great many reactions which occur between substances in different phases, and these are known as heterogeneous reactions. Numerous reversible, heterogeneous reactions are known, and it is pertinent now to bestow consideration on how far the law of mass action can be applied to such cases. The familiar reaction of the decomposition of calcium carbonate thermally – a well-known example of a reversible reaction represented by the equation

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

is considered as an example. Assuming that this reaction occurs in the gaseous phase it is clearly possible to apply the law of mass action law to the equilibrium, and this should have the result:

$$K = \frac{[CaO]\,[CO_2]}{[CaCO_3]}$$

where [CaO], $[CO_2]$ and $[CaCO_3]$ are the concentrations of calcium oxide, carbon dioxide, and calcium carbonate respectively. Some solids possess a measurable vapour pressure and, as in the case of liquids, the vapour pressure is fixed at a constant temperature. Therefore, it is assumed that calcium oxide and carbonate, which are solids under the conditions of the experiment, have a real, though very small, vapour pressure. The partial pressure of a given gas in a mixture of gases is proportional to its volume. It is after Avogadro's hypothesis that it can be said that the volume of a gas in a mixture is proportional to its molecular concentration. It is, therefore, possible to express the concentrations of substances in the vapour phase in terms of their partial pressures, since these are proportional to the concentrations. The expression for the equilibrium constant that assumes:

$$K = \frac{p_{CaO} \cdot p_{CO_2}}{p_{CaCO_3}}$$

where the p's are the partial pressures of the species involved. The vapour pressures of the solids will be constant, at a given temperature, as long as these solids are present; hence in the present case p_{CaO} and p_{CaCO_3} are constants, so that

$$K = p_{CO_2}$$

The system, therefore, is at equilibrium at a given temperature when the partial pressure of carbon dioxide present has the required fixed value. This result is confirmed by experiment which shows that there is a certain fixed dissociation pressure of carbon dioxide for each temperature. The same conclusion can be deduced from the application of phase rule. In this case, there are two components occurring in three phases; hence $F = 2 - 3 + 2 = 1$, or the system has one degree of freedom. It may thus legitimately be concluded that the assumption made in applying the law of mass action to a heterogeneous system is justified, and hence that in such systems the active mass of a solid is constant.

Another common illustration to which the same considerations apply is that of reaction of steam on red hot iron. This reaction is represented by

$$4\,H_2O + 3\,FeO \rightleftharpoons Fe_3O_4 + 4\,H_2$$

Assuming that the active masses of the solids are constant, one has, using the same notation as before:

$$K = \frac{(p_{H_2})^4}{(p_{H_2O})^4} \text{ i.e., } \frac{p_{H_2}}{p_{H_2O}} = K'$$

Again, this result is borne out by experiment, so that the assumptions on which it is founded appear to be well justified.

3.7.2
Van't Hoff Isotherm

The Van't Hoff isotherm is a very useful expression which correlates the free energy change in a reaction occurring at a given temperature to the corresponding equilibrium constant. This expression is used to calculate the equilibrium constant when the free energy change is known, or to obtain the free energy change from the equilibrium constant. It also leads to the definition of the standard free energy change. For the homogeneous reaction, $A + B \rightleftharpoons C + D$, the Van't Hoff isotherm is expressed by:

$$\Delta G = -R\,T \ln K + R\,T \ln Q$$

where ΔG is the free energy change for the reaction with the reactants and the products in arbitrary states; K is the equilibrium constant and Q is the arbitrary reaction quotient defined as

$$Q = \frac{[C]\,[D]}{[A]\,[B]} = \frac{a_C \cdot a_D}{a_A \cdot a_B}$$

Here, the a's refer to the activities in the chosen arbitrary state. The concept of activity is presented separately in a later section. For the present, the activity of a species in a system may just be considered to be a function of its concentration in the system, and when the species is in a pure form (or in its standard state), its activity is taken to be unity. The activities a_C, a_D, a_A, a_B given above correspond to the actual conditions of the reaction, and these may or may not correspond to the state of equilibrium. Two special situations can be considered. In the first, the arbitrary states are taken to correspond to those for the system at equilibrium. Q would then become identical to the equilibrium constant K and, according to the Van't Hoff isotherm, ΔG would then be zero. In the second situation, all the reactants and the products are considered to be present as pure species or in their standard states, and a_A, a_B, a_C, and a_D are all equal to 1. Then $Q = 1$ and the free energy change is given by

$$\Delta G = -R\,T \ln K = R\,T \ln 1$$

Since ln 1 = 0, the equation simplifies to

$$\Delta G = -R\,T \ln K = \Delta G^0$$

where ΔG^0 denotes the standard free energy for the reaction taking place at a constant temperature T. The Van't Hoff isotherm can then be expressed as

$$\Delta G = \Delta G^0 + R\,T \ln \frac{a_\mathrm{C} \cdot a_\mathrm{D}}{a_\mathrm{A} \cdot a_\mathrm{B}}$$

The importance of the Van't Hoff isotherm lies in the fact that it gives the direction of a chemical reaction. If under a given set of conditions ΔG is positive, then the reaction cannot take place under these conditions. It may, however, occur if the conditions (activities) are suitably altered to make ΔG negative.

It can be seen from the Van't Hoff isotherm that the sign of ΔG depends on the relative values of K and Q. The latter must be smaller than the former for the reaction to be spontaneous. This will be so because ΔG would then be negative. If the conditions are such that $Q > K$, the reaction will not be possible. There are, however, two ways by which this situation can be altered. First, the activities of the products may be decreased and/or those of the reactants increased, in order that the value of Q may be made smaller than that of K. Second, the temperature may be changed in such a manner as to increase K sufficiently so that the condition $Q < K$ is satisfied and ΔG becomes negative. When this happens, the reaction will occur.

A significance analogous to what has been described can be given to the standard free energy, ΔG^0, of a reaction. If ΔG^0 is negative, a given reaction, with all the reactants and products in their respective chosen standard states, can occur spontaneously. If ΔG^0 is positive, the reaction cannot take place under the given conditions.

The result of deviation from unit activity is illustrated by the reduction of magnesia (MgO) with silicon. According to data provided, ΔG^0 for

$$2\,\mathrm{MgO\,(s)} + \mathrm{Si\,(s)} = 2\,\mathrm{Mg\,(G)} + \mathrm{SiO_2\,(s)}$$

at 1200 °C is about +65 kcal. This implies that there is a very little chance of using silicon as a reducing agent to produce magnesium from magnesia. However, the actual free energy change (ΔG) accompanying this reaction is provided by

$$\Delta G = \Delta G^0 + R\,T \ln \frac{P^2_{\mathrm{Mg\,(G)}} \cdot a_{\mathrm{SiO_2\,(s)}}}{a^2_{\mathrm{MgO\,(s)}} \cdot a_{\mathrm{Si\,(s)}}}$$

The relationship above points out the fact that if $P_{\mathrm{Mg\,(G)}}$ and $a_{\mathrm{SiO_2\,(s)}}$ can be brought down sufficiently, ΔG can be made negative even though ΔG^0 is positive. The Pidgeon process for the commercial production of magnesium lowers P_Mg by operating the process at a pressure of about 10^{-4} atm and by having CaO present in order to reduce the activity of the silica in a slag as the orthosilicate $2\,\mathrm{CaO} \cdot \mathrm{SiO_2}$. A basic slag would give $a_{\mathrm{SiO_2}}$ as less than 0.001. The high affinity of CaO for $\mathrm{SiO_2}$ brings down the possibility of loss of MgO as magnesium silicate. A convenient method of introducing CaO into the system is to use calcined dolomite, which is a mixed carbonate of magnesium and calcium, as the source of magnesium.

$$CaCO_3 \cdot MgCO_3 \text{ (dolomite)} \xrightarrow{\text{Heating}} CaO \cdot MgO$$

$$2\,CaO \cdot MgO + Si = 2\,Mg\,(G) + 2\,CaO \cdot SiO_2$$

In the process, ferrosilicon is used rather than pure silicon. Apart from being a cheaper source of silicon, the iron in ferrosilicon is dissolved as FeO in the slag, thus lowering the liquidus temperature of the slag. The magnesium is evolved as a gas, which is condensed in massive form without reoxidation. This example clearly shows that if the activities of reactants or products differ significantly from unity, the Van't Hoff isotherm throws much better insights into the thermodynamic possibilities of the reaction than ΔG^0 and the Ellingham diagram. This indeed is a dramatic example of how, by manipulation of the activities of the reactants, seemingly unfavourably disposed reactions can be steered or led towards favourable disposition.

3.7.3

Van't Hoff Isochore

The Van't Hoff isotherm establishes the relationship between the standard free energy change and the equilibrium constant. It is of interest to know how the equilibrium constant of a reaction varies with temperature. The Van't Hoff isochore allows one to calculate the effect of temperature on the equilibrium constant. It can be readily obtained by combining the Gibbs–Helmholtz equation with the Van't Hoff isotherm. The relationship that is obtained is

$$\frac{d\ln K}{dT} = \frac{\Delta H^0}{R\,T^2}$$

The rate of change of the equilibrium constant with temperature is seen to depend on the standard heat of the reaction.

Integration can be carried out by first rearranging the relationship shown above to

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta H^0}{R} \quad \text{or} \quad \frac{d(\log K)}{d(1/T)} = -\frac{\Delta H^0}{2.303\,R}$$

The integrated form of the above equations, on the assumption that ΔH^0 is temperature-dependent, is

$$\log K = -\frac{\Delta H^0}{2.303\,R}\,\frac{1}{T} + \text{Constant}$$

Both the integrated and differential forms show that a plot of log K against $1/T$ should yield a straight line with a slope equal to $-\Delta H^0/2.303\,R$. Thus, a measured value of ΔH^0 can be employed to calculate the equilibrium constant at temperatures other than that for which it is given. Conversely, it is possible to use measurements of the equilibrium constant at a number of temperatures to evaluate the standard enthalpy change for the reaction.

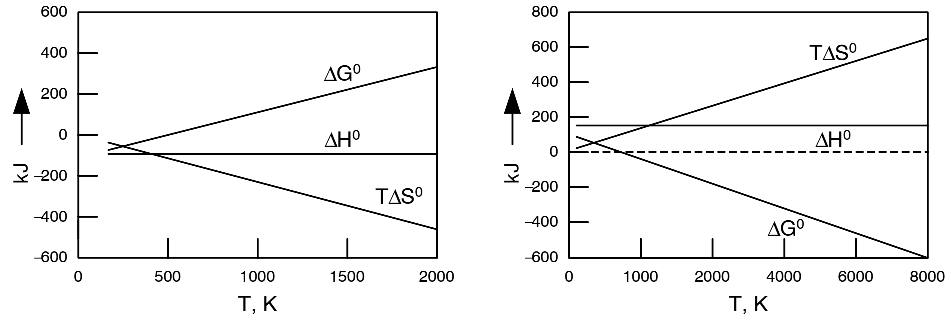
When much larger temperature ranges are considered, the basis of the dependence of the equilibrium constant on temperature can more clearly be seen by returning to the relationships

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 \quad \text{and} \quad G^0 = -R\,T\ln K$$

or

$$R\,T \ln K = -\Delta H^0 + T\,\Delta S^0$$

The above equation is valid at any temperature when values of ΔH^0 and $T\,\Delta S^0$ appropriate to that temperature are used. Generally, the $T\,\Delta S^0$ term, as might be expected from the presence of the explicit T factor, is the more temperature-dependent. At high temperatures this term dominates the ΔH^0 term to provide an RTlnK value that is increasingly positive or negative, depending on whether ΔS^0 for the reaction is positive or negative. Thus at high temperatures the equilibrium constant generally becomes increasingly greater if ΔS^0 is positive or smaller if ΔS^0 is negative. Examples of these behaviours are shown by the reactions used as illustrations in Figures 3.3 (A) and (B). A graphical representation of the variation of ln K with $1/T$ for exothermic and endothermic reactions is shown in Figure 3.3 (C).

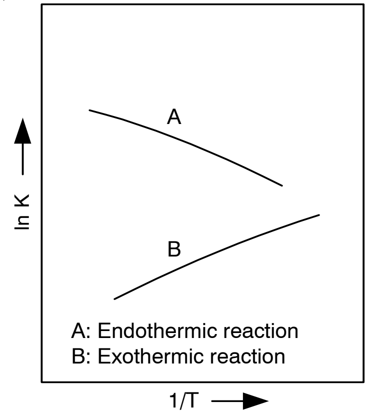


Reaction: N_2 (g) + 3 H_2 (g) = 2 NH_3 (g)

(A)

Reaction: H_2O (g) + C (s) = CO (g) + H_2 (g)

(B)



(C)

Figure 3.3 The temperature dependence of ΔG^0, ΔH^0, and $T\,\Delta S^0$ over large temperature ranges; the behaviour (A) for negative ΔS^0, (B) positive ΔS^0 and (C) variation of ln K with $1/T$ for exothermic and endothermic reactions.

3.7.4
Le Chatelier's Principle

Chemical equilibria being of a dynamic type, equilibrium states are altered by changes in the variables controlling them. The effect of such changes can be interpreted qualitatively on the basis of a principle which was enunciated independently by Le Chatelier in 1885 and by Braun one year later. It states that when a system in a state of dynamic equilibrium is subjected to a stress imposed by variation in anyone of the variables controlling the equilibrium state, the system will tend to adjust itself in such a way as to minimize the effect of the stress. The variables of interest in this connection are temperature of the system, pressure on the system, and concentrations for the reactants and products taken individually.

In order to illustrate this principle, let the effect of temperature on the equilibrium constant of an exothermic reaction, involving the oxidation of a metal to its oxides, be considered. Upon increasing the temperature of this reaction some of the metal oxides will dissociate into the metal and oxygen and thereby reduce the amount of heat released. This qualitative conclusion based on Le Chatelier's principle can be substantiated quantitatively from the Van't Hoff isochore.

The equation

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H^0}{R\,T^2}$$

in essence indicates that the effect of temperature on K is determined by the sign and the magnitude of ΔH^0 for the reaction. If ΔH^0 is positive, i.e., if the reaction is endothermic, then K increases with increasing temperature. If, on the other hand, ΔH^0 is negative, i.e., if the reaction is exothermic, then K decreases with increasing temperature. Le Chatelier's principle described above essentially gives the direction of the variation of K with temperature.

It may be added here that Le Chatelier's principle is quite general in nature, and that its applicability is not restricted only to chemical equilibria. It can also be applied to physical equilibria, as for example, to explain qualitatively the effects of temperature and pressure on solubility or the effect of pressure on the melting of a solid.

The content provided to the present topic on chemical equilibrium may be concluded with the following summarized presentation:

(1) The equilibrium constant, K, is affected by the temperature of the system but not by the pressure of the system, the presence or otherwise of inert substances or the kinetics of the reaction.

(2) Although the equilibrium constant is not affected by pressure or by inerts, these variables can influence the equilibrium concentration of the reactants and the products and the equilibrium conversion of the reactants.

(3) A very large value of K ($K >> 1$) signifies that almost complete conversion is possible and that the reaction can be considered to be irreversible. Very small values of K ($K << 1$) indicate that the reaction would not occur to any appreciable extent.

(4) As the temperature increases, the equilibrium conversion increases for endothermic reactions and decreases for exothermic reactions.

(5) In gas reactions, as the pressure increases the conversion increases when the number of moles is reduced with the progress of the reaction; the conversion decreases when the number of moles increases with the reaction.
(6) For all reactions a reduction in the amount of inerts present acts in the same way as an increase in pressure acts in the case of gas reactions.

3.8
Free Energy–Temperature Diagrams

3.8.1
Variation of Free Energy with Temperature

In all metallurgical processing, heterogeneous reactions and the approach to equilibrium between two or more phases are of great importance. Much of the information on equilibrium is contained in the equilibrium constant which, as mentioned earlier, is related to the standard free energy change by the equation

$$\Delta G^0 = -R\,T \ln K$$

and to the corresponding entropy and enthalpy changes by the relation

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0$$

The change, ΔG^0, in the standard free energy with temperature is due to the changes with temperature of ΔH^0 and ΔS^0, and, of course, to the change in the temperature itself. Both ΔH^0 and ΔS^0 change with temperature if the total heat capacity of the reactants is not the same as that of the products. In view of the expressions, given earlier, regarding the variation of ΔH^0 and ΔS^0 with temperature, the above equation can be written as

$$\Delta G^0 = \Delta H^0_{298} + \int_{298}^{T} \Delta C_p \, dT - T\Delta S^0_{298} - \int_{298}^{T} \frac{\Delta C_p}{T} \, dT$$

In this equation the subscript 298 refers to the values of the properties at 298 K and $\Delta C_p = \Sigma\, S_{P_{\text{products}}} - \Sigma\, C_{P_{\text{reactants}}}$. The occurrence of phase changes, if any, between 298 K and T would lead to the introduction of additional terms, accounting for the appropriate enthalpy and entropy changes. The term ΔC_p is usually small but seldom zero. Plots of ΔG^0 versus T are, therefore, slightly curved. The term ΔC_p can usually be expressed as a function of temperature by an empirical equation, and the inclusion of this in the expression for ΔG^0 leads to the following types of relations:

$$\Delta G^0 = \text{Constant} + a\,T \log T + b\,T^2 + C\,T^{-1} + e\,T$$

and

$$\Delta G^0 = A + B\,T \log T + C\,T$$

where a, b, c, e and A, B, C are constants. It may, however, be mentioned that uncertainties in the experimental data available for constructing the above equations are such that the use of a simpler equation of the type

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0$$

does not introduce significantly large errors. $\Delta H^{0\prime}$ and $\Delta S^{0\prime}$ in the above equation are the average values of ΔH^0 and ΔS^0 in the temperature range of 298 K to T, which has been considered. This simpler equation has an added advantage in that it quickly indicates the enthalpy and entropy changes involved.

3.8.2
Ellingham Diagrams

A particular case of the free energy change accompanying a chemical reaction is the standard free energy of formation, which is the free energy change accompanying the formation of one mole of a compound from the constituent elements, all being in their standard states. The free energies of formation of the elements in their standard states are, by convention, taken to be zero. As discussed in the previous section, the free energies of formation change with temperature and, without any serious loss of accuracy, this temperature dependence can be taken to be linear.

In 1944 Ellingham compiled, for the first time, diagrams depicting the temperature dependence of the standard free energies of formation of numerous oxides and sulphides. In the discussion presented here, attention will be confined to the oxide reaction

$$\mathrm{M\ (s) + O_2\ (g) \rightarrow MO_2\ (s)}$$

and the essential features will be brought out in terms of a few illustrative free energy versus temperature lines (Ellingham lines) drawn for this reaction. Figure 3.4 shows one such plot. The plot is a straight line graph because

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0$$

is of the form $y = m\,x + c$ (with $m = -\Delta S^0 = -(S - S)$ where S is the total entropy of the products and S is the total entropy of the reactants, and $c = \Delta H^0$). The intercept of the graph on the y axis is ΔH where $\Delta \mathrm{H}$ is the standard enthalpy at 0 K. At 0 K, $\Delta G = \Delta H$. The slope of the graph is $-\Delta S^0$. Thus when the entropy is increasing (DS is positive), the slope of the graph is negative ($m = -(+D\ S) = -D\ S$). This situation is illustrated by lines 2 and 4 in Figure 3.4. Line 2 corresponds to an endothermic reaction with the entropy increasing. Line 4 corresponds to an exothermic reaction with entropy increasing. When the entropy is decreasing (ΔS is negative) the slope will be positive ($m = -\ (-\Delta S) = +\Delta S$). This situation is illustrated by lines 1 and 3 in Figure 3.4 Line 1 corresponds to an endothermic reaction with entropy decreasing (ΔG is always positive), and line 3 shows an exothermic reaction with entropy decreasing. The quantity plotted is free energy per mole of oxygen rather than per mole of the oxide. This facilitates a simple comparison, when data for more than one element are plotted, of the oxygen affinity of the different elements and enables one to obtain the free energy change corresponding to a reaction of the type $\mathrm{M + NO \rightarrow MO + N}$ by simple subtraction of the standard free energy values for the two compounds. Such a diagram allows one to read directly the value of ΔG^0 at any temperature T_1, and thus has the advantage of combining a great deal of information in a very simple presentation.

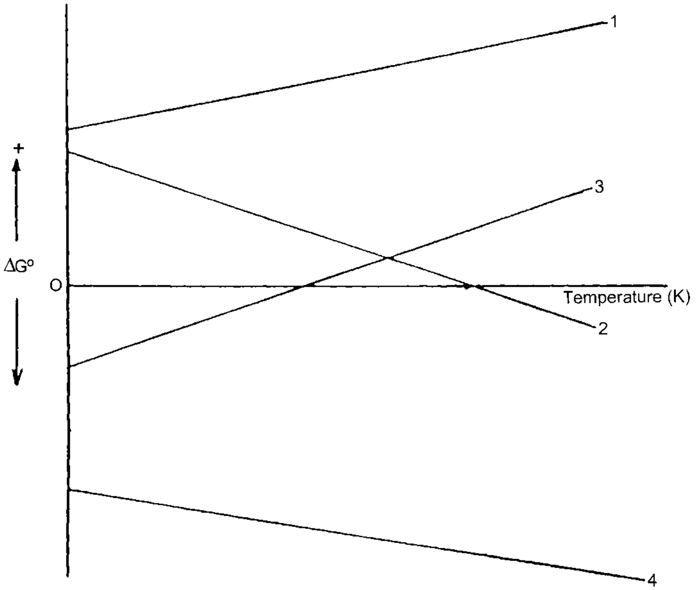


Figure 3.4 Effect of the sign of ΔH^0 and ΔS^0 on Ellingham lines.

In an Ellingham diagram covering a wide temperature range, sharp changes in the slope of the line (ΔG^0 versus T plot) occur at certain temperatures. At these temperatures phase transformations take place in the reactants or in the products. As the slope of the line corresponds to $-\Delta S^0$, where ΔS^0 is the entropy change associated with oxide formation, the magnitude of the change in slope is determined by the value of the entropy change for the transformation. Since the entropy changes markedly at the melting and the boiling points of a metal as well as of its oxides, a change in the slope of the line in the Ellingham diagram may be anticipated at these temperatures. The various possibilities are shown in Figure 3.5 and Table 3.2. When the metal undergoes a phase change with rising temperature, its entropy

Table 3.2 Entropy change scenario.

Process	***Entropy change***	***Remarks***
Metal melting:		
M (s) + 0.5 O_2 (G) → MO (s)	$-S_1$	
M (s) → M (l)	$+S_2$	
M (l) + 0.5 O_2 (G) → MO (s)	$S = -S_1 - S_2$	More negative
Oxide melting:		
M (s) + 0.5 O_2 (G) → MO (s)	$-S_1$	
MO (s) → MO(l)	$+S_2$	
M (s) + 0.5 O_2 (G) → MO (l)	$S = -S_1 - S_2$	Less negative

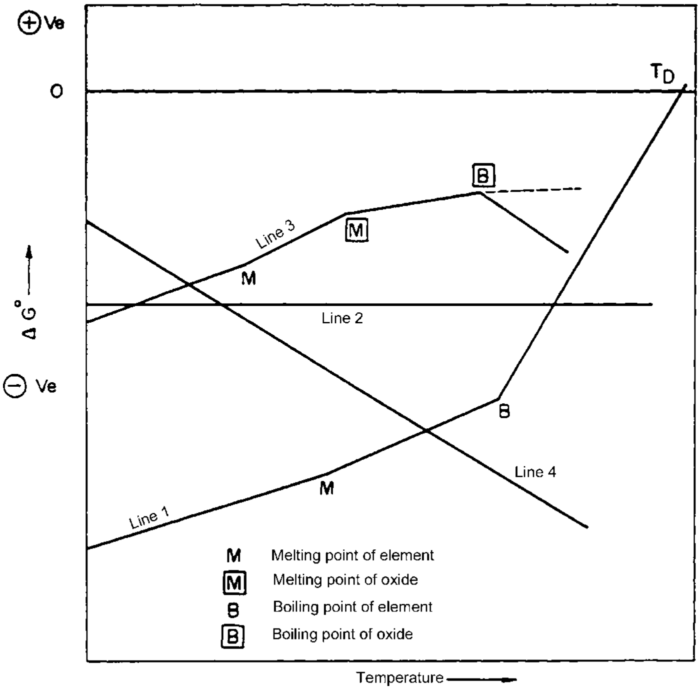


Figure 3.5 Slopes of Ellingham lines.

increases by an amount equal to the enthalpy of the phase change divided by the absolute temperature at which the change occurs. When the phase change occurs in the reactants, augmentation of the entropy of the reactants results in the slope ($m = -\Delta S^0 = S - S_p^0$) becoming a larger positive value. Line 1 represents a typical case of phase transformation in reactant. If, on the other hand, there is a phase transformation in the product the slope becomes a smaller positive value because here the entropy of the product is augmented (S becomes more and m becomes a smaller positive value or even a negative value). In Figure 3.5, line 3 represents a typical case of phase transformation in the product. As regards the phase change, boiling results in a far greater augmentation of entropy than melting. Thus in the figure, sharper changes in slope occur at points marked B and **B** than at points marked M and **M**. Line 2 illustrates the special case where there is almost no entropy change associated with the oxidation reaction and where no phase transformation of the metal or its oxide occurs in the range of temperatures considered. Line 4 in the diagram pertains to another special situation which arises when oxidation causes an increase in entropy. For such reactions, ΔS^0 is positive and the slope of the Ellingham line is negative. The oxide becomes stabler as the temperature is increased. Typical examples of “line 1” behaviour are provided by magnesium, calcium, and zinc. The classic example of “line 2” behaviour is exhibited by carbon dioxide. However, this type of behaviour is not exhibited by any metal. The oxides of metals like lead and cadmium are examples of “line 3” behaviour. “Line 4” behaviour is exhibited by carbon monoxide, and volatile suboxides of several refractory metals.

From the Van't Hoff isotherm it follows that for the oxidation reaction considered, the standard free energy change at temperature T is given by

$$\Delta G^0 = -R\,T \ln \frac{a_{\mathrm{MO_2}}}{a_{\mathrm{M}}\,P_{\mathrm{O_2}}}$$

where $P_{\mathrm{O_2}}$ is the equilibrium pressure of oxygen. Since MO_2 and M are pure solids,

$$a_{\mathrm{MO_2}} = a_{\mathrm{M}} = 1$$

Thus,

$$\Delta G^0 = -R\,T \ln \frac{1}{P_{\mathrm{O_2}}}$$

When the right-hand side of the above equation is zero, i.e., when either $T = 0$ or $P_{\mathrm{O_2}}$ equals one atmosphere, ΔG^0 must be zero. The intersection of the standard free energy change versus temperature line with the temperature axis, when $\Delta G^0 = 0$, gives the temperature at which the oxygen equilibrium pressure, $P_{\mathrm{O_2}}$, is equal to one atmosphere. This temperature is known as the decomposition temperature of the oxide and is denoted as T_{D} on line 1 in Figure 3.5.

When ΔG^0 is negative for the oxidation reaction, the oxide is stabler than the metal and oxygen mixture. When this standard free energy change for the reaction is positive, the oxide is unstable and converts to the metal and oxygen. The temperature range of stability of the metal oxide under standard conditions is, therefore, the range over which ΔG^0 is negative.

Having considered the temperature range of stability of an oxide under standard conditions, i.e., under 1 atmosphere oxygen pressure, it is interesting to analyze the range of oxygen pressures over which the oxide would remain stable at a given temperature. Using the Van't Hoff isotherm for the oxide reaction, the free energy change in the reaction can be expressed in terms of the standard free energy change and the oxygen pressure as

$$\Delta G_{\mathrm{T}} = \Delta G_{\mathrm{T}}^0 - R\,T \ln P_{\mathrm{O_2}}$$

At a given temperature ΔG_{T}^0 is constant, but the value of ΔG_{T} can be changed by varying the $P_{\mathrm{O_2}}$ value. When $P_{\mathrm{O_2}}$ is progressively increased to values exceeding 1 atmosphere, the value of $R\,T \ln P_{\mathrm{O_2}}$ becomes more and more positive and ΔG_{T} becomes more and more negative with respect to ΔG_{T}^0. Thus, an oxide which is unstable under standard conditions can be made stable by increasing the oxygen pressure sufficiently, without changing the temperature. On the other hand, when $P_{\mathrm{O_2}}$ is decreased to values less than 1 atmosphere, the value of $R\,T \ln P_{\mathrm{O_2}}$ becomes more and more negative and ΔG_{T} becomes more and more positive with respect to ΔG_{T}^0. Thus, an oxide which is stable under standard conditions can be made unstable by decreasing the oxygen pressure sufficiently, without changing the temperature.

A standard free energy versus temperature diagram for oxides is often presented with a scale for oxygen pressures. Such a diagram is shown in Figure 3.6. This scale is designed to

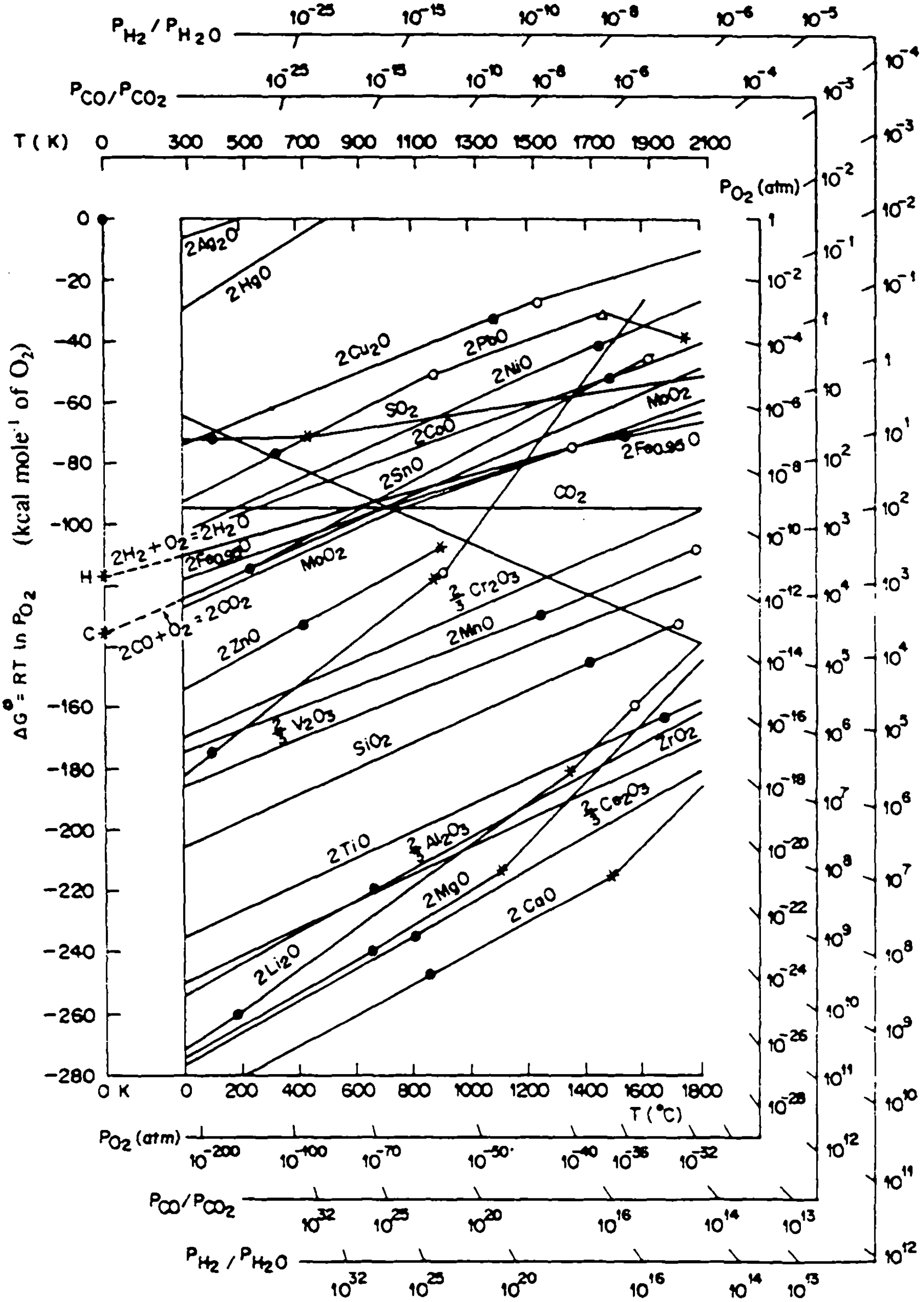


Figure 3.6 Free energy–temperature diagram with scales showing oxygen pressures, CO/CO_2 and H_2/H_2O pressure gas ratios.

enable a direct reading to be obtained of the oxygen pressure in equilibrium with any particular metal–metal oxide system at any chosen temperature. A line joining the point O at the top left hand corner of the diagram to the point on the oxygen scale corresponding to 10^{-8} atmosphere pressure gives the free energy change, ΔG_T, at any given temperature for the change of pressure of 1 mole of oxygen from 1 atm (P_1) to 10^{-8} atm (P_2). In this situation

$$\Delta G_T = R\,T \ln \frac{P_2}{P_1} = R\,T \ln 10^{-8}$$

Considering the intersection of this line with the Ellingham line for the reaction

$$4\ \mathrm{Cu\ (s)} + \mathrm{O_2\ (1\ atm)} = 2\ \mathrm{Cu_2O\ (s)}$$

one finds that the lines intersect at 900 °C. At this temperature, therefore, ΔG_T becomes equal to zero for the process

$$4\ \mathrm{Cu\ (s)} + \mathrm{O_2}\ (10^{-8}\ \mathrm{atm}) = 2\ \mathrm{Cu_2O\ (s)}$$

and pure solid copper, pure solid cuprous oxide and oxygen at 10^{-8} atm pressure remain in equilibrium together. Alternately, by fixing the temperature, say at 1000 °C, the equilibrium oxygen pressure can be read out from the oxygen scale by locating the point on it which is collinear with the point O and the point on the Cu-Cu_2O line at 1000 °C. The value so read is 10^{-6} atm. Thus, by subjecting cuprous oxide to less than 10^{-6} atm pressure at 1000 °C, or to less than 10^{-8} atm pressure at 900 °C, it can be reduced to pure copper. At oxygen pressures higher than these values the metal will be oxidized.

A common method for fixing the oxygen pressure at such low values in a system is to use a gas mixture comprising CO and CO_2 or H_2 and H_2O. A CO–CO_2 mixture results in the reaction

$$2\ \mathrm{CO} + \mathrm{O_2} = 2\ \mathrm{CO_2}$$

and depending on the pressures of CO_2 and CO, the oxygen pressure becomes fixed at any temperature because the equilibrium constant for the reaction is

$$K = \frac{P_{CO_2}^2}{P_{CO}^2\ P_{O_2}}$$

and from Van't Hoff isotherm

$$\Delta G^0 = -R\,T \ln K$$

or

$$K = \exp\left(\frac{-\Delta G^0}{R\,T}\right)$$

so that

$$P_{O_2} = \frac{P^2_{CO_2}}{P^2_{CO}} \exp\left(\Delta G^0 / R\,T\right)$$

where ΔG^0 is the standard free energy change in the above reaction at temperature T. The line drawn for the reaction

$$2\ CO\ (1\ atm) + O_2\ (1\ atm) = 2\ CO_2\ (1\ atm)$$

in Figure 3.6 is validated as long as CO and CO_2 pressures are equal to each other irrespective of their actual values. The lines of CO/CO_2 pressure ratios of 10/1, 100/1, etc., will lie below this ($CO/CO_2 = 1$) line by the extent given by the relationship

$$\Delta G^0_T = 2\,R\,T \ln 10$$

and

$$\Delta \Gamma^0_T = 2\,R\,T \ln 100\ , \text{etc.}$$

All these lines will radiate from the point C in the diagram. At this point the linear extension of the CO–CO_2 line intersects the temperature axis at the absolute zero temperature. At the other end of the diagram, these lines pass through the CO/CO_2 pressure scale at the points marked 1/1, 10/1, $10^2/1$, etc. To read, then, the CO/CO_2 (pressure) ratio in gases in equilibrium with any oxide system at any temperature, the point on the CO/CO_2 scale which is co-linear with the point C and the point on the oxide line at the chosen temperature is read. If the point falls in between the markings 10/1 and $10^2/1$, the actual value can be obtained by logarithmic interpolation between 10/1 and $10^2/1$. For example, a gas mixture with a CO/CO_2 ratio of $10^3/1$ is in equilibrium with Zn(l) and ZnO(s) at about 650 °C. At 900 °C, the equilibrium CO/CO_2 ratio, according to the diagram, is $10^{2.5}/1$. When the CO/CO_2 ratio in the gas mixture is greater than these values, zinc oxide is reduced to the metal. Ratios less than these values will result in the oxidation of zinc metal.

The H_2/H_2O scale in the diagram is similarly useful. The point H is used in this case as the origin in place of the point C of the CO/CO_2 scale or O of the oxygen scale.

It may be pointed out here that in addition to oxides, Ellingham diagrams have been constructed for sulfides, halides, carbides, nitrides, silicides, phosphates, sulfates and carbonates. The basis for constructing these diagrams is essentially the same as that described for oxides, and the purpose of these diagrams is also similar. They readily provide information regarding the temperature range of stability of the compounds of interest under standard conditions. A very useful feature of an Ellingham diagram is that it can provide, to a first approximation, information pertaining to the relative stabilities of compounds of the same type formed by different metals. A knowledge of the relative stabilities of compounds of different metals over a range of temperatures provides guidelines regarding the possibility of reducing the compounds to the corresponding metals. This aspect has been treated in detail in Chapter 4. It may, however, be mentioned in this context that although the ΔG^0 versus T diagrams are somewhat akin to important road maps providing very useful information as described, they do have some limitations. Some of these are listed here.

(1) The diagrams pertain to reactions in which the reactants and the products are in their standard states. In practice, the activities of the participants in the reactions may not be unity and this can lead to results quite different from those corresponding to the "standard states" situation.
(2) The diagrams show the direction in which equilibrium lies, but they do not specify the conditions under which it would be reached.
(3) All possible reactions cannot be included in a diagram, as a consequence of limitations on its scale. It is, therefore, wise to check out all different species present to ensure that a vital reaction is not missed or overlooked in the evaluation of a proposed process.
(4) No information on the kinetics of the reactions can be obtained from the diagrams. Although a reaction may be chemically possible, the rate at which it may occur could be so slow as to make it practically inoperative.
(5) Compounds whose formation lines are represented in the diagrams are assumed to be stoichiometric which often is not true.
(6) The diagram has ignored the possibility of interaction between reactants and products leading to compound formation.

3.9
Solutions

A solution is a mixture of two or more substances. The substances involved are mixed so intimately (on the atomic scale) that it is not possible to distinguish their individual properties. A solution constitutes a single phase, as distinct from heterogeneous systems which contain several phases. A solution, however, differs from a chemical compound in that its composition is not fixed but can vary over a range. It is customary to designate the major component of a solution as the solvent, and the minor ones as the solutes. A solvent as well as a solute can be a gas, a solid or a liquid. Depending upon the state of the solute and/or the solvent, several types of solutions may exist.

It is relevant here to examine some examples of the various types of solutions encountered in metallurgy. Molten phases play a prominent role in extractive metallurgy. In a smelting process, for instance, the valuable components of a resource material enrich one molten phase, whereas the gangue and other impurities are discarded in another, called the slag phase. Many alloy systems, incorporating typically solutions that are solid, figure very importantly in physical metallurgy. There are also gases in metals which provide examples of solutions consisting of solids or liquids as solvents and gases as solutes.

The behaviour of most metallurgically important solutions could be described by certain simple laws. These laws and several other pertinent aspects of solution behaviour are described in this section. The laws of Raoult, Henry and Sievert are presented first. Next, certain parameters such as activity, activity coefficient, chemical potential, and relative partial and integral molar free energies, which are essential for thermodynamic detailing of solution behaviour, are defined. This is followed by a discussion on the Gibbs–Duhem equation and ideal and nonideal solutions. The special case of nonideal solutions, termed as a regular solution, is then presented wherein the concept of excess thermodynamic functions has been used.

3.9.1
Raoult's Law

A fundamental property of a substance is the tendency for its atoms or molecules to spread into the surrounding space. A consequence of this property is the observed vapor pressure of liquids and solids. In order to understand the effects of the formation of a solution on this property, reference may be drawn to a solution consisting of two substances, A and B, with A being the solvent and B the solute. If the vapor pressure, P_A, of the solvent over the solution is considered, it is clear that it must be proportional to the amount of A present in the solution. Thus,

$$P_A \propto \frac{N_A}{N_A + N_B}$$

or

$$P_A = K \frac{N_A}{N_A + N_B}$$

The ratio $N_A/(N_A + N_B)$ represents the mole fraction of the solvent in the solution, where N_B and N_A are the numbers of moles of the solute B and the solvent A respectively present in the solution, and K is a constant. In the case of the pure solvent $N_B = 0$ and the fraction $N_A/(N_B + N_A)$ is equal to 1. This leads to the equality $K = P_A^0$ (where P_A^0 is the vapor pressure of the pure solvent A). The expression for the vapor pressure of the solvent now takes the following form

$$P_A = P_A^0 \frac{N_A}{N_B + N_A}$$

so that,

$$\frac{P_A}{P_A^0} = \frac{N_A}{N_B + N_A}$$

By similar arguments, the expression for the vapour pressure of the solute can be written as

$$\frac{P_B}{P_B^0} = \frac{N_B}{N_B + N_A}$$

All these are mathematical expressions of Raoult's law. According to this law, the vapor pressure of a component of the solution is directly proportional to the mole fraction of that component in the solution. The constant of proportionality is the vapor pressure of the component in its pure state. Usually, Raoult's law is expressed as

$$P_A = P_A^0 X_A$$

or

$$P_B = P_B^0 \, X_B$$

where X_A is the mole fraction of the component A and X_B is the mole fraction of the component B. Plots of these equations, the vapor pressure versus composition relations, for a Raoultian solution, are shown in Figure 3.7 The figure shows plots of the vapour pressures of the components A and B and also of the total vapour pressure of both A and B as a function of composition. According to Dalton's law of partial pressures, the total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituent gases.

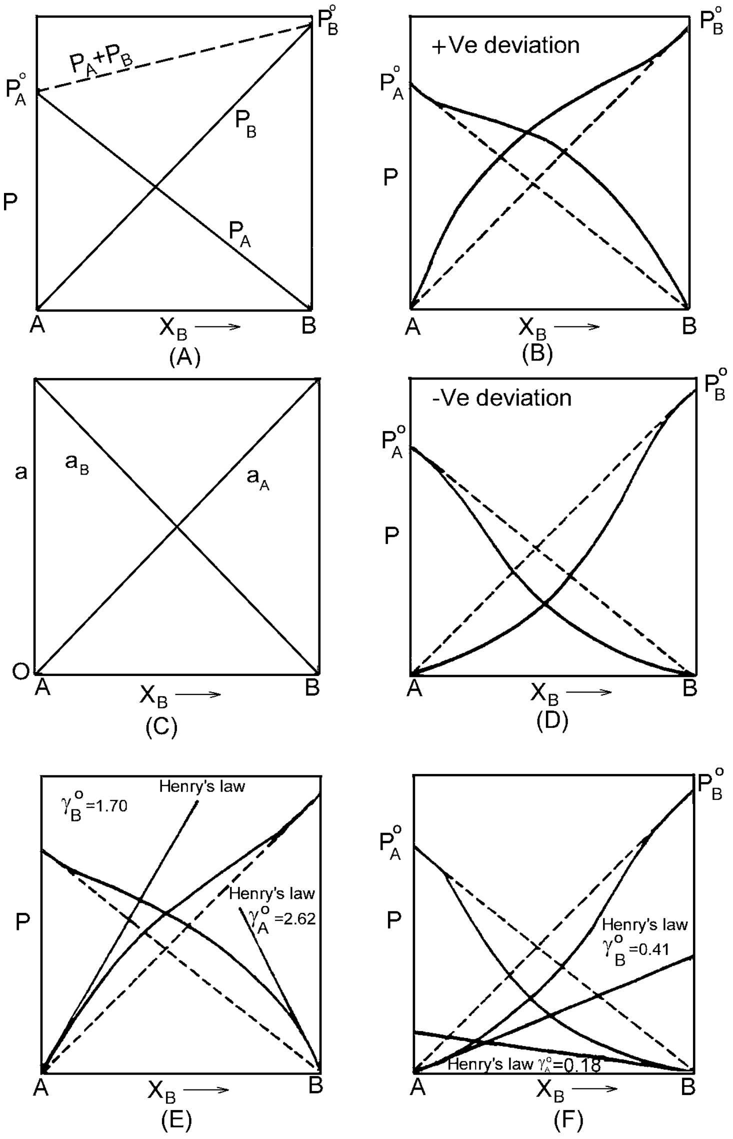


Figure 3.7 Illustration of Raoult's and Henry's laws in binary solution.

The partial pressure is defined as the pressure each gas would exert if it alone were to occupy the entire volume occupied by the mixture at the same temperature. Thus, the total pressure exerted by A and B is equal to the sum of the partial pressure of A, P_A, and partial pressure of B, P_B

$$P_{\text{Total}} = P_A + P_B$$

It can be readily shown that

$$P_A = X_A\,(\nu)\,P_{\text{Total}} \text{ and}$$

$$P_B = X_B\,(\nu\,)\,P_{\text{Total}}$$

where $X_A(\nu)$ and $X_B(\nu)$ are the mole fractions of A and B in the vapor mixture. Dalton's law, which is valid strictly for ideal gases, can be considered applicable to the vapor mixture as in the present case because at low pressures and high temperatures vapours behave like ideal gases.

3.9.2
Henry's Law

Henry's law is more general than Raoult's law. Continuing with the example of the binary solution formed by the components A and B, Henry's law can be stated as follows: the vapor pressure of a component over a solution is proportional to its mole fraction. For the component A, this relation is given by

$$P_A \propto X_A$$

or

$$P_A = K_A\,X_A$$

where K_A is a constant characteristic of the component and the solution at a given temperature. For the other component, B, the law can likewise be written as

$$P_B = K_B\,X_B$$

In general, therefore, for any component, *i*,

$$P_i = K_i\,X_i$$

Henry's law is obeyed by either of the components, and not by both the components at the same time. Besides, Henry's law is obeyed by the solute over only a limited range of concentrations, usually in the dilute solution range. The solute is said to exhibit Henrian behaviour in the concentration range over which it obeys Henry's law.

The Henrian behaviour of a component in a binary solution is illustrated schematically in Figure 3.7 wherein two types of Henrian behaviour have been indicated. In one type the constant K_B is larger than P_B^0, and the Henry's law line lies above the Raoult's law line. In the other type, $K_B < P_B^0$ and the Henry's law line lies below the Raoult's law line. In this context, Raoult's law may be considered as a special case of Henry's law with $K_B = P_B^0$.

3.9.3
Sievert's Law

The dissolution of gases in metals is an important area that warrants special attention in metallurgy. The presence of very minor amounts of such gases as nitrogen, oxygen, and hydrogen has a conspicuous effect on the properties of metals such as niobium, tantalum, zirconium, and titanium. Molten metals produced in the presence of air typically contain significant quantities of dissolved nitrogen, oxygen, and hydrogen (from the water vapor present in air). It is usually necessary to remove these gases prior to solidification, because their solubilities in the solid metal are much smaller than those in the liquid metal. Consequently, on solidifying a metal with a high concentration of dissolved gases, voids are formed in the solid from the evolved gas bubbles; these could degrade the mechanical properties of a casting and additional processing would be required to eliminate such voids. These examples underline the practical importance of studies on the solubility of gases in metals.

A diatomic gas, nitrogen for instance, dissociates into atoms when it dissolves in a metal. This dissociation can be represented as

$$N_2\ (g) = 2\ N\ (\text{dissolved species})$$

The equilibrium constant, K, for this process, is

$$K = \frac{c_N^2}{P_{N_2}}$$

where c_N is the concentration of atomic nitrogen in the metal (equal to a constant times X_N, where X_N is the atom fraction of nitrogen present in the metal) and P_{N_2} is the (partial) pressure of nitrogen gas in equilibrium in the solution. On rearranging the terms, one obtains,

$$X_N = (P_{N_2})^{0.5} \cdot \text{constant}$$

Similar relationships can be written for the dissolution of hydrogen and oxygen. These relationships are expressions of Sievert's law which can be stated thus: the solubility of a diatomic gas in a liquid metal is proportional to the square root of its partial pressure in the gas in equilibrium with the metal. The Sievert's law behaviour of nitrogen in niobium is illustrated in Figure 3.8. The law predicts that the amount of a gas dissolved in a metal can be reduced merely by reducing the partial pressure of that gas, as for example, by evacuation. In practice, however, degassing is not as simple as this. Usually, Sievert's law is obeyed in pure liquid metals only when the solute gas is present in very low concentrations. At higher concentrations deviations from the law occur.

3.9.4
Activity and Activity Coefficient

Expressing the concentrations of the components of a solution in terms of mole fractions or atom fractions is adequate only in some limiting cases of solution behaviour. A more

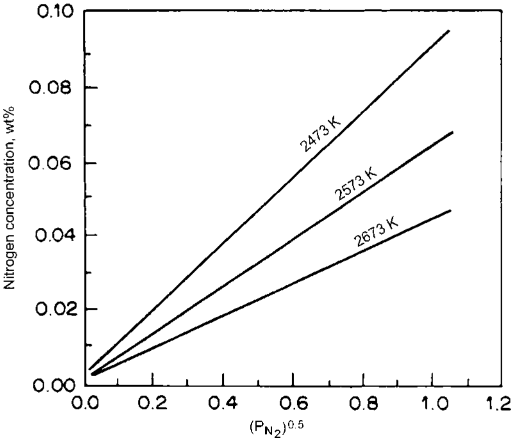


Figure 3.8 Sievert's law behaviour of nitrogen in niobium at high temperatures.

general and also more accurate method of expressing concentrations of components in a solution is by specifying their activities. The activity, a_i, of a component, i, in a solution is defined as the ratio of the partial pressure, P_i, of the component in solution to the partial pressure, P_i^0, of the pure component at the same temperature.

$$a_i = \frac{P_i}{P_i^0}$$

It can be immediately seen from the above relationship that when a component obeys Raoult's law, its activity is equal to its mole fraction

$$a_i = X_i$$

Similarly, when Henry's law is obeyed,

$$a_i = k_i X_i$$

where k_i is a constant for the solute i at a given temperature. It is related to K_i the proportionality constant given earlier, by the relationship

$$k_i = \frac{K_i}{P_i^0}$$

These relationships are alternative expressions of Raoult's and Henry's laws. Raoultian and Henrian behaviours of a component in a solution, in terms of activity, are shown schematically in Figure 3.7.

The two cases relating the activity of a component to its mole fraction, given above, are specific examples of a more general way of relating activity to mole fraction. The activity and the mole fraction of a component in a solution are related through a parameter known as the activity coefficient.

The activity coefficient, γ_i, of the component, i, in a solution is defined as the ratio of its activity, a_i, to its mole fraction, X_i,

$$\gamma_i = \frac{a_i}{X_i}$$

It can be immediately seen that for components exhibiting Raoultian behaviour, the activity coefficient is equal to unity. The Henry's law constant k_i is nothing but the activity coefficient γ_i. Noting that Henrian behaviour is exhibited when the component i is present in very low concentrations, the constant γ_i is also expressed in this case as γ_i^0 and is known as the activity coefficient at infinite dilution. Henry's law may now be stated as

$$a_i = \gamma_i^0 X_i$$

The meaning and significance of g_i^0 are illustrated in Figure 3.7.

3.9.5
Free Energy of Formation of a Solution

When two pure substances are mixed, they form a solution if the free energy change for the process is negative. The process of formation of a solution between two substances, A and B, can be represented as

$$A + B = AB$$

and

$$\Delta G^M = G_{AB} - G_A - G_B$$

Here, ΔG^M is the free energy change for the above process and is called the free energy of mixing. G_{AB} is the free energy of the solution, while G_A and G_B are the free energies of the pure components A and B respectively. A solution forms if $G_{AB} < (G_A + G_B)$ i.e., if ΔG^M is negative.

For any solution the three thermodynamic properties of major importance are the enthalpy, the entropy, and the free energy of the solution. Usually these properties are given for the formation of one mole of the solution at constant temperature and pressure, and they are referred to as integral thermodynamic properties. The free energy of mixing (ΔG^M) is related to the corresponding enthalpies (ΔH^M) and entropies (ΔS^M) by the equation

$$\Delta G^M = \Delta H^M - T\,\Delta S^M$$

If G_A is the value of the free energy per mole of A as it occurs in the solution and G_B is the value of the free energy per mole of B as it occurs in the solution, then the value of the free energy of the solution (here a binary solution consisting of A and B is considered) is the sum $n_A\, G_A + n_B\, G_B$ where n_A and n_B are the number of moles of A and B respectively present in the solution. If one considers one mole of the solution, one should use the mole fractions of A and B instead of n_A and n_B. Representing the mole fractions of A and B by X_A and X_B respectively, the free energy of one mole of the solution $G_{A\text{-}B}$ is given by

$$G_{A\text{-}B} = X_A\, G_A + X_B\, G_B$$

The terms G_A and G_B are formally defined as the partial molar free energies of A and B respectively in the solution.

It will be relevant at this point to elaborate on the partial molar free energy of the component A in the binary solution A-B. The partial molar free energy of the component A in the solution is defined as the increase in the free energy of the solution A-B when one mole of A is added to a large quantity of the solution at a given temperature and pressure. A large quantity of the solution is mentioned in this definition to ensure that the addition of one mole of A does not cause a measurable change in the composition of the solution. Mathematically, the partial molar free energy, G_A, of the component A, is expressed as

$$\bar{G}_A = \left(\frac{\partial G}{\partial n_A} \right)_{T,P,n_B}$$

where G is the free energy of the solution, n_A is the number of moles of A, n_B of B and the subscripts shown outside the bracket imply that T, P and n_B are maintained constant as n_A is varied. The partial molar free energy of B, G_B, can be expressed in a similar manner. The partial molar free energy is also known as the chemical potential and written as μ. It is relevant to mention here that the concept of the chemical potential has been the basis of the modern trend to approach and establish the relationship between the free energy and the equilibrium constants in chemical equilibria. The traditional approach, as mentioned earlier, has involved the introduction of the concept of the equilibrium constant, the application of the law of mass action and the use of the Van't Hoff isotherm.

One must recognize that the partial molar free energy is not a measurable quantity because the absolute value of the free energy is not measurable. However, the relative partial molar free energy, ΔG_A^M, defined as follows, is measurable

$$\Delta \bar{G}_A^M = \bar{G}_A - G_A^0$$

where G_A^0 is the molar free energy of A in its reference or standard state. Generally, the reference state selected is the stable form of the pure component at the temperature of the system. The quantity, ΔG_A^M is also known as the partial molar free energy of mixing or as the partial molar free energy of solution of the component A. In a similar way the expression for the relative partial molar free energy, ΔG_B^M is

$$\Delta \bar{G}_B^M = \bar{G}_B - G_B^0$$

Besides the partial molar and the relative partial molar free energies of the components, some other important thermodynamic properties are the partial molar and the relative partial molar enthalpies and entropies. The partial molar enthalpy and entropy of the component A are defined by

$$\bar{H}_A = \left(\frac{\partial H}{\partial n_A} \right)_{T,P,n_B}$$

and

$$\bar{S}_A = \left(\frac{\partial S}{\partial n_A} \right)_{T,P,n_B}$$

The relative partial molar enthalpy, $\Delta H_{\mathrm{A}}^{\mathrm{M}}$, and the relative partial molar entropy, $\Delta S_{\mathrm{A}}^{\mathrm{M}}$, are defined as

$$\Delta\bar{H}_{\mathrm{B}}^{\mathrm{M}} = \bar{H}_{\mathrm{B}} - H_{\mathrm{B}}^{0}$$

and

$$\Delta\bar{S}_{\mathrm{B}}^{\mathrm{M}} = \bar{S}_{\mathrm{B}} - S_{\mathrm{B}}^{0}$$

The relative partial molar free energy of A is written in terms of the integral molar free energy of the solution as

$$\Delta\bar{G}_{\mathrm{A}}^{\mathrm{M}} = \left(\frac{\partial \Delta G^{\mathrm{M}}}{\partial n_{\mathrm{A}}}\right)_{\mathrm{T,P,n_B}}$$

The corresponding expressions for the relative partial molar enthalpy and entropy of the component A are

$$\Delta\bar{H}_{\mathrm{A}}^{\mathrm{M}} = \left(\frac{\partial \Delta H^{\mathrm{M}}}{\partial n_{\mathrm{A}}}\right)_{\mathrm{T,P,n_B}}$$

$$\Delta\bar{S}_{\mathrm{A}}^{\mathrm{M}} = \left(\frac{\partial \Delta S^{\mathrm{M}}}{\partial n_{\mathrm{A}}}\right)_{\mathrm{T,P,n_B}}$$

In the binary solution considered, the free energy of the system before mixing is the sum of the free energies of the pure components:

$$n_{\mathrm{A}}\, G_{\mathrm{A}}^{0} + n_{\mathrm{B}}\, G_{\mathrm{B}}^{0}$$

After mixing (i.e., after the formation of the solution) the free energy of the system is given by

$$n_{\mathrm{A}}\, \bar{G}_{\mathrm{A}} + n_{\mathrm{B}}\, \bar{G}_{\mathrm{B}}$$

The free energy of formation (or free energy of mixing) of the solution is now equal to the free energy after mixing minus the free energy before mixing:

$$n_{\mathrm{A}}\, \bar{G}_{\mathrm{A}} + n_{\mathrm{B}}\, \bar{G}_{\mathrm{B}} - n_{\mathrm{A}}\, G_{\mathrm{A}}^{0} + n_{\mathrm{B}}\, G_{\mathrm{B}}^{0}$$

When the formation of one mole of the solution is considered, the integral molar free energy of mixing, ΔG^{M}, is given by

$$\Delta G^{\mathrm{M}} = X_{\mathrm{A}}\, \bar{G}_{\mathrm{A}} + X_{\mathrm{B}}\, \bar{G}_{\mathrm{B}} - X_{\mathrm{A}}\, G_{\mathrm{A}}^{0} - X_{\mathrm{B}}\, G_{\mathrm{B}}^{0}$$

or

$$\Delta G^{\mathrm{M}} = X_{\mathrm{A}}\, (\bar{G}_{\mathrm{A}} - G_{\mathrm{A}}^{0}) + X_{\mathrm{B}}\, (\bar{G}_{\mathrm{B}} - G_{\mathrm{B}}^{0})$$

or

$$\Delta G^{M} = X_A \, \bar{G}_A^{M} + X_B \, \bar{G}_B^{M}$$

where ΔG_A^{M} and ΔG_B^{M} are the relative partial molar free energies of A and B respectively. The quantity ΔG^{M} is, as noted earlier, the integral molar free energy of mixing or the integral molar free energy of solution.

The relative partial molar free energy of mixing of a component is nothing but the free energy change due to the transfer of one mole of the component from the pure state to the solution. This transfer can be considered in three steps. In the first step, one mole of the pure component A is evaporated at temperature T to vapor at pressure P_A^0. The G for this process is zero if P_A^0 is the equilibrium vapor pressure of pure A at temperature T. In the second step, the pressure of 1 mole of vapor is reduced to a value P_A, without changing the temperature. The free energy change for this step is that due to the isothermal change in pressure, $\Delta G = R\,T \ln(P_A / P_A^0)$. In the third step, one mole of vapor A at pressure P_A is condensed into solution at temperature T. If P_A is the equilibrium pressure of A over the solution at temperature T, the free energy change for this step also is zero. Thus, the relative partial molar free energy of mixing becomes equal to the free energy change due to the change of vapor pressure from P_A^0 to P_A. In other words,

$$\Delta \bar{G}_A^{M} = R\,T \ln \frac{P_A}{P_A^0} = R\,T \ln a_A$$

The equality of a_A and P_A / P_A^0 has been explained earlier. It may be recalled that the activity of the component A in the solution is defined by this equality. For the binary solution A-B, the integral molar free energy of mixing is then

$$\Delta G^{M} = X_A \,(R\,T \ln a_A) + X_B \,(R\,T \ln a_B)$$

or

$$\Delta G^{M} = R\,T\,(X_A \ln a_A + X_B \ln a_B)$$

3.9.6
Gibbs–Duhem Equation

As mentioned earlier, the partial molar free energies of mixing are measurable quantities, and so are the integral molar free energies of mixing. The measurement usually involves the experimental determination of the activity of one of the components. It is not necessary to determine experimentally the activities of both the components because once the activity of one of the components is known over a range of concentrations, including the pure component, the activity of the other component can be calculated by using the well known Gibbs–Duhem equation.

The Gibbs–Duhem equation is one of the most extensively used relations in thermodynamics. It is written in the following equivalent forms for a binary solution at constant temperature and pressure:

$$X_A \, \mathrm{d}\bar{G}_A + X_B \, \mathrm{d}\bar{G}_B = 0$$

$$X_A\,d\bar{G}_A^M + X_B\,d\bar{G}_B^M = 0$$

$$X_A\,d\ln a_A + X_B\,d\ln a_B = 0$$

and

$$X_A d\ln\gamma_A - X_B\,d\ln\gamma_B = 0$$

Amongst the various relations given above, the last is the one which is actually used to calculate activity coefficients. For calculating the activity coefficient of the component, A, when the activity coefficient versus composition relationship for the other component, B, is known, the equation is used in the following form:

$$d\ln\gamma_A = \frac{X_B}{X_A}\,d\ln\gamma_B$$

and

$$\ln\gamma_{A|X_A=X_A} = -\int_{\ln\gamma_B\ \text{at}\ X_A=1}^{\ln\gamma_B\ \text{at}\ X_A=X_A} \frac{X_B}{X_A}\,d\ln\gamma_B$$

The integration is performed graphically as shown in Figure 3.9 by plotting $\ln g_B$ against the mole fraction ratio X_B/X_A.

The relationships presented thus far for partial, integral and relative partial molar free energies are applicable in a similar manner to entropy, enthalpy and also volume.

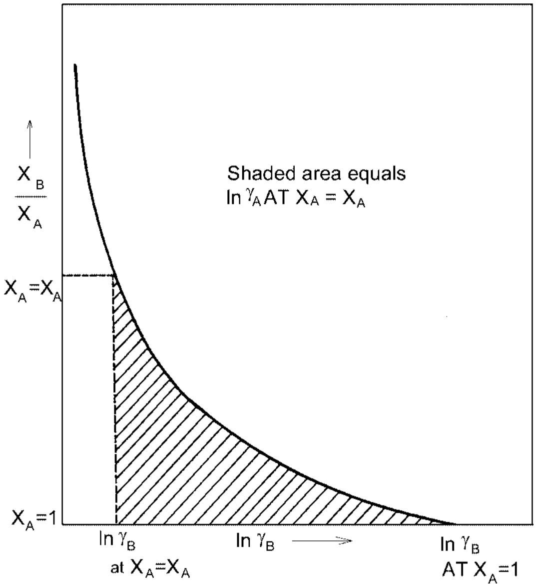


Figure 3.9 Graphical integration of Gibbs–Duhem equation.

3.9.7
Ideal Solution

In an ideal solution the components obey Raoult's law. The activity equals the mole fraction:

$$a_i = X_i$$

The partial and integral molar free energies of mixing are, therefore, given by

$$\Delta\overline{G}_A^{M,id} = R\,T \ln X_A$$

$$\Delta\overline{G}_B^{M,id} = R\,T \ln X_B$$

$$\Delta G^{M,id} = R\,T(X_A \ln X_A + X_B \ln X_B)$$

The equality of activity and mole fraction in an ideal solution has interesting consequences. These consequences, in fact, are the characteristics of an ideal solution, and are presented in the following.

At constant temperature and composition, the variation of free energy with pressure is related to the volume of the system as

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

Expressing this equation in terms of relative partial molar quantities, the following relationships are obtained:

$$\Delta\overline{V}_i^M = \left(\frac{\partial \Delta\overline{G}_i^M}{\partial P}\right)_T = \left[\frac{\partial(R\,t \ln X_i)}{\partial P}\right]_T$$

As the mole fraction is not a function of pressure, $\Delta V_i^M = 0$ and so

$$\Delta V^M = X_A\,\Delta V_A^M + X_B\,\Delta\overline{V}_B^M$$

is also equal to zero. There is thus no volume change associated with the formation of an ideal solution. The enthalpy of formation of an ideal solution is also zero. This follows from the Gibbs–Helmholtz equation

$$\left[\frac{\partial\left(\frac{\Delta\overline{G}_i^M}{T}\right)}{\partial T}\right]_{P,x} = -\frac{\Delta\overline{H}_i^M}{T^2}$$

i.e.,

$$\frac{d(R \ln X_i)}{dT} = -\frac{\Delta\overline{H}_i^M}{T^2} = 0$$

because X_i is independent of temperature. Since ΔH_A^M and ΔH_B^M are both equal to zero, the integral molar enthalpy of formation of an ideal solution, $\Delta H^{M,id}$, is also equal to zero:

$$\Delta H^M = X_A \, \Delta \bar{H}_A^{M,id} + X_B \, \Delta \bar{H}_B^{M,id} = 0$$

The entropy of formation of an ideal solution at a given temperature can be obtained from the following equation

$$\Delta G^{M,id} = \Delta G^{M,id} - T\Delta S^{M,id}$$

since $H^{M,id} = 0$,

$$\Delta S^{M,id} = -\frac{\Delta G^{M,id}}{T}$$

As,

$$\Delta G^{M,id} = R\,T\,(X_A \ln X_A + X_B \ln X_B)$$

$$\Delta S^{M,id} = -R\,(X_A \ln X_A + X_B \ln X_B)$$

But,

$$\Delta S^{M,id} = X_A \, \Delta \bar{S}_A^{M,id} + X_B \, \Delta \bar{H}_B^{M,id}$$

Thus, it follows that,

$$\Delta \bar{S}_A^{M,id} = -R \ln X_A$$

and

$$\Delta \bar{S}_B^{M,id} = -R \ln X_B$$

These results also follow from the relation

$$\left(\frac{\partial \Delta \bar{G}^{M,id}}{\partial T} \right)_P = -\Delta S^{M,id}$$

The variation of the entropy of formation of an ideal solution with composition is shown in Figure 3.10. It is again a characteristic of an ideal solution that the partial $(\Delta S_A^{M,id}, \Delta S_B^{M,id})$ and the integral molar $(\Delta S^{M,id})$ entropies of its formation are independent of temperature.

3.9.8
Nonideal Solutions

An ideal solution is an exception rather than the rule. Real solutions are, in general, nonideal. Any solution in which the activity of a component is not equal to its mole fraction is called non-ideal. The extent of the nonideality of a solution, i.e., the extent of its deviation from

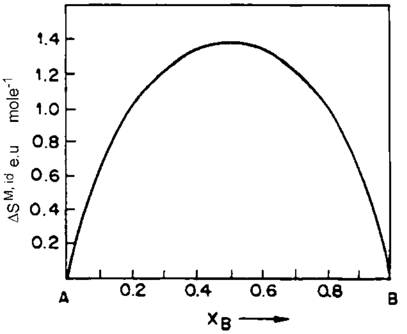


Figure 3.10 The entropy of formation of an ideal solution.

the ideal behaviour, is easily quantified in terms of the value of the activity coefficient. For an ideal solution the value of the activity coefficient, γ, is equal to one. In a nonideal solution, γ can have values greater than or less than unity. When the activity coefficient exceeds unity, the component is said to exhibit a positive deviation from Raoult's law; likewise, when $\gamma < 1$, the component is said to exhibit a negative deviation from Raoult's law. While the relative partial molar entropies and free energies of formation of an ideal solution can be readily calculated from the mole fraction values, in the case of nonideal solutions a knowledge of the activity coefficients is necessary to calculate such functions. This is because for any solution, the relative partial molar free energy is given by

$$\Delta \bar{G}_i^M = RT\ln a_i$$

and since,

$a_i = \gamma_I\, X_i$one has

$$\Delta \bar{G}_i^M = RT\ln\gamma_i + RT\ln X_i$$

It may be noted that for an ideal solution, $\gamma_i = 1$, so that $\ln\gamma_i = 0$ and $\Delta G_i^M = RT\ln X_i$. Generally, the activity coefficient of a component in a real solution varies both with composition and with temperature. The variation with temperature is given by the Gibbs–Helmholtz equation, as shown below. Expanding ΔG_i^M in terms of mole fractions and activity coefficients, i.e., using the relationship

$$\Delta \bar{G}_i^M = RT\ln\gamma_i + RT\ln X_i$$

and applying the Gibbs–Helmholtz equation, one obtains

$$\frac{\partial}{\partial T}(R\ln X_i) + \frac{\partial}{\partial T}(R\ln\gamma_i) = -\frac{\Delta \bar{H}_i^M}{T^2}$$

The first term on the left hand side in the above equation is equal to zero because X_i is independent of temperature. Hence

$$\frac{\partial}{\partial T}(R\ln\gamma_i) = -\frac{\Delta\bar{H}_i^M}{T^2}$$

or

$$\frac{\partial(R\ln\gamma_i)}{\partial\left(\frac{1}{T}\right)} = -\frac{\Delta\bar{H}_i^M}{T^2}$$

and a nonzero heat of formation of the solution (i.e., a nonzero enthalpy of mixing) is an indication of its nonideality. The determination of the activity coefficient is central to the determination of the thermodynamic properties of real solutions. In addition to the experimental determination of the quantity, several solution models have been propounded to estimate this quantity and thus explain the solution behaviour. The most important model in this context is the regular solution model of Hildebrand.

3.9.9
Regular Solution

A particular type of nonideal solution is the regular solution which is characterized by a nonzero enthalpy of mixing but an ideal entropy of mixing. Thus, for a regular solution,

$$\Delta\bar{H}_i^M \neq 0$$

and

$$\Delta\bar{S}_i^M \neq -R\ln X_i$$

For such solutions, Hildebrand defined the following equations to relate the activity coefficients to the solution composition

$$R\,T\ln\gamma_A = \alpha\,(1 - X_A)^2$$

and

$$R\,T\ln\gamma_B = \alpha\,(1 - X_B)^2$$

where α is a constant independent of temperature and composition.

A particularly elegant way of describing regular solutions is through the use of what are known as excess functions. Any thermodynamic function can be thought of as being composed of two parts – an ideal part and an excess part. For example, the integral molar free energy of mixing of a real solution can be written as

$$\Delta G^M = \Delta G^{M,id} + G^{XS}$$

where G^{XS} represents the excess part. It follows immediately that

$$G^{XS} = \Delta G^M - \Delta G^{M,id}$$

or

$$G^{XS} = \Delta H^M - T\,\Delta S^M + T\,\Delta S^{M,id}$$

so that

$$G^{XS} = \Delta H^{M}$$

for a regular solution. The excess integral molar free energy of a regular solution can be seen to be due to activity coefficients having values other than unity, because

$$G^{XS} = \Delta G^{M} - \Delta G^{M,id}$$

or,

$$G^{XS} = R\,T(X_A \ln X_A + X_B \ln X_B) + R\,T(X_A \ln \gamma_A + X_B \ln \gamma_B) - R\,T(X_A \ln X_A + X_B \ln X_B)$$

i.e.,

$$G^{XS} = R\,T\,(X_A \ln \gamma_A + X_B \ln \gamma_B)$$

Using Hildebrand's relationship, $R\,T \ln \gamma_A = \alpha\,(1 - X_A)^2$ and $R\,T\,\gamma \ln_B = \alpha\,(1 - X_B)^2$ in this equation, one obtains, since $X_A + X_B = 1$,

$$G^{XS} = \alpha\, X_A\, X_B$$

so that

$$\Delta H^{M} = \alpha\, X_A\, X_B$$

Thus the integral molar excess free energy of mixing as well as the enthalpy of mixing are independent of temperature for a regular solution.

3.10
Phases in Equilibria

For a system at equilibrium, the free energy change, ΔG, at constant temperature and pressure is zero. Let two phases, α and β, of the same substance, in equilibrium at a temperature T and pressure P, be considered. If the two phases are reversibly converted into one another ($\alpha \rightleftharpoons \beta$) by withdrawing or supplying heat, the system is always in equilibrium, and ΔG is zero. It readily follows that the molar free energy of the substance in the two phases in equilibrium is the same

$$G_\alpha = G_\beta$$

where G_α and G_β are the free energies per mole of the substance in the two phases. If the temperature is raised from T to $T + \mathrm{d}T$, then in order that the system stays in equilibrium, the pressure must be changed from P to $P + \mathrm{d}P$. The system will still be at equilibrium under the new conditions and the free energies per mole in the changed situation can be written as

$$G_\alpha + \mathrm{d}G_\alpha = G_\beta + \mathrm{d}G_\beta$$

Subtraction of the previous ($G_\alpha = G_\beta$) equation from this yields,

$$\mathrm{d}G_\alpha = \mathrm{d}G_\beta$$

Substituting for $\mathrm{d}G$ the expression derived earlier

$$\mathrm{d}G_\alpha = V_\alpha\,\mathrm{d}P - S_\alpha\,\mathrm{d}T$$

and

$$\mathrm{d}G_\beta = V_\beta\,\mathrm{d}P - S_\beta\,\mathrm{d}T$$

and using the relation $\mathrm{d}G_\alpha = \mathrm{d}G_\beta$,

$$V_\alpha\,\mathrm{d}P - S_\alpha\,\mathrm{d}T = V_\beta\,\mathrm{d}P - S_\beta\,\mathrm{d}T$$

Rearrangement of the terms leads to the relation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{S_\beta - S_\alpha}{V_\beta - V_\alpha}$$

The quantity $(S_\beta - S_\alpha)$ is the entropy change in the phase change and hence $(S_\beta - S_\alpha) = \Delta S = L/T$, where L is the latent heat per mole associated with the phase change at temperature T. Taking this into account, the above relationship can be expressed as

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T\,(V_\beta - V_\alpha)}$$

This equation is called the Clapeyron equation and can be applied to any two phases in equilibrium, e.g., solid and liquid, liquid and vapor, solid and vapor or two crystalline forms of the same solid. Thus for the equilibrium

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L_\mathrm{v}}{T\,(V_\mathrm{v} - V_\mathrm{l})}$$

where L_v is the molar heat of vaporization, V_v and V_l are respectively the molar volumes of the vapor and the liquid phases, T is the boiling point of the liquid and $\mathrm{d}P/\mathrm{d}T$ is the rate of change of the vapor pressure of the liquid with temperature.

It is of interest to consider the variation of vapor pressure with temperature. The vapor pressure of a liquid is constant at a given temperature. It increases with increasing temperature upto the critical temperature of the liquid. The liquid is completely in the vapor state above the critical temperature. The variation of the vapor pressure with temperature can be expressed mathematically by the Clapeyron–Clausius equation. Clausius modified the Clapeyron equation in the following manner by assuming that the vapor behaves like an ideal gas.

If the temperature is not near the critical temperature, the volume of a liquid can be considered to be negligibly small compared with the volume of the vapor. The Clapeyron equation then becomes

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L_\mathrm{v}}{T\,V_\mathrm{v}}$$

If it is assumed that the vapor behaves like an ideal gas, then

$$V_v = \frac{R\,T}{P}$$

Substituting this relation in the previous equation,

$$\frac{dP}{dT} = \frac{L_v\,P}{R\,T^2}$$

Now, using the mathematical identity

$$\frac{dP}{dT} = P \cdot \frac{d\ln P}{dT}$$

the equation may be written in the form,

$$\frac{d\ln P}{dT} = \frac{L_v}{R\,T^2}$$

This equation is called the Clapeyron–Clausius equation. For many purposes this is rearranged and integrated between the temperature limits T_1 and T_2, corresponding to the pressure limits P_1 and P_2,

$$\int_{\ln P_1}^{\ln P_2} = \int_{T_1}^{T_2} \frac{L_v}{R} \cdot \frac{dT}{T^2}$$

If it is assumed that the molar heat of vaporization is independent of temperature, then the equation integrates to

$$\ln\frac{P_2}{P_1} = -\frac{L_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

The above equation, on rearrangement and replacement of ln by $\log_{10}$, becomes

$$2.303\,\log_{10}\frac{P_2}{P_1} = -\frac{L_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where P_1 and P_2 are the vapor pressures at temperatures T_1 and T_2 respectively.

3.11
Phase Rule

The main focus has thus far been on homogeneous systems which are both physically and chemically uniform. It is only appropriate that due attention is also given to the study of heterogeneous systems, which consist of two or more homogeneous parts or “phases” that are physically distinct. It has already been seen that the equilibria in homogeneous systems (homogeneous equilibria) can be studied satisfactorily by means of the well-known law of mass action. The equilibria in heterogeneous systems (heterogeneous equilibria), on the other hand, are usually examined with the help of two well-known and important generalizations, namely, the phase rule and the distribution law. While the distribution law has been dealt with in Chapter 5, the text at the present stage concentrates on the phase rule

The phase rule as has been pointed out in the preceding paragraph deals with the behavior of heterogeneous systems at equilibria. It essentially includes three special terms. These are: (i) number of phases in the system (P); (ii) the number of components for the system (C); and (iii) the number of degrees of freedom available to the system (F). A system for the present purpose could be any substance or combination of substances, which is set apart from its surroundings or other substances, such that its equilibrium state may be studied. The simplest way to express the rule in the form of an equation combining the three terms is as follows:

$$F = C - P + 2 \quad \text{or} \quad P + F = C + 2$$

where the available variables besides the concentration factors, are only two, the temperature and the pressure.

A heterogeneous system is made up of two or more different parts, each of which is homogeneous in itself and is separated from others by bounding surfaces. These homogeneous and physically distinct portions of a heterogeneous system in equilibrium are termed *phases*. The following may be cited as some examples: (i) freezing water has three phases, ice, water and vapour in equilibrium; (ii) a mixture of two or more gases is homogeneous and constitutes one phase only; (iii) two immiscible liquids in contact form two different phases; and (iv) a heterogeneous mixture of solid substances consists of as many phases as there are substances present.

The conception of *components* is rather more difficult to comprehend. By the term components of a system one does not mean the number of constituents i.e., the chemical entities present in the system. Pertinent to the statement of the phase rule, the number of components is defined as the minimum number of independently variable chemical constituents which is sufficient to express the composition of each and every one of the phases present in any state of equilibrium. When determining the number of components in terms of the chemical constituents, it should be borne in mind that zero and negative quantities of components are permitted. Some simple cases may be considered in order to make the definition clear. First let the case of the freezing of water be taken. There are three phases, namely, ice, water and water vapor, in equilibrium at the start of freezing. Even though the system has three phases, each of these is made of only one chemical constituent, viz., H_2O which is, therefore, the only constituent present. Although hydrogen and oxygen enter into the constitution of water they cannot be regarded as components: first, because they are combined in definite proportions (2 : 1) to form water and their amounts cannot be independently varied; and secondly, because they do not take part in the equilibrium. The system ice – water-vapour is, therefore, a one-component system. As a second example, the case of the decomposition of calcium carbonate ($CaCO_3 \rightarrow CaO + CO_2$) is considered. Three different substances (solid calcium carbonate, solid calcium oxide and carbon dioxide gas) are present, but they are not all to be considered components (in the phase rule sense) since they are not mutually independent. If two of them are chosen, the composition of the third is defined by the equation

$$CaCO_3 = CaO + CO_2$$

so that the number of components is two. As a third example, the case of the dissociation of solid ammonium chloride into gaseous ammonia and hydrogen chloride (NH_4Cl (s) $\rightarrow$ NH_3 (g) + HCl (g)) may be considered. In this case, the two phases present are solid NH_4Cl and a homogeneous gaseous mixture in which the constituents of ammonium chloride are present in the same proportion in which they are present in the solid state. The phase rule does not make a distinction between a chemical compound and a mixture in which its constituents are present in the same proportion as long as that mixture is homogeneous. The composition of both the phases can, therefore, be represented by the same chemical entity, NH_4Cl, and the system can be taken to be a one-component system. It can be taken to be a two-component system if NH_3 and HCl are not present in equivalent proportions. A few other examples can be considered by way of distinguishing between phases and components. It is known that copper and nickel are so similar that they are completely soluble over the entire composition range. Such a system exhibits only a single phase in the solid state (solid solution), and has two components (Cu and Ni). For material systems involving compounds instead of elements, the compounds can be components. For example, MgO and NiO form solid solutions in a way similar to that for Cu and Ni. In this illustration, the two components are MgO and NiO.

A system in equilibrium is influenced by such variables as the pressure, the temperature, and the compositions of the phases. The minimum number of variable factors (i.e., pressure, temperature, and compositions of the phases) which must be specified in order that a system at equilibrium can be completely defined is called the number of degrees of freedom. It is also sometimes called the variance. For a system in which ice, water, and water vapor are in equilibrium, there is no degree of freedom because the system can exist only at a definite temperature and a definite pressure. A pure metal at its precise melting point has no degrees of freedom. In this situation, the metal exists in two phases in equilibrium, that is, in solid and liquid phases simultaneously. Such systems are called invariant systems. When only a two-phase equilibrium, e.g., between ice and water vapor, or between water and water vapor has to be maintained, the phase rule shows that the degree of freedom is one. This equilibrium can occur over a range of temperatures or pressures. However, once the temperature is specified, the pressure becomes automatically fixed since at any given temperature the two-phase equilibrium can occur only at a particular pressure. In the same way, once the pressure is specified, the temperature of the system is automatically fixed. This is a typical behaviour of a system with one degree of freedom, or a univariant system. For a given sample of gas, only two variables are required to define its condition completely. Since pressure, volume and temperature are related by the gas equation, $P\,V = R\,T$, fixing the values of any two variables would automatically fix the value of the third variable. The two fixed variables are said to be arbitrary or independent, while the third variable which can be calculated from the condition of equilibrium is called the dependent variable. The system, therefore, has two degrees of freedom, and such systems are called bivariant. Thus systems are described as being invariant, univariant, bivariant, and trivariant according to the number of degrees of freedom of zero, one, two, or three respectively.

3.11.1
Applications

The conditions of equilibrium in a system can be very well studied by applying the phase rule equation $F = C - P + 2$. For a clear understanding of the rule and its applications, a graphical representation has proved to be very useful. Graphical representations of this type (or phase diagrams as they are more popularly known) are classified according to the number of components in the system. Single-component systems have unary diagrams, two-component systems have binary diagrams, three-component systems give rise to ternary diagrams, and so on.

In the case of a unary or one-component system, only temperature and pressure may be varied, so the coordinates of unary phase diagrams are pressure and temperature. In a typical unary diagram, as shown in Figure 3.11, the temperature is chosen as the horizontal axis by convention, although in binary diagrams temperature is chosen as the vertical axis. However, for a one-component system, the phase rule becomes $F = 1 - P + 2 = 3 - P$. This means that the maximum number of phases in equilibrium is three when F equals zero. This is illustrated in Figure 3.11 which has three areas, i.e., solid, liquid, and vapour In any

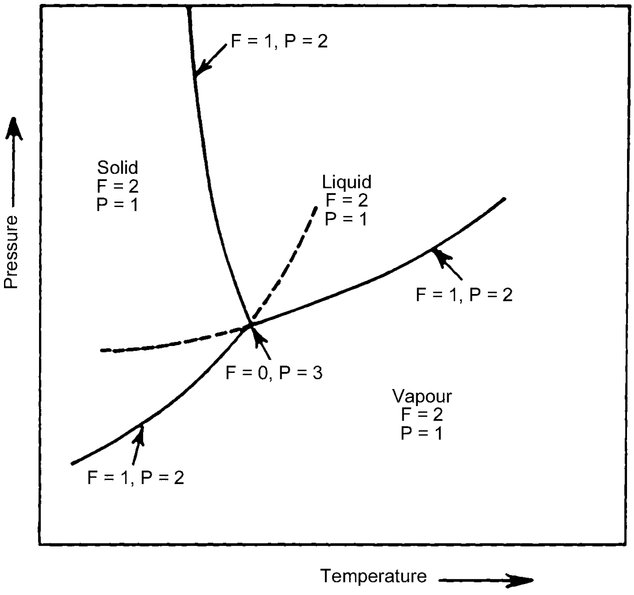


Figure 3.11 Phase diagram for a one-component system (unary phase diagram).

one of these areas or phases, temperature or pressure may be varied with no change in phase as there are two degrees of freedom ($F = 3 - P$; here, $F = 3 - 1 = 2$). For two phases to continue to coexist, only temperature or pressure can be varied independently ($F = 3 - 2 = 1$). The common point where three phase boundaries intersect where $F = 3 - 3 = 0$, corresponds to a specific temperature and a specific pressure, and it is only at this point that all the three phases, i.e., solid, liquid, and vapour, coexist in equilibrium. A two-phase equilibrium is possible only along the phase boundaries.

In a two-component system, when both the components exist in one phase, the number of degrees of freedom assumes the value of three ($F = 2 - 1 + 2$). In such a system not only the pressure and temperature but also the composition of the phases may alter. With three variable factors influencing the equilibrium, a graphical representation is quite complicated. Pressure, temperature and composition could be represented by three axes at right-angles, yielding space models or solid equilibrium diagrams. For the sake of obtaining simple phase diagrams, one considers only two of the variable factors at a time, keeping the third one as constant. In this way one can have pressure-temperature (P–T), temperature-composition (T–C) and pressure-composition (P–C) diagrams. Of these three types of diagram, diagrams (T–C) are most commonly used in metallurgy, and in such cases the pressure is kept constant at a value of one atmosphere. Since the degrees of freedom in such a case are reduced by one, the corresponding phase rule equation can be written as

$$F = C - P + 1$$

Such systems are called condensed systems.

One may now take up some specific examples and describe them from the point of view of the phase rule. In the case of a pure metal at its melting point, $C = 1$ and $P = 2$ (solid + liquid), giving $F = 1 - 2 + 1 = 0$, as has been noted previously. An example of metallurgical interest is the system involving lead and silver. Molten silver and lead mix together in all proportions, giving a homogeneous solution. These elements do not react chemically to form compounds, and the four possible phases taking part in the equilibrium are (i) solid silver; (ii) solid lead; (iii) solution of silver and lead; and (iv) vapor of silver and lead. The system is evidently a two component system, as the compositions of the various phases can be represented by the two-chemical species, silver and lead. The boiling points of these two metals being quite high, the gaseous phase is practically absent in this system and, therefore, pressure can have little effect on the equilibrium. In such a case, only the two remaining variables – temperature and concentration – need be considered, with pressure kept at the atmospheric value. This situation corresponds to a condensed system. The complete T–C diagram of the system is given in Figure 3.12. The diagram consists of two curves, AO and BO. The curve AO shows the effect of the addition of lead on the melting point of pure silver and may be designated as the melting point or the freezing point curve of silver. The curve BO likewise may be called the melting point or the freezing point curve of lead. All along the curve AO there are two phases, solid silver and liquid, in equilibrium; therefore $F = C - P + 1 = 2 - 2 + 1 = 1$, indicating that the system is univariant. Likewise, along the curve BO the system is univariant. The curves AO and BO meet at O which, being common to both curves, represents the conditions under which solid silver, solid lead and the liquid solution coexist. The degree of freedom here is zero; that is, the system is invariant. The point O corresponds to a temperature which is lower than the melting point of either com-

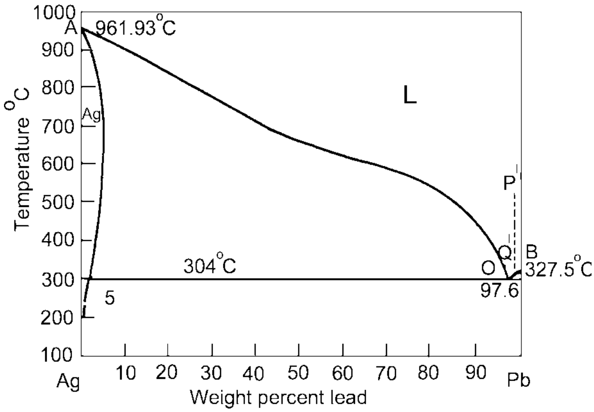


Figure 3.12 The lead–silver phase diagram.

ponent. Thus, an alloy of silver and lead corresponding to the point O (97.6% Pb, 2.4% Ag) will melt at 303 °C, a temperature lower than the melting point of silver (961.93 °C) and that of lead (327.5 °C). The point O, which can be attained in the above manner, is called the *eutectic point*. It is the lowest temperature at which the liquid phase can exist. If the liquid is cooled below this temperature, both the components separate simultaneously in the solid form, without any change of composition.

It is pertinent to add that based on the facts contained in this diagram, a process called Parke's process has been developed by which desilverization of lead is accomplished. Let the point P” represent the molten argentiferous lead containing a very small amount of silver. On cooling, one travels along the dotted line P′Q′ until the temperature corresponding to the point Q′ on the curve OB is reached, when lead starts to separate. On further lowering of temperature more lead separates as a solid phase until the eutectic point O is reached where an alloy containing about 2.4% of silver is obtained. This is then subjected to cupellation.

The coverage thus far has provided an account of the usefulness of phase rule to classify equilibria and to establish the number of independent variables or degrees or of freedom available in a specific situation. In the following paragraphs the equilibria used in mass transfer are analyzed in terms of phase rule in the case of leaching, drying and crystallisation.

Two situations are found in leaching. In the first, the solvent available is more than sufficient to solubilize all the solute, and, at equilibrium, all the solute is in solution. There are, then, two phases, the solid and the solution. The number of components is 3, and $F = 3$. The variables are temperature, pressure, and concentration of the solution. All are independently variable. In the second case, the solvent available is insufficient to solubilize all the solute, and the excess solute remains as a solid phase at equilibrium. Then the number of phases is 3, and $F = 2$. The variables are pressure, temperature and concentration of the saturated solution. If the pressure is fixed, the concentration depends on the temperature. This relationship is the ordinary solubility curve.

In drying a water-wet solid, free liquid water may or may not be present. If it is, there are in all three phases-vapour, liquid and solid- and three components, so $F = 2$. At constant pressure a unique relationship exists between temperature and concentration of water in the vapour, just as in air–water contacts. The water present in hygroscopic solids or in natural substances such as wood may be in a loose combination with the solid, with no liquid water present. Then there are two phases and three components, and $F = 3$. The variables are temperature, pressure, and the concentrations of water in vapour and solid. If temperature and pressure are fixed, these concentrations can be plotted on an equilibrium curve.

As far as crystallization is concerned, there are two components, solvent and solute, and $F = C = 2$. The solid phase is pure, and variables are concentrations, temperature, and pressure. Fixing one, the pressure, leaves either concentration or temperature as an independent variable. The relationship between temperature and concentration is the usual solubility curve.

3.12
Thermodynamic Data Presentation

Thermodynamic data conveyed in different diagrammatic forms or presentations are immensely useful. One obvious advantage is that these graphical portrayals allow rapid evaluation of thermodynamic functions, without having the need to go into tedious comparative calculations. The more frequently used diagrams are (i) Ellingham diagrams; (ii) Predominance diagrams; and (iii) Pourbaix diagrams. The diagrams due to Ellingham have been dealt with and illustrated to a good measure in the present chapter and also in Chapter 4. These diagrams have subsequently been produced more elaborately by those due to Richardson and Jeffes and to many others. An important addition that came with equally profound impact is the predominance diagram. These diagrams are used to great effect in Chapter 4. The account on Pourbaix diagrams appears exclusively in Chapter 5. However, it may just be mentioned at this stage that the Pourbaix diagram is in essence one form of Predominance diagram that has been found particularly very useful in hydrometallurgy. Alternatively, it may be best described as what one comes across in the application of predominance diagrams to aqueous solutions when examining their importance in producing metals hydrometallurgically. The list of graphical presentations in a sense seems fit to be extended to include those depicting phase rule as applied to, for example, to single-, two-, three-, or multi-component systems. Some of these particular areas have been dealt with at length appropriately in Section 3.12.

3.13
Introduction (Kinetics)

A well-recognized strength of thermodynamics is that it can predict whether or not a particular reaction occurs, under specified conditions, and the relative amounts of the reactants and the products that would be present when equilibrium is reached. The thermodynamic approach, however, does not provide an indication of the rate at which the equilibrium would be reached. This information is provided by reaction kinetics.

The relevance of reaction kinetics becomes immediately apparent if one takes into account the fact that, to a first approximation, the size of a plant required to produce a certain amount of material is inversely proportional to the kinetics of the reaction leading to such production. This is because the time required for a given amount of material to be produced increases with decreasing reaction rate. The inherent costs involved in keeping the production plant running are also time-dependent. Thus, the economic aspects of any process are influenced by the process kinetics. Besides this, the kinetics of a reaction must be known if one has satisfactorily to design equipment to implement reactions on an industrial scale. Of course, if the reaction is fast enough such that the system is essentially at equilibrium, the design is very much simplified and thermodynamic information alone is sufficient.

Chemical kinetics is usually subdivided into the study of either homogeneous reactions or heterogeneous reactions. Homogeneous reactions occur entirely within one phase, be it a solid, a liquid, or a gas. A simple example of a homogeneous reaction is the neutralization of an acid by a base in an aqueous medium ($H^+ + OH^- \rightarrow H_2O$). A most important homogeneous reaction in solid-state metallurgy is true lattice diffusion. A reaction is heterogeneous if it needs the presence of at least two phases to proceed at the rate it does. It is immaterial whether the reaction takes place in one, two, or more phases, or at an interface, or whether the reactants and the products are distributed among the phases or are all contained within a single phase. All that matters is that at least two phases are necessary for the reaction to proceed as it does. Reference is drawn to the reaction between the gases nitrogen and hydrogen to produce ammonia. Since the reaction involves only a gas phase one might be inclined to call it a homogeneous reaction. However, the reaction proceeds at useful rates only at the surface of the solid catalyst introduced into the chemical reactor; the reaction is, therefore, better categorized as a heterogeneous one because it involves two phases (the gas phase and the solid catalyst). There is a very significant difference with regard to the manner or mode of occurrence of homogeneous and heterogeneous reactions. Unlike homogeneous reactions, heterogeneous reactions take place at the interfaces between phases. The simple example of the oxidation of solid carbon by carbon dioxide can be considered in this particular context. In the bulk of the gas there is no carbon present, so that the reaction, $C + CO_2 = 2\,CO$, does not take place there. Similarly, within the carbon particles (provided they are not porous) there is no carbon dioxide and so no reaction takes place there either. The reaction is confined to the interface between the gaseous and the solid phases (i.e., the surfaces of the carbon particles).

3.14
Rate of Reaction

The terms rate, speed, and velocity are all synonymous in chemical kinetics, though this is not so in mechanics. It takes different periods of time to complete different reactions. The neutralization reaction between acids and bases, mentioned earlier as an example of homogeneous reactions, takes place almost instantaneously at room temperature and under atmospheric pressure. However, it takes many days for iron to rust under these conditions. Thus, the rates of reactions that may take place under the same conditions of temperature and pressure may differ very significantly. When carbon or sulfur or phosphorus burns in air and in pure oxygen, the same reaction products are obtained, but the rate of the reaction is much faster in oxygen than in air. This is simply a consequence of the concentration of oxygen in air being lower. Examples abound to highlight the fact that chemical reactions between solids are accelerated when the sizes of their particles are reduced. Examples such as these underline the necessity and importance of the knowledge of the duration of a given chemical reaction. Before examining such details however, a very pertinent question is how to define the rate of a reaction in a meaningful and useful way. Various definitions of the rate of a reaction are available, all of which are interrelated and involve intensive rather than extensive quantities. The rate of reaction is a function of the state of the system:

$$r_\mathrm{i} = f\,(\text{state of the system})$$

The form of this functional relationship remains the same, no matter how the rate of the reaction is defined. It is only the constants of proportionality and their dimensions that change while switching over from one definition to another.

3.15
Homogeneous Reactions

It may be recalled that in homogeneous reactions all reacting materials are found within a single phase, be it gas, liquid or solid; if the reaction is catalytic, then the catalyst must also be present within the phase. Thus, there are a number of means of defining the rate of a reaction; the intensive measure based on unit volume of the reacting volume (V) is used practically exclusively for homogeneous systems. The rate of reaction of any component i is defined as

$$r_\mathrm{i} = \frac{1}{V}\left(\frac{\mathrm{d}N_\mathrm{i}}{\mathrm{d}t}\right)_{\text{by reaction}} = \frac{(\text{moles of } i \text{ which appear by reaction})}{(\text{unit volume})\ (\text{unit time})}$$

By the definition given above, if i is a reaction product the rate is positive, but if it is a reactant which is being used up, the rate is negative; thus $-r_\mathrm{i}$ is the rate of disappearance of the reactant.

The progress of this category of reactions is expected to depend on the composition of the materials within the phase as well as the temperature and pressure of the system. The rate of homogeneous reaction should not be affected by the shape of the container, the surface properties of the solid materials in contact with the phase, and the diffusion characteristics of the fluid. Thus the rate of reaction of component i may be expressed as

$$\begin{aligned} r_\mathrm{i} &= f\,(\text{state of the system}) \\ &= f\,(\text{temperature, pressure, composition}) \end{aligned}$$

This generally simplifies to

$$r_\mathrm{i} = f\,(\text{temperature, composition})$$

3.15.1
Rate Equation

If the temperature and other experimental variables do not change, then the rate of a reaction is a function of the concentrations of the reactants, which implies that it is a function of time. This is so because these concentrations change continuously with time as the reaction progresses. It is not convenient to use the numerical values of the reaction rate in discussions on reaction kinetics because it is necessary to refer each value to the corresponding concentration, i.e., to the appropriate stage of the reaction. This difficulty is circumvented by expressing the results in terms of a rate equation which gives the functional dependence of the reaction rate on the concentration. Such rate equations are of considerable importance because they provide concise expressions for the course of the reaction and can be applied for computing reaction times, yields, and optimum economic conditions. Very often they also provide an insight regarding the mechanism by which the reaction proceeds.

Rate equations are differential equations of the general form $\mathrm{d}c_i/\mathrm{d}t = k\,f\,(c_1, c_2, \dots c_n) = k\,f\,(c)$, where i is the particular product or reactant, and c_i is its molar concentration (N_i/V). The constant k goes by a number of names such as velocity coefficient, velocity constant specific reaction rate, rate constant, etc., of the particular reaction. Physically, it stands for the rate of the reaction when the concentrations of all the reactants are unity. The function $f(c)$ and the rate constant k are determined from experimental data.

The rate or the kinetic equations actually result from the law of mass action which states that, at a constant temperature, the rate of a chemical reaction is directly proportional to the product of the concentrations of the reactants. In order to elaborate, by way of illustration the reaction between hydrogen and chlorine, represented in the following manner, is considered:

$$\mathrm{H_2 + Cl_2 = 2\,HCl}$$

According to the law, the rate of the reaction is as follows:

$$r = k\,C\,(\mathrm{H_2}) \cdot C\,(\mathrm{Cl_2})$$

where $C\,(\mathrm{H_2})$ and $C\,(\mathrm{Cl_2})$ are the molar concentrations of $\mathrm{H_2}$ and $\mathrm{Cl_2}$ respectively that have entered the reaction. There is, however, one error in this particular representation. This reaction actually occurs in two stages:

$$\mathrm{Cl + H_2 = HCl + H}$$

$$\mathrm{H + Cl_2 = HCl + Cl}$$

Using these data, it is possible to have a kinetic equation for each stage; these equations are as follows:

$$r_1 = k \cdot C\,(\mathrm{Cl}) \cdot C\,(\mathrm{H_2});\quad r_2 = k_2\,C\,(\mathrm{H}) \cdot \mathrm{C}\,(\mathrm{Cl_2})$$

It is evident that kinetic equations may not be derived from chemical equations, since the latter only indicate which substances enter the reaction and in what quantities, and which substances are formed; they provide no indication as to the mechanism of the reaction.

In many instances, the rate of progress of reaction, involving say substances A, B, ..., D, can be approximated by an expression of the following type:

$$\gamma_A = k\, c_A^a\, c_B^b \ldots c_D^d\,, \quad a + b + \ldots + d = n$$

where a, b, ..., d are not necessarily related the stoichiometric coefficients. One calls the powers to which the concentrations are raised the "order of reaction". Thus, the reaction is a^{th} order with respect to A, b^{th} order with respect to B, and n^{th} order overall.

Another term often used in reaction kinetics is "molecularity". In order to distinguish this term from order of a reaction, present reference is drawn to the formation of NH_3 from H_2 and N_2, as shown in the equation below:

$$1.5\ H_2 + 0.5\ N_2 \rightleftharpoons NH_3$$

The above equation shows that 1.5 molecules of H_2 react with 0.5 molecules of N_2 to form one molecule of NH_3. The total number of molecules of the reactants involved is two, and it is referred to as the molecularity of the reaction. Experimentally, the rate has been found to follow the equation.

$$r = K\,[H_2]^{1.5}\,[N_2]^{0.5}$$

The order of the above reaction is, therefore, 1.5 + 0.5 = 2. This is typical of situations where the order of reaction and the molecularity of the reaction are the same. It may, however, be noted that the form of rate law, which determines the order of a reaction, can only be derived by actual experiment, and that may or may not be equal to the molecularity of the reaction as provided by the equation representing that reaction. Thus, a general reaction

$$a\,A + b\,B \rightarrow C + D$$

and the reaction rate law as determined experimentally is represented as

$$r = [A]^x\,[B]^y$$

$(a + b)$ is the molecularity of the reaction and $(x + y)$ is its order of reaction. Thus, the order of reaction, as has been cited in the paragraph earlier, is defined as the sum of the powers of concentrations of reactants in the rate law equation as determined experimentally. Now let the following reaction be considered:

$$2\ NO\ (g) + 2\ H_2 \rightarrow N_2\ (g) + 2\ H_2O$$

It is found by experiment that the formation of N_2 shows a fourfold increase if the concentration of NO is doubled, whereas it shows a twofold increase if the concentration of H_2 is doubled. Thus the rate equation may be given as:

$$r = k\,[NO]^2\,[H_2]^1$$

The order of the reaction is 2 + 1 = 3, whereas the molecularity of the reaction, as given by the equation is 4. This reaction can be treated as a representative example which shows that the order of a reaction is strictly an experimental quantity, being concerned solely with the manner in which the rate depends on concentration. In other words, the order of a reaction should be regarded as a mathematical convenience and not as a fundamental property of the reaction. It must be mentioned here that the order of a reaction corresponds to the experimental rate equation, while the molecularity of a reaction refers to the theoretical mechanism by which it occurs. It may also be appreciated that the molecularity of a reaction must always have an integral value and will never be zero; in contrast, the order for a particular component need not be a whole number, it can be fractional and can also be apparently zero, despite the fact the component actually takes part in the reaction. It will be instructive to consider a few more specific examples in this context.

A reaction of solid copper with oxygenated atmosphere to form an oxide layer on the surface of copper is shown below:

$$4\,\mathrm{Cu} + \mathrm{O_2} = 2\,\mathrm{Cu_2O}$$

In the above example, the concentration of copper remains constant (pure copper) so that the reaction rate could be expected to depend on the partial pressure of oxygen in the atmosphere ($P_{\mathrm{O_2}}$). This would be a first order reaction, but experimental determination of the dependence of the rate on $P_{\mathrm{O_2}}$ shows that the rate is approximately proportional to $P_{\mathrm{O_2}}^{1/7}$ implying a fractional order.

The oxidation of nitrogen oxide through the reaction,

$$2\,\mathrm{NO}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\,\mathrm{NO_2}\,(g)$$

appears to be of the second order with respect to NO, but of the zero order with respect to the other reactant, $\mathrm{O_2}$. Zero order with respect to oxygen does not mean that oxygen is not associated with the reaction, but there is no apparent experimental dependence. This situation can occur when oxygen is present in such a large excess that its concentration changes negligibly during the course of the reaction. In the instance of the same reaction performed with equimolar amounts of the reacting gases the reaction will appear to be first order with respect to oxygen.

3.15.2
Rate-Controlling Step

It is apparent from the last example cited in previous section that there is not necessarily a connection between the kinetic order and the overall stoichiometry of the reaction. This may be understood more clearly if it is appreciated that any chemical reaction must go through a series of reaction steps. The addition of these elementary steps must give rise to the overall reaction. The reaction kinetics, however, reflects the slowest step or steps in the sequence. An overall reaction is taken as for an example:

$$2\,X + Y \rightleftharpoons Z$$

The above reaction is supposed to be actually taking place through the following elementary reaction steps,

$$X + Y \rightleftharpoons XY \qquad K_1 = \frac{[XY]}{[X]\,[Y]} \qquad \text{Step 1}$$

$$XY + Y \rightleftharpoons YXY \qquad K_2 = \frac{[YXY]}{[XY]\,[Y]} \qquad \text{Step 2}$$

$$YXY + X \rightleftharpoons Z + Y \qquad K_3 = \frac{[Z]\,[Y]}{[YXY]\,[X]} \qquad \text{step 3}$$

From the three reaction steps cited above the overall reaction is:

$$2\,X + Y \rightleftharpoons Z$$

The constants K_1, K_2 and K_3 are the equilibrium constants for the reaction steps 1, 2, and 3 respectively, and XY and YXY are the intermediaries formed during the course of the reaction. A number of scenarios about the reaction rate may be envisaged. If the first reaction step is the slowest in the sequence then the observed reaction rate law will be given by

$$r_1 = k_1\,[X[\,[Y]$$

If the second reaction step is the slowest the rate will be given by

$$r_2 = k_2\,[XY]\,[Y]$$

However, the concentration of XY is apparently unknown since it is an intermediate complex.

If the reaction step 2 is slow, the reaction step 1 must be relatively fast and therefore approach equilibrium. Thus, from the equation for the reaction step 1 $[XY] = K_1\,[X]\,[Y]$ and substituting into the equation for r_2 the following relationship is obtained:

$$r_2 = K_1\,k_2\,[X]\,[Y]^2$$

If the reaction step 3 is the rate-limiting step then the rate is given by

$$r_3 = k_3\,[X]\,[YXY]$$

In the above case both the reaction steps 1 and 2 are virtually at equilibrium so that the concentration of YXY present may be expressed in terms of the concentrations of the reactants and the rate constants in these previous steps, i.e., $[YXY] = K_2\,[XY]\,[Y] = K_2\,K_1\,[X]\,[Y]^2$. Thus substituting for $[YXY]$ the rate law for the reaction step 3 is given by

$$r_3 = k_3\,K_2\,K_1\,[X]^2\,[Y]^2$$

3.15.3
Order of Reaction

In kinetics, reactions are classified as being first, second, third, etc. order depending on the way the rate of the reaction is related to the concentration terms in the rate equation. If the rate of reaction is apparently independent of concentration, the reaction is said to be of zero order.

3.15.3.1 First-order Reactions

A first-order reaction may be represented schematically as:

$$\mathrm{A} \rightarrow \text{Products}$$

It is assumed that at the beginning of the reaction ($t = 0$) the concentration of A is a and that of P (products) is zero. If after time t the concentration of P is x, that of A would be $(a - x)$. The rate of formation of P is $\mathrm{d}x/\mathrm{d}t$. A first-order reaction can be expressed as:

$$\frac{dx}{dt} = k\,(a - x)$$

Separation of the variables leads to the following:

$$\frac{dx}{a - x} = k\,dt$$

and integration of the above provides the following:

$$-\ln\,(a - x) = k\,t + c$$

where c is the integration constant which may be evaluated by using the boundary condition that when t is equal to zero, x is zero; hence

$$-\ln a = c$$

Substituting this value of c in the equation, $-\ln\,(a - x) = k\,t + c$, the relationship turns out as:

$$\ln a - \ln\,(a - x) = k\,t$$

or

$$\ln\frac{a}{a - x} = k\,t$$

and

$$k = \frac{2.303}{t}\log\frac{a}{a - x}$$

This is the integrated rate equation for a first-order reaction. When dealing with first-order reactions it is customary to use not only the rate constant, k for the reaction but also the related quantity half-life of the reaction. The half-life of a reaction refers to the time required for the concentration of the reactant to decrease to half of its initial value. For the first-order reaction under consideration, the relation between the rate constant k and the half-life $t_{0.5}$ can be obtained as follows:

The integrated rate equation is

$$\ln\frac{a}{a - x} = k\,t$$

when $t = t_{0.5}$, $a - x = a/2$. Thus,

$$k\,t_{0.r} = \ln\frac{a}{a/2}$$

or

$$t_{0.r} = \frac{\ln 2}{k}$$

The above equation implies that the half-life of a first-order reaction is independent of concentration. This result in only true for a first-order reaction.

3.15.3.2 **Second-Order Reactions**

There can arise two possibilities in the case of reactions of the second order; the rate may be proportional to the product of two equal initial concentrations or to the product of two different initial concentrations. The first case corresponds to a situation where a single reactant is involved, the process being represented as:

$$2\,\mathrm{A} \rightarrow P$$

It may also be pertinent to a reaction between two different reactants,

$$\mathrm{A} + \mathrm{B} \rightarrow P$$

provided that their initial concentrations are the same. In such circumstances the rate may be written as:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k\,(a - x)^2$$

where x is the amount of A that has reacted in unit volume at time t, and a is the initial amount of A. Integration of this rate equation and application of the boundary condition that $x = 0$ at $t = 0$ leads to

$$t = \frac{1}{k}\,\frac{x}{a\,(a - x)}$$

In this case also, $t_{0.5}$ of the reaction may be considered. At $t = t_{0.5}$, $x = a/2$ and also $a - x = a - a/2 = a/2$ and therefore

$$t_{0.5} = \frac{a/2}{k\,a \cdot a/2} = \frac{1}{a\,k}$$

The half-life is thus seen to depend on the initial concentration for the second order reaction considered. This is in contrast to first-order reaction where the half-life is independent of concentration. For this reason half-life is not a convenient way of expressing the rate constant of second-order reactions.

Reactions of higher orders than two are less common, though some third-order reactions are encountered. Proceeding in a similar way for reaction of n^{th} order,

$$n\,\mathrm{A} \rightarrow \text{Products}$$

the corresponding equation evolves as:

$$t = \frac{1}{(n - 1)\,k}\left[\frac{1}{(a - x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

and the expression for half-life $t_{0.5}$ (setting $x = 0.5\,a$) comes out as:

$$t_{0.5} = \frac{2^{n-1} - 1}{(n - 1)\, k\, a^{n-1}}$$

The equation involving t for the general case of a reaction of the n^{th} order as shown above applies to any value of n except $n = 1$, for this case the treatment leading to exponential equation shown in first-order reaction ($\ln a/(a - x) = k\,t$) must be employed. The equation is applicable for $n = 2$. Other cases, including those of nonintegral orders, can easily be worked out. The half-life, $t_{0.5}$, is seen to be inversely proportional to k in all cases, and inversely proportional to the $(n - 1)^{\text{th}}$ power of the concentration.

3.15.3.3 **Consecutive Reactions**

Reactions of higher order are very rare, and most of the complicated reactions take place in stages. Such reactions which occur in stages are called consecutive or successive reactions and are very common. If a substance A is reacted to yield a product C via the formation of an intermediate substance B, then the overall process consists of the two reactions shown below:

(i) A → B (ii) B → C

If the rate of reaction (i) is very much greater than the rate of reaction (ii), then the rate of the total reaction from A to C is practically the same as that of the slower reaction (ii).

It will be of interest to present mathematically the picture of the course of consecutive reactions. In the simplest case the substance A considered in the present example undergoes a first-order reaction to yield C; the reverse reactions are neglected. The reaction occurring in two first-order steps can now be written as:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_1'} \mathrm{C}$$

At $t = 0$	a	o	o	moles L^{-1}
At $t = t$	x	y	z	moles L^{-1}

The concentration changes involved are shown in Figure 3.13 and are governed by the differential ratio equations given below:

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = k_1\, x$$

$$+\frac{\mathrm{d}y}{\mathrm{d}x} = k_1\, x - k_1\, Y$$

$$+\frac{\mathrm{d}z}{\mathrm{d}x} = k_1\, Y$$

The evaluation of x, y and z at any time t is a complicated series of mathematical steps. A statement of results will serve for the present purpose:

$$x = a\, e^{-k_1 t}$$

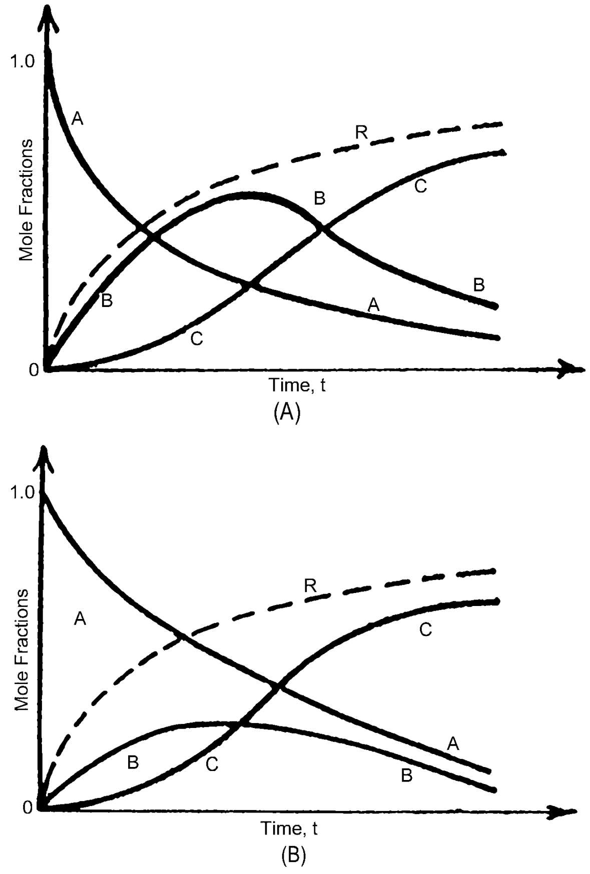


Figure 3.13 Consecutive reaction (A) $k_1 = 2\,k'_1$, (B) $= 0.5\,k'_1$.

$$y = \frac{k_1\ A}{k_1' - k_1}\left(e^{-k_1 t} - e^{-k_1 t}\right)$$

$$z = \frac{a}{k_1 - k_1}\left[k_1\left(1 - e^{-k_1 t}\right) - k_1\left(1 - e^{-k_1 t}\right)\right]$$

In such reactions, while the concentration of A consistently falls and that of C consistently rises, the concentration of B passes through a maximum. Thus, the ratio of B to C is different at different times. Curves R in Figure 3.13 indicate the rate of formation of B in the absence of subsequent steps.

3.15.3.4 **Reversible Reactions**

A homogeneous irreversible reaction is characterized by a large value of the equilibrium constant so that the reverse reaction can be ignored and the reaction can be considered to proceed only in the forward direction. There is practically no major problem in the measurement of the rate of reaction which progresses only in one direction. It is, however, known that in a reversible reaction the reverse reaction takes place under the same set of conditions as the forward reaction. In such reactions the rates of the forward reactions are high initially and gradually decrease as time proceeds. As the products accumulate, the backward reactions set in and their rates slowly increase. Ultimately, a stage is reached when the rates of the backward and forward reactions become equal; this stage corresponds to the equilibrium state. This situation causes a serious disturbance in the measurement of reaction rates. In this case the rate of the reverse reaction must be taken into account in determining the overall reaction. Various combinations of forward and reverse reactions are possible, the simplest being the case when a first-order reaction is reversed by another first-order reaction. In order to present the fact mathematically, an illustrative reference is drawn to a hypothetical first-order reaction,

$$A \underset{k_r}{\overset{k_f}{\longleftrightarrow}} B$$

If the above reaction starts using pure A of concentration a, and if after time t the concentration of B is x, then that of A would be $a - x$. The rate of the forward reaction (r_f) is

$$r_f = k_f\,(a - x)$$

and the rate of the reverse reaction (r_r) is

$$r_r = -k_r\,x$$

where k_f and k_r are respectively the rate constants for the forward and the reverse reactions. The overall or net rate of production of B is thus

$$\frac{dx}{dt} = k_f\,(a - x) - k_r\,x$$

The overall rate of the reaction at equilibrium is zero, and this situation is represented by:

$$k_f\,(a - x') = k_r\,x'$$

where x' is now the net amount of A which has reacted to form B at the position of equilibrium (the concentration of B is then x'). Elimination of k_r by using the two previous equations, one obtains

$$\frac{dx}{dt} = \frac{k_f\,a}{x'}\,(x' - x)$$

The above equation is of the same form as given previously in the case of first-order kinetics, and its solution is

$$\frac{x'}{a}\ln\frac{x'}{x' - x} = k_f\,t$$

If, therefore, x' is determined from equilibrium measurements, k_f can be calculated from the determination of x as a function of time, and k_r can then be obtained from the equilibrium constant.

3.15.4
Temperature Effect

So far, what has been examined is the effect of the concentrations of the reactants and the products on the reaction rate at a given temperature. That temperature also has a strong influence on reaction rates can be very effectively conveyed by considering the experimentally found data on the formation of water from a mixture of hydrogen and oxygen. At room temperature the reaction will not take place; hence the reaction rate is zero. At 400 °C it is completed in 1920 h, at 500 °C in 2 h, and at 600 °C the reaction takes place with explosive rapidity. In order to obtain the complete rate equation, it is also necessary to know the role of temperature on the reaction rate. It will be recalled that a typical rate equation has the following form:

$$-r_{\mathrm{i}} = -\frac{1}{V}\frac{\mathrm{d}N_{\mathrm{i}}}{\mathrm{d}t} = k\,f(c)$$

In this equation it is the reaction rate constant, k, which is independent of concentration, that is affected by the temperature; the concentration-dependent terms, $f(c)$, usually remain unchanged at different temperatures. The relationship between the rate constant of a reaction and the absolute temperature can be described essentially by three equations. These are the Arrhenius equation, the collision theory equation, and the absolute reaction rate theory equation. This presentation will concern itself only with the first.

The Arrhenius equation is given by

$$k = A \exp\left(-\frac{E}{R\,T}\right)$$

where A is a constant for a particular reaction (the preexponential constant, also called as the frequency factor), and so is E (called the activation energy); k is the reaction rate constant, R the gas constant, and T the absolute temperature. The equation can be applied successfully to many homogeneous gas reactions, reactions involving solutions and heterogeneous reactions, and can be used in equivalent alternative forms such as

$$\ln k = \ln A - \frac{E}{R\,T}$$

A plot of ln k versus reciprocal temperature (Arrhenius plot) gives a straight line. The slope of this straight line is $-E/R$, and therefrom E can be readily determined. Differentiating the above equation with respect to temperature, one obtains

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{E}{R\,T^2}$$

It can be seen from this relationship that the greater is E for a reaction, the greater will be the increase in the rate of the reaction with temperature. When a reaction is performed at two different temperatures, T_1 and T_2, the Arrhenius equation can be written in the following manner:

$$\log \frac{k_2}{k_2} = \frac{E}{2.303\,R}\left(\frac{T_2 - T_1}{T_1\,T_2}\right)$$

From the coverage made thus far, it may be of interest to record in one place the different factors which influence the rate of chemical reactions. The rate of chemical reaction depends essentially on four factors. The nature of reactants and products is one. For example, certain physical properties of the reactants and products govern the rate. As a specific example in this context mention may be of oxidation of metals. The volume ratio of metallic oxide to metal may indicate that a given oxidation reaction will be fast when the oxide is porous, or slow when the oxide is nonporous, thus presenting a diffusion barrier to the metal or to oxygen. The other two factors are concentration and temperature effects, which are detailed in Sections. The fourth factor is the presence of catalysts.

3.16
Heterogeneous Reactions

In the case of heterogeneous reactions, there are two complicating factors that must be taken into account beyond what is normally considered in homogeneous systems.

The first of these factors pertains to the complications introduced in the rate equation. Since more than one phase is involved, the movement of material from phase to phase must be considered in the rate equation. Thus the rate expression, in general, will incorporate mass transfer terms in addition to the usual chemical kinetics terms. These mass transfer terms are different in type and number in different kinds of heterogeneous systems. This implies that no single rate expression has a general applicability.

The second factor pertains to the contacting patterns for multiphase systems. Many combinations of contacting patterns are possible, even for a two-phase system. Each of the many ways of contacting two phases has associated with it a specific form of performance equation which must be developed for that particular contacting pattern.

In a bid to introduce formally the heterogeneous reaction, the following reaction is considered:

$$X(1) + Y(2) = XY(1)$$

The numbers in the parentheses indicate the phases in which the reactants and the products are soluble. Since X does not dissolve in phase 2 and Y in phase 1, their only possible meeting place is the interface between the two phases, 1 and 2. It is necessary to transport atoms of X and of Y to the interface. The reaction product XY has also to be transported away from the interface. The reaction would otherwise come to a halt due to the accumulation of XY at the interface. Each of these individual processes mentioned may be addressed as kinetic steps and for the reaction cited, these steps are: (a) the transfer of X from the bulk of phase 1 to the interface; (b) the transfer of Y from the bulk of phase 2 to the interface; (c) chemical reaction at the interface; and (d) the transfer of XY from the interface into the bulk of phase 1 (say). The steps listed can be grouped into two categories. The steps (a), (b), and (d) are mass transfer processes, while the step (c) is a chemical reaction step. A simpler situation is encountered in many of the reactions in process metallurgy. Phase 1 is a gas and phase 2 is a solid or a liquid; so also is the reactant *Y*. The reaction steps now become: (i) the transfer of *X* from phase 1 to the interface; (ii) chemical reaction at the interface; and (iii) the transfer of the product from the interface to the bulk of phase 1. The steps (i) and (iii) are mass transfer processes, and step (ii) is a chemical reaction step. The discussions and conclusions pertinent to steps (i) to (iii) are easily extendable to the more general case comprising as steps (a) to (d) described previously.

The kinetic steps described above for the generalized reaction are in series. Any one step in the series, if prevented from occurring, would also prevent the overall reaction from occurring. The overall process can be compared with an electrical series circuit where the various resistances are taken to represent the various kinetic steps leading to the overall reaction. If the resistance of a step is large, then it is considered to be a slow one. Just as the magnitude of the electric current passing through a series circuit is mainly determined by the largest resistance, similarly the slowest kinetic step has the strongest influence on the overall rate. The slowest kinetic step, which dictates the overall rate, is called the rate-controlling or the rate-limiting step. The conclusions arrived at would be quite different if the kinetic steps were in parallel instead of being in series. In this case, the step with the minimum resistance would influence the overall rate the most markedly; this is unlike the series situation, where the step with the maximum resistance is responsible for governing the overall rate. It is, difficult however, to conceive of a process which is either entirely series or entirely parallel in nature. Most processes encountered bear an analogy to a circuit having a series–parallel combination of resistances, and invariably the slowest step in series would be the rate-controlling one. An example of such a series–parallel combination is the desulfurization reaction in an iron blast furnace. The reaction is:

$$\text{S (liq. iron)} + \text{O}^{2-} \text{ (slag)} = \text{S}^{2-} \text{ (slag)} + \text{O (liq. iron)}$$

For the above reaction to proceed, oxygen should not be allowed to accumulate in the liquid iron. Its removal takes place by reaction with the other elements present in liquid iron:

$$\text{Mn (liq. iron)} + \text{O (liq. iron)} = \text{MnO (slag)}$$

$$\text{Si (liq. iron)} + 2\ \text{O (liq. iron)} = \text{SiO}_2 \text{ (slag)}$$

$$\text{C (liq. iron)} + \text{O (liq. iron)} = \text{CO (slag)}$$

All the above reactions are in parallel, but the individual steps in them as well as the kinetic steps of the sulfur oxidation reaction are in series.

In addition to the steps enumerated earlier, there are two other factors that may influence the overall reaction rate significantly; these are heat transfer and changes in the structure of solid during the reaction. Heat is either produced or consumed in many fluid–solid reactions. The heat of reaction has to be transferred from the surroundings to where the reaction occurs or vice versa. This transfer of heat involves: (i) convection and/or radiation between the surrounding and the surface of the solid; and (ii) conduction within the solid. This heat and the chemical reaction that takes place may bring about sintering or some other changes in the nature and extent of porosity in the solid. This would influence the overall reaction rate significantly.

3.16.1
Rate Equation

In general the rate equation for a heterogeneous reaction accounts for more than one process. The present consideration is directed to the general problem of combining the rates for processes of different kinds. Let r_1, r_2, ..., r_n be the rates of changes for the individual processes that are to be accounted for by an overall rate. If the changes occur by parallel paths, then the overall rate will be greater than the rate for any individual path. In fact, if the different parallel paths are independent of each other, the overall rate will be simply the sum of all the individual rates, or

$$r_{\text{overall}} = \sum_{i=1}^{n} r_{\text{i}}$$

On the other hand, if the overall change requires that a number of steps occur in succession, then at steady state all these steps will proceed at the same rate. Thus,

$$r_{\text{overall}} = r_1 = r_2 = \ldots = r_n$$

In some heterogeneous reactions, for instance, in noncatalytic fluid–solid reactions, the resistances to the reaction may be taken to occur in series. However, in some other reactions, such as catalytic solid–solid reactions, more complicated series–parallel relationships among the resistances must be considered.

It is important to appreciate the fact that when two or more reaction rates are to be compared and/or combined, they should be defined in the same manner. For instance, if it is required to combine a mass transfer step and a reaction step, then the rates corresponding to both should be defined in an identical manner. Since the mass transfer rate by definition is the flow of material per unit time normal to a unit surface

$$J_{\text{transfer}} = \frac{1}{S}\frac{\mathrm{d}N_{\text{i}}}{\mathrm{d}t}$$

the reaction rate should also be expressed in terms of unit area as

$$J_{\text{reaction}} = \frac{1}{S}\frac{\mathrm{d}N_{\text{i}}}{\mathrm{d}t}$$

rather than in terms of unit volume, as is customary for homogeneous reactions.

Another pertinent point is that while combining or comparing rates one often does not know the concentrations of materials at intermediate positions, and the rates have to be expressed in terms of the overall concentration differences. This can be readily done if the rate expressions for all the reactions under consideration are linear in concentrations or concentration differences. If some of the functional relationships are nonlinear, then the resultant rate expression may be very complicated.

As an example of combining linear rate expressions one could consider the irreversible reaction

$$g\ (\text{gas}) + s\ (\text{solid}) \rightarrow g'\ (\text{gas})$$

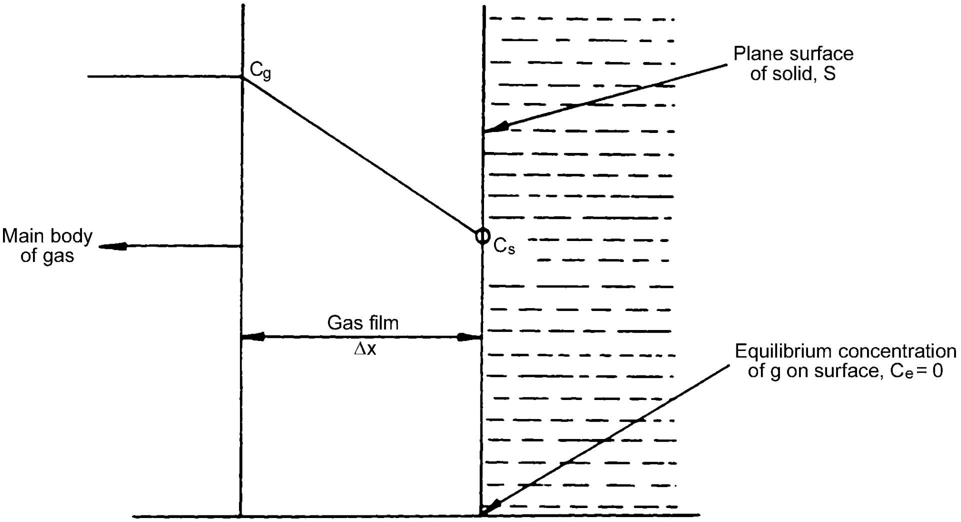


Figure 3.14 Schematic of a gas–solid reaction.

which takes place in the manner illustrated schematically in Figure 3.14. Atoms or molecules of the gas g diffuse from the main body of the gas through a stagnant gas film on to the plane surface of the solid s. On this surface the gas g reacts with the solid s to yield the gaseous product g′, which then diffuses back into the main body of the gas through the gas film adjacent to the solid surface. The flux of g diffusing to the surface of s would be given by

$$J_g = \frac{1}{s}\frac{dN_i}{dt} = -D\frac{\Delta C}{\Delta x} = -\frac{D}{\Delta x}(C_g - C_s) = -k_g\,(C_g - C_s)$$

The reaction under consideration is of the first order with respect to g and based on unit surface the reaction rate is given by

$$J_s = \frac{1}{S}\frac{dN_i}{dt} = -k_s\,C_s$$

where k_s is the reaction rate constant based on unit surface. Under steady-state conditions the rate of arrival of the gas to the surface should be equal to the reaction rate at the surface, the processes being in series. Therefore,

$$J_g = J_s$$

so that

$$k_g\,(C_g - C_s) = k_s\,C_s$$

One therefore obtains

$$C_s = \frac{k_g}{k_g + k_s}\,C_g$$

Thus,

$$J_g = J_s = \frac{1}{S}\frac{dN_i}{dt} = \frac{k_s\, k_g\, C_g}{k_g + k_s}$$

$$= -\frac{1}{1/k_g + 1/k_s} \cdot C_g = -k_o\, C_g$$

where k_o is the overall rate constant. It could be seen from this result that $1/k_g$ and $1/k_s$ are additive resistances. It so happens that the addition of resistances to obtain an overall resistance applies only to the situation where the rate is a linear function of the driving force and where the processes occur in series.

Next, as an example of combining nonlinear rate expressions one could consider the same reaction as before, assuming that the reaction is of the second order with respect to the gas phase reactant g. In this case, for the mass transfer step, one has

$$J_g = -k_g\,(C_g - C_s)$$

and for the reaction step

$$J_s = -k_s\, C_s^2$$

under steady-state conditions

$J_g = J_s$so that

$$k_g\,(C_g - C_s) = k_s\, C_s^2$$

Solving this quadratic equation in C_s one obtains

$$C_s = \frac{-k_g + (k_g^2 + 4\, k_s\, k_g\, C_g)^{0.5}}{2\, k_s}$$

Substitution of this value of C_s in the expression for J_g yields

$$J_g = J_s = -\frac{k_g}{2\, k_s}\,[2\, k_s\, C_g + k_g - (k_g^2 + 4\, k_s\, k_g\, C_g)^{0.5}]$$

It would be seen that if the individual rate expressions are not all linear, then the individual resistances are not additive but combine in a complex manner.

Chemical reaction rates may show large variations from reaction to reaction, and also with changes of temperature. It is often found that one or the other of the steps involved in the overall process offers the major resistance to its occurrence. Such a slow step controls the rate of the process. As a simplification such a rate-controlling step can be considered alone. In an alternative procedure the nonlinear relationship between rate and concentration is approximated to a linear relationship. To do this the nonlinear rate is expanded in the form of a Taylor's series and only the linear terms are retained.

Table 3.3 Noncatalyzed heterogeneous reaction types of importance in chemical metallurgy.

Reactions	***Type***	***Examples***	
Solid (S) → Gas (G)	1. Adsorption (physical and chemical)	Carbon reactions	$C + 0.5\ O_2 \rightarrow CO$
		Carbonyl formation	$Ni + 4\ CO \rightarrow Ni(CO)_4$
	2. $S + G_1 \rightarrow G_2$	Chlorination	$Nb + 2.5\ Cl_2 \rightarrow NbCl_5$ $Nb_2O_5 + 5\ C + 5\ Cl_2 \rightarrow 5\ CO$
		Fluorination	$UF_4 + F_2 \rightarrow UF_6$
	3. $G_1 \rightarrow S + G_2$	Decomposition of metal carbonyl	$Ni(CO)_4 \rightarrow Ni + 4\ CO$
	4. $S_1 + G \rightarrow S_2$	Oxidation of metals	$NX + 0.5\ m\ O_2 = X_nO_m$ (where X represents a metal)
		Reaction of oxides with sulfur oxide	$2\ Fe_3O_4 + 0.5\ O_2 = 3\ Fe_2O_3$
		Oxidation of sulfides to sulfates	$XS + 2\ O_2 \rightarrow XSO_4$ (where X represents a metal)
		Hydration of oxides	$MgO + H_2O \rightarrow Mg(OH)_2$
		Formation of calcium carbonitride	$CaC_2 + N_2 \rightarrow CaCN_2 + C$
		Formation of complex chlorides	$2\ KCl + TiCl_4 \rightarrow K_2TiCl_6$
		Ammoniation of phosphates	$NH_4H_2PO_4 + NH_3 \rightarrow (NH_4)_2HPO_4$
	5. $S_1 \rightarrow S_2 + G$	Decomposition reactions upon heating	$Al_2O_3 \cdot 2\ SiO_2 \cdot 2\ H_2O \rightarrow Al_2O_3 + 2\ SiO_2 + 2\ H_2O$ (kaolin) $FeS_2 \rightarrow FeS + S$ $CaCO_3 \rightarrow CaO + CO_2$ $Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3\ SO_3$
	6. $S_1 + G_1 \rightarrow S_1 + G_2$	Reduction of oxides	$MoO_3 + H_2 \rightarrow MoO_2 + H_2O$
		Reduction of halides	$FeCl_2 + H_2 \rightarrow Fe + 2\ HCl$
		Reduction of sulfides	$FeS_2 + H_2 \rightarrow FeS + H_2S$
		Oxidation of sulfides	$NiS_2 + H_2 \rightarrow NiS + SO_2$
		Miscellaneous	$2\ TaC + 4.5\ O_2 \rightarrow Ta_2O_5 + 2\ CO_2$ $ZrC + 2\ O_2 \rightarrow ZrO_2 + CO_2$
Solid (S) – Liquid (L)	1. $S \rightarrow L$	Melting	
	2. $S + L_1 \leftrightarrow L_2$	Dissolution–crystallization	
	3. $S + L_1 \rightarrow L_2$	Leaching	$CaCO_3 + 2\ H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$
	4. $S_1 + L_1 \rightarrow S_2 + L_2$	Cementation	$Cu + ZnSO_4 \rightarrow CuSO_4 + Zn$
Solid (S) – Solid (S)	1. $S_1 \rightarrow S_2$	Sintering; phase transformation	
	2. $S_1 + S_2 \rightarrow S_3 + G$	Reduction of oxides by carbon	$CaO + 3\ C \rightarrow CaC_2 + CO$
	3. $S_1 + S_2 \rightarrow S_3 + S_4$	Reduction of oxides by halides by metals	$Cr_2O_3 + 2\ Al \rightarrow Al_2O_3 + Cr$
Liquid (L) – Gas (G)	1. $L \leftrightarrow H$	Distillation–condensation absorption	
	2. $L_1 + G_1 \rightarrow L_2 + G_2$	Steelmaking pneumatically	L-D process for steelmaking
	3. $L_1 + G \rightarrow L_2$	Absorption of gases in water	Dissolution of gases like hydrogen chloride, ammonia and carbon dioxide in water
Liquid (L) – Liquid (L)	1. $L_1 \leftrightarrow L_2$	Solvent extraction	UO_2^{2+} (aq) + 2 NO_3^- (aq)+2 TBP (org) $\rightleftharpoons$ $UO_2(NO_3)_2 \cdot 2$ TBP (org)
		Slag-metal reactions	Electroslag refining
		Liquid metal-liquid metal extraction	Parkes process, (molten Zn is added to molten Pd containing Ag which is selectively transferred to Zn)

3.16.2
Types of Reactions

The various types of heterogeneous reactions are shown in Table 3.3. They are broadly grouped as solid–gas, solid–liquid, solid–solid, liquid–gas, and liquid–liquid reactions. The different types included in each group are also shown in the compilation. Some representative processes have been indicated as examples. It may be pointed out that in the group of solid–liquid reactions a specific mention of what is known as autocatalytic reactions has not been made. The autocatalytic processes occur when the liquid product reacts further with the solid undergoing reaction. The dissolution of copper in dilute sulfuric acid (or aqueous ammonia) in the presence of oxygen may be cited as an example:

$$\mathrm{Cu} + 2\ \mathrm{H}^+ + 0.5\ \mathrm{O}_2 \rightarrow \mathrm{Cu}^{2+} + \mathrm{H}_2\mathrm{O}$$

The cupric ions formed react further with metallic copper to form cuprous ions:

$$\mathrm{Cu} + \mathrm{Cu}^{2+} \rightarrow 2\ \mathrm{Cu}^+$$

which are readily oxidized by oxygen to regenerate the cupric ions:

$$2\ \mathrm{Cu}^+ + 2\ \mathrm{H}^+ + 0.5\ \mathrm{O}_2 \rightarrow 2\ \mathrm{Cu}^{2+} + \mathrm{H}_2\mathrm{O}$$

Therefore, the amount of copper dissolved will increase as the process continues.

Further discussions presented in this chapter on the kinetic aspects of heterogeneous reactions will be confined to fluid-particle reactions. The text will attempt to lay a foundation for the subject, and the background knowledge gained will be helpful in studying the kinetics and mechanisms of processes belonging to the other groups of reactions. A large amount of reference material is available with regard to each of these reactors.

3.16.3
Heat and Mass Transfer

The transfer of heat and/or of mass occurs in a variety of natural as well as man-made processes, and has an important bearing on many of the designs and processes pertinent to chemical metallurgy. In this context the laws of conservation of mass, energy and momentum play a vital role because the application of these fundamental principles enables one to determine how much mass, energy and momentum are transferred in any particular process. The job essentially involves the setting up of a balance between the quantities entering, leaving and being accumulated in the system. The rate of transfer has to be related to the driving force which brings about the transfer, and the relationships arrived at must be taken into consideration judiciously in order to work out the dimensions of the equipment to be used for accomplishing a particular task. The transfer of heat, mass and momentum, in the ultimate analysis, generally involve interactions at the molecular level.

In a practical sense, all operations that are carried out in metallurgy, chemical, engineering and many other disciplines involve the production or absorption of energy in the form of heat. The laws directing the transfer of heat and the types of systems that have for their main aim the control of heat flow are therefore of great consequential. When two bodies at different temperatures are brought into thermal communication, heat transfers from the body at higher temperature to that at the lower temperature. The resultant transfer is always in the direction of the temperature lowering. The mechanisms of heat transfer are three: conduction, convection, and radiation.

Heat *conduction* involves the transfer of energy from molecule to molecule in a substance, the direction of the energy transfer being down the temperature gradient. This is frequently the only heat transfer mechanism in solids. For example, the flow of heat through the brick wall of a furnace takes place by conduction as far as the solid wall is concerned. In liquids and gases (i.e., fluids), conduction usually operates in conjunction with other mechanisms. Convection involves the transfer of energy through the motion of fluid from high-temperature regions to low-temperature regions and vice versa; many molecules move as aggregates, carrying with them energy, mass, and momentum. The forces used to create *convection* currents in fluids are of two types. If the currents are the result of buoyancy forces produced by differences in density and the differences in density are in turn caused by temperature gradients in the fluid medium, the action is called natural convection. If the currents are set in motion by the action of a mechanical device, as for example, a pump or an agitator, the flow is independent of density gradients, the action is called forced convection. The heating of water by a hot surface is one of the very familiar examples of heat transfer mainly by convection. The flow of air across a heated radiator is an example of natural convection, while heat flow to a fluid pumped through a heated pipe is an example of forced convection. The two kinds of force may operate simultaneously in the same fluid, and natural and forced convection then occur together. It is very rare that heat transfers through fluids by pure conduction without some convection, this arising because of the eddies produced by the changes of density with temperature. Based on this fact, the terms "conduction" and "convection" are often used together, although in many cases as has already been pointed out as examples are preponderantly convection. *Radiation* refers to the transfer of energy through space by means of electromagnetic waves. If radiation is passing through empty space, it is not transformed to heat or any other form of energy, and it is not diverted from its path. If, however, matter appears in its path, the radiation will be transmitted, reflected, or absorbed. The absorbed energy is the one which quantitatively transforms into heat. For example, fused quartz transmits practically all the radiation heat that falls on it; however, a matte surface will absorb most of the radiation received by it and will transform such absorbed energy quantitatively into heat.

3.16.3.1 **Conduction**

The mechanism of conduction is most easily understood by the study of conduction through homogeneous isotropic solids, because in this case convection is not present. As a simple illustration of heat transfer by conduction, let a flat parallel-sided plate of a uniform solid material, whose flat faces are maintained at temperatures T_1 and T_2 respectively ($T_1 > T_2$) be considered (Figure 3.15). Heat would be transferred from the face at the higher temperature (T_1) to that at the lower temperature (T_2). Let the rate of this transfer be $\mathrm{d}Q/\mathrm{d}t$, and the area of the plate perpendicular to the direction of heat flow be S. If L is the plate thickness, then it is found that $\mathrm{d}Q/\mathrm{d}t$ is proportional to $(T_1 - T_2) \cdot S/L$. In other words,

$$\frac{1}{S} \cdot \frac{\mathrm{d}Q}{\mathrm{d}t} \propto -(T_2 - T_1)/L$$

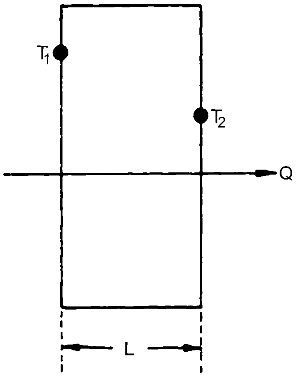


Figure 3.15 Heat transfer by conduction through a parallel-sided plate.

Let an element of the plate of thickness dL be considered, and let the temperature difference across this element be dT, then

$$\frac{1}{S}\cdot\frac{\mathrm{d}Q}{\mathrm{d}t} \propto -\frac{\mathrm{d}T}{\mathrm{d}L}$$

This means that the heat transfer flux is proportional to the negative temperature gradient. If the positive L direction is chosen as the direction of heat flow, then temperature decreases along this direction and dT/dL is negative. One can write

$$\frac{1}{S}\cdot\frac{\mathrm{d}Q}{\mathrm{d}t} = -k\frac{\mathrm{d}T}{\mathrm{d}L}$$

The constant of proportionality k is known as the thermal conductivity of the material and the above relationship is known as Fourier's law for conduction in one dimension. The thermal conductivity k is the heat flux which results from unit temperature gradient in unit distance. In s.i. units the thermal conductivity, k, is expressed in $\mathrm{Wm^{-1}\,K}$. Integration of Fourier's law yields

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{T_1 - T_2}{L/k\,S} = \frac{T_1 - T_2}{R}$$

In this rate equation ($T_1 - T_2$) represents the driving force and $L/k\ S$ (= R) represents the thermal resistance for conduction.

Now, let heat flow by conduction through a flat wall consisting of three parallel-sided layers of thicknesses L_1, L_2 and L_3 be considered (Figure 3.16). Let the thermal conductivities of the three layers be k_1, k_2, and k_3 respectively. Let δT_1 be the drop in temperature across the first layer, δT_2 that across the second layer, and δT_3 that across the third layer. If δT is the total temperature drop over all the three layers then

$$\delta T = \delta T_1 + \delta T_2 + \delta T_3$$

Considering that heat flow occurs through an area S in all the layers, one can write by applying Fouriers' law

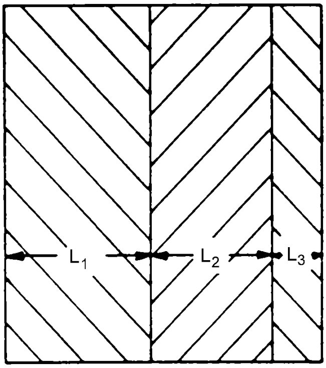


Figure 3.16 Thermal resistances in series.

$$\delta T_1 = \frac{L_1}{k_1\, S} \cdot \frac{\mathrm{d}Q_1}{\mathrm{d}t}$$

$$\delta T_2 = \frac{L_2}{k_2\, S} \cdot \frac{\mathrm{d}Q_2}{\mathrm{d}t}$$

$$\delta T_3 = \frac{L_3}{k_2 S} \cdot \frac{\mathrm{d}Q_3}{\mathrm{d}t}$$

where $\mathrm{d}Q_i/\mathrm{d}t$ gives the rate of heat flow across the ith layer. Adding the above expressions one obtains

$$\delta T = \delta T_1 + \delta T_2 + \delta T_3 = \frac{L_1}{k_1\, S} \cdot \frac{\mathrm{d}Q_1}{\mathrm{d}t} + \frac{L_2}{k_2\, S} \cdot \frac{\mathrm{d}Q_2}{\mathrm{d}t} + \frac{L_3}{k_3\, S} \cdot \frac{\mathrm{d}Q_3}{\mathrm{d}t}$$

Since the heat that passes through the first layer must pass through the second and subsequently through the third layer, one must have

$$\frac{\mathrm{d}Q_1}{\mathrm{d}t} = \frac{\mathrm{d}Q_2}{\mathrm{d}t} = \frac{\mathrm{d}Q_3}{\mathrm{d}t} = \frac{\mathrm{d}Q}{\mathrm{d}t}$$

In view of the above, one arrives at the result

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{\delta T}{L_1/k_1\, S + L_2/k_2\, S + L_3/k_3\, S} = \frac{\delta T}{R_1 + R_2 + R_3}$$

where R_1, R_2 and R_3 are the thermal resistances for conduction for the three layers. This shows that the overall resistance equals the sum of the individual resistances, analogous to the case of the flow of electric current through a series combination of resistances.

In the case of a porous solid, the rate of heat transfer by conduction can be expressed in the following manner:

$$\frac{\text{Heat transfer rate per unit area}}{\text{Temperature gradient}} = -k_e$$

where k_e is the effective thermal conductivity and the gas in the pore space is assumed to be in thermal equilibrium with the solid.

It may be pointed out here that estimating k_e in terms of the thermal conductivity of the solid (k) and its porosity (ε) may be quite difficult, particularly when the porous solid is an aggregate of fine particles.

3.16.3.2 **Convection**

Let a simple case of heat transfer by convection be considered. Let it be assumed that the surface of a solid at temperature T_1 is in contact with a flowing fluid at temperature T_2 ($T_1 > T_2$) as indicated in Figure 3.17. Let $\mathrm{d}Q/\mathrm{d}t$ represent the rate of heat transfer by convection from the solid over a finite area of solid–fluid contact, S. In such a situation it is found in many cases that $\mathrm{d}Q/\mathrm{d}t$ is proportional to $S \cdot (T_1 - T_2)$, so that

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = h\,S\,(T_1 - T_2)$$

Here the proportionality constant h is called the convective heat transfer coefficient. In S.I. units, h is expressed in Wm^{-2} K. The rate equation may be expressed as

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{(T_1 - T_2)}{1/h\,S} = \frac{T_1 - T_2}{R}$$

The temperature difference, $T_1 - T_2$, is the driving force in this case, the quantity $1/h\,S$ ($= R$), is known as the thermal resistance for convective heat transfer, and h is called the surface coefficient.

The treatment given above is a very simplified one. It may be recalled that when fluid flow is of such a nature that the value of the Reynolds number exceeds a certain critical value, the character of the flow changes from viscous flow to turbulent flow. Even when

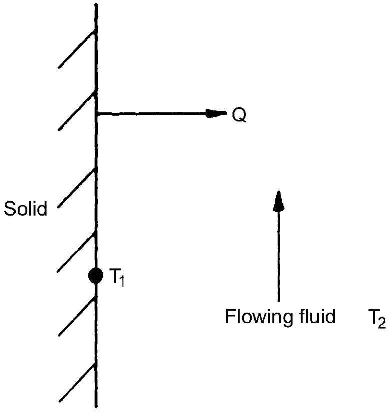


Figure 3.17 Heat transfer by convection.

turbulent flow occurs, there remains a thin fluid film adjacent to the wall of the container which persists in exhibiting viscous flow. In turbulent flow, the turbulence may be caused by various means by using an agitator or a stirrer, by pumping the fluid through a pipe (forced convection), by the convection currents set up when an otherwise static body of fluid is heated (natural convection) and so on. When heat passes through the container wall into the fluid, the relatively stagnant fluid film adjacent to the wall plays an important role in determining the rate at which heat is this film by conduction and the thermal conductivities of fluids are rather low. Even though the film is usually quite thin, because of its poor thermal conductivity it offers a large resistance to the flow of heat. Beyond this film, a rapid equalization in temperature is brought about by the turbulence. The temperature distribution across a column of flowing fluid, which is being heated or cooled, depends on the velocity distribution across the same column of fluid. Let a situation be considered where heat flows from a hot fluid into a cold fluid through a solid conducting wall. The temperature gradients corresponding to this situation are shown schematically in Figure 3.18. The broken lines *aa* and *bb* on the two sides of the wall represent the boundaries of the fluid films exhibiting viscous flow. All parts of the fluids to the right of aa and to the left of bb are in turbulent flow. The temperature gradient from the bulk of the hot fluid to the solid wall is represented in Figure 3.18 by the profile T_A T_B T_C; T_A is the maximum temperature in the hot fluid, T_B is the temperature at the boundary of the viscous film aa, and T_C is the temperature at the interface of the solid wall and the fluid film. Likewise, the profile T_D T_E T_F represents the temperature gradient from the solid wall to the bulk of the cold fluid. In heat

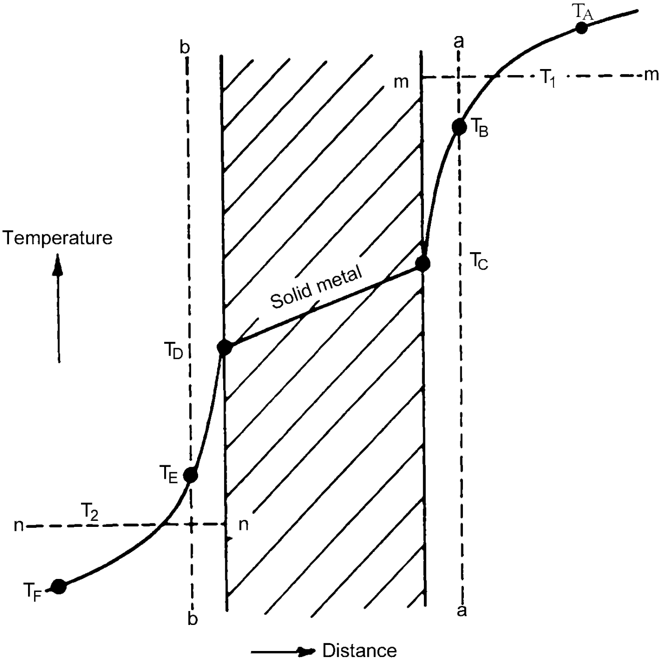


Figure 3.18 Temperature gradients in forced convection.

transfer calculations the temperature of the fluid is taken to be the average temperature which would be obtained by completely mixing the fluid. On the right-hand side of the wall let this average fluid temperature be denoted by T_1 ($T_A > T_1 > T_B$) which is indicated by the straight line mm in Figure 3.18. Similarly, the average temperature of the colder fluid on the left of the wall is taken to be T_2 ($T_E < T_2 < T_F$) which indicated by the horizontal line nn in Figure 3.18. Inside the wall, the temperature gradient T_C T_D is due to heat flow by conduction. In most cases ($T_C - T_D$) is much less than ($T_A - T_F$). Let it be assumed that the rate of flow of heat from the hot to the cold fluid is given by $\mathrm{d}Q/\mathrm{d}t$. This must be the same as the rate of heat flow from the hot fluid to the wall and from the wall to the cold fluid. Let the area of the wall on the high temperature side, in a plane normal to the heat flow direction, be S_1 and let the area on the low temperature side be S_2; then the surface coefficient on the hot side is given by

$$h_1 = \frac{1}{S_1\,(T_1 - T_C)} \cdot \frac{\mathrm{d}Q}{\mathrm{d}t}$$

and similarly, the surface coefficient on the cold side is given by

$$h_2 = \frac{1}{S_2\,(T_D - T_2)} \cdot \frac{\mathrm{d}Q}{\mathrm{d}t}$$

If the average area of the solid wall be S_m, then the thermal resistance of the wall would be $L/k\,S_m$. Thus in the situation represented by Figure 3.18 one has to deal with three thermal resistances: that on the side of the hot fluid ($1/h_1\,S_1$), that of the solid wall ($L/k\,S_m$), and that on the side of the cold fluid ($1/h_2\,S_2$).

Drawing an analogy with the case of heat flow by conduction through a three-layered wall discussed earlier, one can write

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{\delta T}{\left(\dfrac{1}{h_1\,S_1}\right) + \left(\dfrac{L}{k\,S_m}\right) + \left(\dfrac{1}{h_2\,s_2}\right)}$$

Multiplying the numerator and the denominator on the right-hand side of the above expression by the area S_1,

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{S_1 \cdot \delta T}{\left(\dfrac{1}{h_1}\right) + \left(L\,\dfrac{S_1}{k\,S_m}\right) + \left(\dfrac{S_1}{h_2\,S_2}\right)}$$

One can now define the overall heat transfer coefficient U_1 as

$$U_1 = \frac{1}{\left(\dfrac{1}{h_1}\right) + \left(\dfrac{L\,S_1}{k\,S_m}\right) + \left(\dfrac{S_1}{h_2\,S_2}\right)}$$

so that

$$\frac{dQ}{dt} = U_1\ S_1\ \delta T$$

From this relationship it is clear that the rate of heat transfer is the product of three factors: the overall heat transfer coefficient; the area of the hot surface; and the temperature drop. If instead of S_1 either S_2 or S_m had been chosen, one would have obtained the heat transfer coefficients based on these areas, namely, U_2 or U_m. It follows that a definite area must be chosen and that the overall heat transfer coefficient is automatically based on the chosen area. The choice is, in general, arbitrary.

In a situation where the solid wall is tubular in shape, L is the wall thickness, S_1 is proportional to the corresponding diameter d_1, and S_2 is proportional to its corresponding diameter d_2.

In this case,

$$U_1 = \frac{1}{\left(\frac{1}{h_1}\right) + \left(d_1\ \frac{L}{d_m\ k}\right) + \left(\frac{d_1}{d_2\ h_2}\right)}$$

and similar equations can be written for U_2 and U_m.

Any relationship used for the prediction of the surface coefficient in a given situation must take into consideration the various properties of the fluid and the conditions of its flow germane to the problem. The factors to be considered might comprise the pipe diameter and various characteristics of the fluid such as its density, its viscosity, its thermal conductivity, its specific heat and so on. Very often problems relating to heat transfer are very complex and it is not feasible to assemble these factors in the form of an equation that is entirely based on theoretical reasoning. A very useful method for arranging these properties in an equation is that of dimensional analysis. This method shows in what relation to each other some of these factors should appear and makes it possible to arrange them into various "dimensionless" groups. A brief discussion on such groups has been provided in a later section.

3.16.3.3 **Radiation**

The transfer of heat by radiation in general can be said to occur simultaneously with heat transfer by convection and conduction. Transfer by radiation tends to become more important than that by the other two mechanisms as the temperature increases. It is useful to gain an appreciation of the basic definitions of the energy flux terms, the surface property terms and their relationships while discussing radiative heat transfer. With this objective, reference may be made to Table 3.4 in which these are presented.

The amount and type of thermal energy radiated by a surface increase rapidly with temperature. For solid surfaces and for liquids (other than those occurring in the form of extremely thin films), the radiant energy emitted is continuous and is distributed over all wavelengths. The major portion of the energy, however, is concentrated within a relatively narrow range of wavelengths. The amount of energy in the range of visible radiation is negligible compared to that associated with thermal radiations. In this context it is useful to refer to Figure 3.19 which shows the effect of temperature on the amount and the distribu-

Table 3.4 Basic definitions.

Terms	*Symbol*	*Definition*	*Remarks*
Emissive power	E	Total thermal radiation energy emitted by a surface per unit time per unit surface area	The three terms, Emissive power (E), Irradiation (G), and Radiosity (J) are all energy fluxes (i.e., rate of energy transfer per unit area). The three terms, Absorptivity (α), Reflectivity (ρ), and Transmissivity (τ), are all surface properties and are dimensionless
Irradiation	G	Total thermal radiation energy incident on a surface per unit time per unit area	
Radiosity	J	Total thermal radiation energy leaving a surface (emitted and reflected) per unit time per unit area	
Absorptivity	α	Fraction of incident radiant energy which is absorbed	
Reflectivity	ρ	Fraction of incident radiant energy which is reflected	
Transmissivity	τ	Fraction of incident radiant energy which is transmitted	

Relationships: (i) $G = \alpha G + \rho G + \tau G$, $1 = \alpha + \rho + \tau$, for opaque solids $\tau = 0$
Therefore $1 = \alpha + \rho$, (ii) $J = E + \rho G$

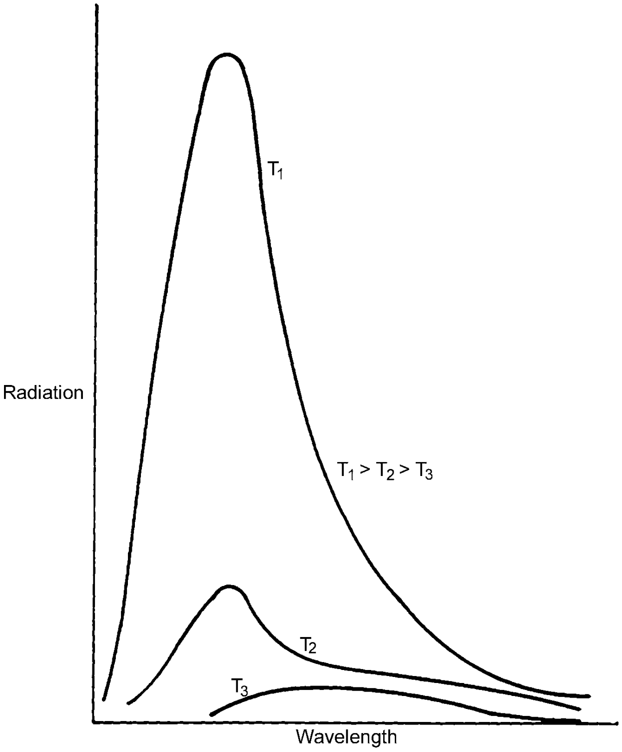


Figure 3.19 Influence of temperature on amount and distribution of black-body radiation.

tion of black body radiation (a black body is defined later). It is seen that each of the curves has a maximum, and that the wavelength corresponding to the maximum shifts to lower values as the temperature increases. The total energy emitted by the surface per unit time per unit area (of surface) is represented by the area under each curve.

When the quantity of energy radiated by a hot body is referred to, it is necessary to make some specifications regarding its physical condition. Not all substances radiate to the same extent at a given temperature. The theoretical substance on which all references are based is called a "black body". This is defined as that body which radiates the maximum possible amount of energy at a given temperature. No actual physical substance is a perfect black body. Further, the term is not related to the colour of the body. If only visible light is taken into consideration black matte substances approach a black body, and light-coloured substances show a wide deviation from it. The name bears this origin. If, however, only thermal radiation is considered, the colour of the body is not related to the quantity of energy it radiates. The inside of a furnace maintained at a uniform temperature, when observed through a small opening, constitutes a black body.

The total quantity of radiation emitted by a black body can be calculated by integrating the curves of Figure 3.19. This has been supplemented by experimental data. The result is the Stefan–Boltzmann law, which is given by

$$Q = b\, S\, T^4$$

where Q is the energy radiated per unit time, S is the area of the radiating surface, and T is its absolute temperature. For black bodies the value of b, the Stefan–Boltzmann constant, is $5.6699 \cdot 10^{-8}\ \mathrm{W/(m^2)(K^4)}$. No actual body radiates quite as much as the black body. For a nonblack body the energy radiated can be expressed as

$$Q = \varepsilon\, b\, \mathrm{S}\, \mathrm{T}^4$$

where ε is the emissivity of the body. ε is defined as the ratio of the emissive power of a body to that of a black body at the same temperature; it is always less than unity, and is also dimensionless.

The energy radiated by a hot body has been the main point of coverage in the presentation made so far. Let attention be now focused on the receipt of energy by a cooler body. When radiation falls on such a body, some of the incident radiation is absorbed to heat, some is reflected, and some may be transmitted. Most opaque solids generally transmit only a negligible amount of the radiation falling on them. The fraction of the incident radiation that is absorbed by a body, is represented by α, its absorptivity, which is always less than unity. If the transmitted radiation is omitted from the present account, it is clear that the sum of the quantities of energy absorbed and reflected by a body should be equal to the radiant energy falling on it. It may be pointed out that it is the complication due to the reflected energy that makes the numerical solution of practical problems rather complicated.

It can be shown that for any substance, (α) is equal to (ε), provided that these quantities are referred to the same temperature. From this result it follows that for a black body, both ε and α must be unity. A black body, therefore, absorbs all the radiation falling on it. This is an important characteristic of a black body.

The value of α for a given surface at a given temperature varies somewhat with the wavelength of the radiation involved. This introduces further complications in practical problems and to avoid them the concept of a "gray body" has been introduced. The absorptivity of such a body at a given temperature is taken to be constant for radiations of all wavelengths.

Let a small black body of area S and at temperature T_2, completely enveloped by a hotter black body at temperature T_1, be considered. In this case, the net amount of heat transferred from the hotter to the colder body equals the algebraic sum of the radiations from the two bodies and is given by

$$Q = b\,S\,(T_1^4 - T_2^4)$$

A qualitative interference that can be drawn from Stefan's law pertains to the effect of high absolute temperatures on the quantities of heat radiated. This aspect is of great practical importance. As the temperature of a body is raised above that of its surroundings, the amount of heat it can radiate to them increases at a phenomenal rate.

The contents in foregoing sections have dealt mainly with the various heat transfer mechanisms. One encounters a inexhaustive virtually list of their applications; examples include conduction in electric-resistance heaters; conduction-convection in heat exchangers (single pass 1-1 exchanger, 1-2 parallel-counter flow heat exchanger), boilers, and condensers (these are special heat-transfer devices used to liquefy vapours by removing their latent heats; typical examples include shell-and-tube condensers and contact condensers); radiation in furnaces and radiant-heat dryers; and of such special methods as dielectric heating. It is often the fact that the device operates under steady-state conditions, but in many processes it works cyclically (typical examples include regenerative furnaces and agitated process reactors).

3.16.3.4 **Mass Transfer by Diffusion**

Just as heat transfer refers to the energy transfer within a system or between a system and its surroundings occurring because of a difference in temperature, mass transfer refers to the transfer of mass (i.e., matter) which occurs within a system or between the system and its surroundings due to a difference in the concentration of a particular component between two points which are not in equilibrium.

In most unit operations it is of considerable importance that material is transferred from one phase to another across a boundary. The transfer of material from a solid phase to a liquid phase (as typically in leaching), or the transfer of material between one liquid phase to another liquid phase (as typically in molten metal and molten slag phases), extraction or between liquid and vapor phases (as typically in distillation) are well-known examples encountered in practice.

The problems relating to mass transfer may be elucidated out by two clear-cut yet different methods: one using the concept of equilibrium stages, and the other built on diffusional rate processes. The selection of a method depends on the type of device in which the operation is performed. Distillation (and sometimes also liquid extraction) are carried out in equipment such as mixer settler trains, diffusion batteries, or plate towers which contain a series of discrete processing units, and problems in these spheres are usually solved by equilibrium-stage calculation. Gas absorption and other operations which are performed in packed towers and similar devices are usually dealt with utilizing the concept of a diffusional process. All mass transfer calculations, however, involve a knowledge of the equilibrium relationships between phases.

A limit to mass transfer is attained if two phases come to equilibrium and the net transfer of material comes to a halt. For a process in practice, which must have a reasonable production rate, equilibrium must be avoided, as the rate of mass at any point is proportional to the compelling or driving force, which is the departure from equilibrium at that point. In order to evaluate driving forces, a knowledge of equilibria between phase is therefore fundamentally important. Several kinds of equilibria are important in mass transfer.

One important mechanism by which mass transfer occurs is diffusion. An experiment to provide an elementary but quite effective description of the mechanism is depicted in Figure 3.20. It shows a pipe with a transparent wall partitioned into two compartments by a removable barrier. One compartment contains a coloured gas *A*, while the other contains a colourless gas *B*. The gas molecules on both sides of the barrier are in constant motion, and on removing the barrier, *A* molecules begin to move into the right-hand half of the pipe and *B* molecules into the left. This is seen as the movement of the colouration to the right, and ultimately the colour becomes uniform throughout the container. The diffusion (of *A* to the right and of *B* to the left) can be thought of as being propelled by concentration gradients. Let a quantitative examination of this phenomenon be attempted by defining the flux of *A* molecules to the right. It is assumed that counting the number of molecules of *A* passing during a brief time interval to the right through some imaginary plane perpendicular to the axis of the pipe and placed at an arbitrary position is possible. The number counted is divided by Avogadro's number, the length of the brief time interval, and the cross-sectional area of the pipe. The number that is obtained by doing so is called the molar flux of *A* at some imaginary plane; let this quantity be represented by the symbol J_A. This flux has the dimensions of moles per unit area per unit time. According to the given definition, the flux J_A is an intensive measure of the rate of diffusion at the point in question.

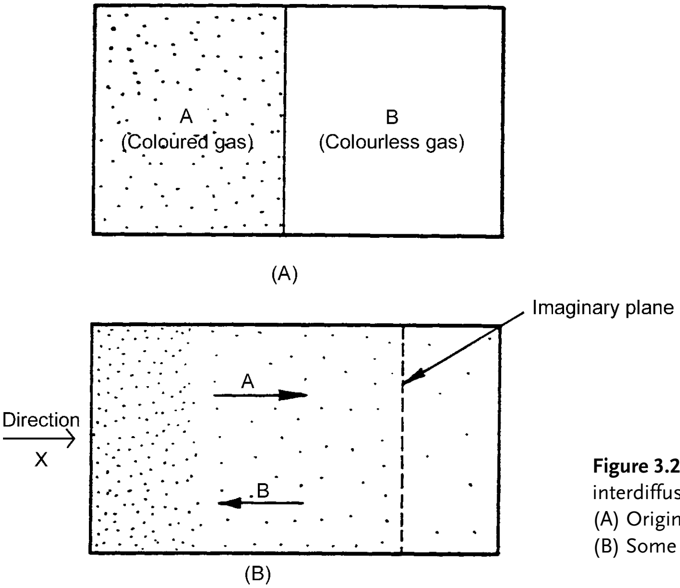


Figure 3.20 Diffusion illustrated by interdiffusion of (A) and (B).
(A) Originally.
(B) Some time after removal of partition.

To inject a general note it may be pointed out that two very important laws, called Fick's laws, form the basis of diffusion theory. The first law can be expressed in the following form:

$$J = -D\frac{\mathrm{d}C}{\mathrm{d}x}$$

where J is the mass of diffusing species passing in unit time through unit area of a plane positioned perpendicularly to the direction of diffusion. The term, J, is identified as the "flux", and is proportional to the concentration gradient $\mathrm{d}C/\mathrm{d}x$ across the plane, where the concentration of the species is C, x is the distance measured in the direction of diffusion. The diffusion coefficient or diffusivity is the constant of proportionality D. In a particular condition, D is the value of J when unit concentration gradient establishes at the plane of measurement. The first law is similar to that relating to the flow of an electric current along a conductor and also the heat transfer by conductance. The second law can be expressed in the following form:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$$

where $\frac{\partial C}{\partial t}$ is the rate of increase in concentration of the diffusion species in a given volume, and is equal to the difference between the flux entering the volume and that going out of the volume, $-\frac{\partial J}{\partial x}$. The equation of above can be written in the following form:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

where D is considered to be constant at constant temperature. It is, however, usually found that D is not constant and varies with the concentration. On account of the difficulty in measuring flow rates under fixed concentration gradients, it is more convenient to apply to Fick's second law and measure the change in concentration with time. Solution of the different equations generated can be achieved under certain boundary conditions which can be closely matched approximately in experimental procedures. The diffusion coefficient or diffusivity is linked to temperature by an expression as given below:

$$D = D_0 \exp\left(-\frac{E_0}{RT}\right)$$

where E_0 is the activation energy for diffusion. The given expression is similar to the well-known Arrhenius equation. The activation energy, E_0, in the solid state represents the energy needed to move the diffusing species from its lower energy site, force neighbouring species apart, and traverse through a transition state which is significantly similar to an activated complex.

Based on Fick's laws, the mathematical representation for the illustration taken is as follows:

$$J_A = -D_{A-B}\,\frac{dC_A}{dx}$$

The subscript A on J shows that it is a flux of A in the x direction of making measurement. The minus sign occurs because the flux is a positive number while the gradient dC_A/dx is negative. If the proportionality constant D_{A-B} is to be positive, the minus sign is a must. The diffusivity or the diffusion constant for the gas pair *A–B* is D_{A-B}; it does not depend on the concentration gradient and (in this case) on the concentration itself, although it does depend on temperature and total pressure. A similar equation can be written to describe the diffusion of *B*:

$$J_B = -D_{A-B}\,\frac{dC_B}{dx}$$

In the experiment described in Figure 3.20 the concentration gradient of *B* is positive, which implies that the last equation indicates a negative flux for the *B* molecules. This is so because diffusion in the positive x direction is treated as positive, and *B* is diffusing in the opposite direction.

The differences in intrinsic diffusivities of components in a two-component mixture give rise to an interesting effect known as the Kirkendall effect. A traditional description of this effect is borne out in terms of the interdiffusion in two metal bars (e.g., *A* and *B*, as shown in Figure 3.21) that are joined to produce a diffusion couple. Markers (such as a metal in the wire form that does not dissolve in either metal) are put at the interface. The two species *A* and *B* diffuse into each other when the assembly is held at some elevated temperature. It is assumed that diffusivity of *A* in *A–B* alloys exceeds that of *B*, so that the flux of *A* to the right past the markers shown in Figure 3.21 exceeds the flux of *B* to the left. The resultant effect is a displacement of the center of mass of the couple with respect to the markers. Indeed, if the marker wires extend outside the couple and the wires were used to suspend the couple, there would be a measurable displacement of the couple to the right by the couple. In practice, it is more common for the couple to be fixed with respect to the laboratory (e.g., by clamping an end of the couple, or merely resting the couple on a surface and relying on friction to immobilize it); whereupon there will be movement of markers with respect to the laboratory. This displacement of marker is more than a laboratory curiosity.

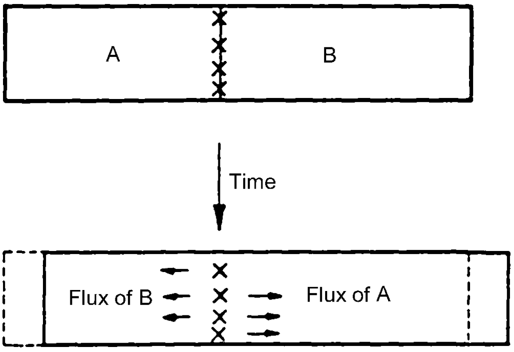


Figure 3.21 Kirkendall effect shown by the movement of inactive markers originally at the interface between two interdiffusing species.

It can be well utilized to identify the transport mechanisms involved with the oxidation of metals. What happens when markers are attached to the surface of a metal which is then exposed to an oxidizing environment is shown in Figure 3.22. The metal is one of many which forms a dense protective oxide film rather than a porous one. Following formation of the protective film, further oxidation is slowed because diffusion must take place through the oxide layer. Two situations can now be envisaged. In the first, as shown in Figure 3.22, metal atoms can diffuse through the oxide film to encounter oxygen with which they react at the outside surface of the oxide layer. In the second, oxygen can diffuse through the oxide film to meet unreacted metal atoms at the metal–metal oxide interface, whereupon reaction occurs at that site. It should be clear that if, as shown in the figure, the first possible mechanism of diffusion were to be operative, the markers would remain at the metal–metal oxide interface. If, on the other hand, the second mechanism operates, the markers would reside at the outside surface. Since the diffusion coefficients of oxygen in metal oxides are small compared to metal diffusion coefficients in the oxide lattice, the most common location of the markers is close to the metal–metal oxide interface.

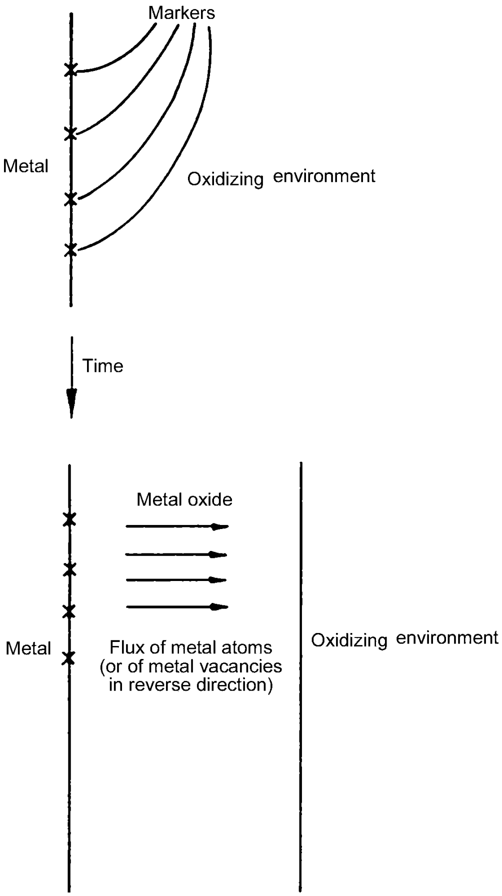


Figure 3.22 Illustration to show how marker experiments can identify the diffusing components (in the case considered they are the metal atoms) during oxidation process.

3.16.3.5 Forced Convection

Consider a situation where a fluid flows past a solid surface from which a component A is being transferred. Such a situation can be encountered in simple processes like drying or dissolution. The bulk of the fluid can be considered to be in turbulent flow, while there is a laminar film adjacent to the solid surface. The major change in the concentration of component A occurs across this laminar film. It is found that the rate of transfer of A (denoted by $\mathrm{d}N_\mathrm{A}/\mathrm{d}t$) is proportional to the surface area, S, and to the difference in the concentration of A in the fluid adjacent to the solid surface and that in the bulk of the fluid. Denoting these concentrations as C_As and C_Ab respectively (Figure 3.23), one can write

$$\frac{\mathrm{d}N_\mathrm{A}}{\mathrm{d}t} \propto S\,(C_\mathrm{As} - C_\mathrm{Ab})$$

or

$$\frac{\mathrm{d}N_\mathrm{A}}{\mathrm{d}t} = k_\mathrm{m}\,S\,(C_\mathrm{As} - C_\mathrm{Ab})$$

where k_m is the mass transfer coefficient corresponding to forced convection. In S.I. units the mass transfer coefficient can be expressed in m s^{-1}. The relationship can also be expressed as

$$n_\mathrm{A} = \frac{1}{S}\frac{\mathrm{d}N_\mathrm{A}}{\mathrm{d}t} = k_\mathrm{m}\,S\,(C_\mathrm{As} - C_\mathrm{Ab})$$

where n_A is a measure of the rate at which mass is transferred per unit surface area of the solid.

The above relationship can also be expressed as

$$\frac{\mathrm{d}N_\mathrm{A}}{\mathrm{d}t} = \frac{(C_\mathrm{As} - C_\mathrm{Ab})}{1/k_\mathrm{m}\,S}$$

In this expression, the numerator corresponds to the "driving force" and the denominator to the "resistance". The mass transfer coefficient, km, has the dimensions of length divided by time which is implied in the unit by which it is expressed.

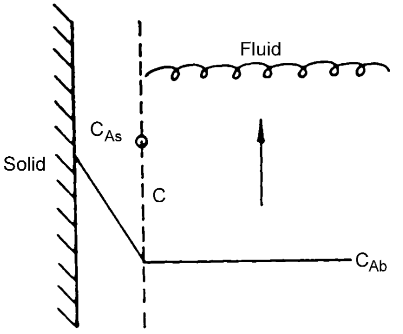


Figure 3.23 Mass transfer by forced convection.

3.16.4
Dimensionless Groups

All physical quantities are measured in appropriate units. These units can be divided into two categories: fundamental or primary units; and derived or secondary units. The latter can be expressed in terms of the former. The choice of primary units is based largely on convenience and may be quite arbitrary; commonly used primary units include those pertaining to length, mass, time and temperature.

All equations that can be derived analytically from basic physical laws are made up of terms that have the same dimensions; in other words, such equations are dimensionally homogeneous. Provided that the same primary units of mass, length, time, temperature, etc. are used throughout, a dimensionally homogeneous equation can be used without regard to conversion factors for any set of primary units. Units satisfying this requirement are called consistent units. Relationships obtained by empirical methods, in which experimental data are correlated by using empirical equations, which are not necessarily dimensionally consistent, are often dimensionally nonhomogeneous and contain terms of varying dimensions. In such dimensionally nonhomogeneous equations there is no advantage in using consistent units; two or more units of length, time etc. may appear in the same equation.

Many physical problems are encountered in engineering, particularly in the context of heat and mass transfer, which cannot be solved fully by mathematical methods or for which no basic theoretical equations can be written. One method of dealing with such problems is that of empirical experimentation. However, this procedure may be extremely laborious, and it may be difficult to process the experimental data into useful relationships that can be used for practical calculations. For tackling problems of this type the method of dimensional analysis often proves to be of great value. This method makes use of the fact that, if a theoretical equation connecting the variables pertinent to a physical process does exist, it must be dimensionally homogeneous. This requirement of dimensional homogeneity makes it possible to gather many factors into a smaller number of dimensional groups of variables. In any given problem, the numerical values of these groups are independent of the dimension system used and the groups themselves, rather than the separate individual factors, appear in the final relationship. Thus the number of independent variables pertinent to the problem is very significantly reduced. Dimensional analysis, which is intermediate between a formal analytical approach and a completely empirical approach, does not usually yield a numerical equation and experimentation must be resorted to in order to complete the solution to the problem. However, the results of such an analysis are available in guiding the experiments and in correlating the experimental data into forms suitable for engineering use.

A number of important dimensionless groups have been arrived at by dimensional analysis and by other means. The numerical value of such a dimensionless group for a given case is independent of the units chosen for the primary quantities as long as consistent units are used within that group. The units used in one group need not be consistent with those used in another.

It must be emphasized that dimensional analysis is used to find the minimum number of dimensionless groups of all the variables known to be relevant to the description of a physical situation and to find the forms of these groups in terms of the specified dimensional variables. However, this analysis cannot be used to determine whether some relevant variables have been left out or whether some irrelevant variables have been included. Neither does this analysis provide guidance as to the most convenient forms of the dimensional groups.

A theorem known as Buckingham's π theorem is very pertinent in the context of dimensionless groups. According to this theorem the number of dimensionless groups is equal to the difference between the number of variables and the number of dimensions used to express them. Any physical equation can be expressed in the form

$$f(\nu_1, \nu_2, \dots \nu_m) = 0$$

where the m variables ν_i ($i = 1, 2, \dots m$) occur in the equation. If the dimensions of these m variables are expressed in terms of n fundamental quantities, then the equation can be transformed to one which contains (m-n) dimensionless groups, $\pi_1, \pi_2, \dots \pi_{m-n}$:

$$F\,(\pi_1, \pi_2, \dots \pi_{m-n}) = 0$$

In this new equation each π term is composed of $(n + 1)$ variables.

Some of the important dimensionless groups pertinent to heat and mass transfer problems are listed in Table 3.5.

In the Rayleigh method of carrying out a dimensional analysis the dependent variable is assumed to be proportional to the product of the independent variables raised to different powers. By equating dimensions, the number of independent dimensionless groups and one set of their possible forms can be obtained. By way of illustration two examples may be considered.

The first example pertains to forced convection in pipe flow. It is found that the rate of heat transfer between the pipe wall and a fluid flowing (turbulent flow) through the pipe depends on the following factors: the average fluid velocity (u) the pipe diameter (d) the

Table 3.5 Some important dimensionless groups.

Name	***Formula***	***Symbol***
Nusselt number	$h\,d/k$	Nu
Reynolds number	$d\,u\,\rho/\mu$	Re
Prandtl number	$C\,\mu/k$	Pr
Grashof number	$g\,d^3\,\beta\,\Delta T\,\rho^2/\mu^2$	Gr
Sherwood number	$k_m\,d/D$	Sh
Schmidt number	$\mu/\rho\,D$	Sc

h	heat-transfer coefficient	μ	viscosity
k_m	mass-transfer coefficient	C	specific heat at constant pressure
d	diameter	g	acceleration due to gravity
k	thermal conductivity	β	coefficient of thermal expansion
u	linear velocity	ΔT	temperature difference
ρ	density	D	diffusivity

fluid density (ρ) the fluid viscosity (μ) the fluid thermal conductivity (k) and the fluid specific heat (C). These variables have to be related to the heat transfer coefficient, h. Following the Rayleigh method, one can write

$$h = K\, u^{\mathrm{m}}\, d^{\mathrm{n}}\, \rho^{\mathrm{p}}\, \mu^{\mathrm{q}}\, k^{\mathrm{r}}\, C^{\mathrm{s}}$$

where K is a dimensionless constant.
From this one has the dimensional relation

$$M\, t^{-3}\, T^{-1} = (L\, t^{-1})^{\mathrm{m}} (L)^{\mathrm{n}} (M\, L^{-3})^{\mathrm{p}}\; (M\, L^{-1}\, t^{-1})^{q}\; (M\, L\, t^{-3}\, T^{-1})^{\mathrm{r}}\; (L^{2}\, t^{-2}\, T^{-1})^{\mathrm{s}}$$

Equating the exponents of each of the fundamental dimensions separately, one obtains

For mass, M: $1 = p + q + r$
For time, t: $-3 = -m - q - 3\,r - 2\,s$
For temperature, T: $-1 = -r - s$
For length, L: $0 = m + n - 3\,p - q + r + 2\,s$

For eliminating n, p, q and r (i.e., four of the six exponents), these could be expressed in terms of m and s in the following manner:

$$n = m - 1$$
$$p = m$$
$$q = s - m$$
$$r = 1 - s$$

Thus one can write

$$h = K\, u^{\mathrm{m}}\, d^{\mathrm{m}-1}\, \rho^{\mathrm{m}}\, \mu^{\mathrm{s}-\mathrm{m}}\, k^{1-\mathrm{s}}\, C^{\mathrm{s}}$$

or

$$\frac{h\,d}{k} = K \left(\frac{d\,u\,\rho}{\mu}\right)^{\mathrm{m}} \left(\frac{C\,\mu}{k}\right)^{\mathrm{s}}$$

In this relationship three dimensionless groups appear:

Nusselt number, $N = \left(\dfrac{h\,d}{k}\right)$

Reynolds number, $\mathrm{Re} = \left(\dfrac{d\,u\,\rho}{\mu}\right)$

Prandtl number, $\mathrm{Pr} = \left(\dfrac{C\,\mu}{K}\right)$

In the second example, let the case of forced convective mass transfer in pipe flow be considered. Let it be assumed that the turbulent flow of the fluid, B, through the pipe is accompanied by a gradual dissolution of the material, A, of the pipe wall. Experimental observations indicate that the mass transfer coefficient, in such a situation, depends on several factors: the velocity, u, the density, ρ, and the viscosity, μ, of the fluid; the internal diameter, d, of the pipe; and the diffusivity, D, of A in B. In other words,

$$k_m = f(u, D, d, \rho, \mu)$$

The dimensions of the variables appearing in the above functional relationship are:

k_m: Lt^{-1}

u: Lt^{-1}

D: $L^2\,t^{-1}$

d: L

ρ: ML^{-3}

μ: $ML^{-1}\,t^{-1}$

Let it be assumed that the functional relationship is of the form

$$k_m = K\,u^m\,D^n\,d^p\,\rho^q\,\mu^r$$

From this one obtains the dimensional relationship:

$$L\,t^{-1} = (L\,t^{-1})^m\,(L^2\,t^{-1})^n\,L^p\,(M\,L^{-3})^q\,(M\,L^{-1}\,t^{-1})^r$$

Equating the exponents for each of the fundamental dimension separately,

L: $1 = m + 2\,n + p - 3\,q - r$

t: $-1 = -m - n - r$

M: $0 = q + r$

In the example under discussion the number of variables is 6 and the number of dimensions is 3, so that the number of dimensionless groups should be (6 – 3) = 3 according to Buckingham's π theorem.

Returning back to the three simultaneous equations obtained earlier by equating the exponents of L, t and M separately, it may be shown that if these are solved to express each exponent in terms of m and r, then one can arrive at the following relationship involving three dimensionless groups:

$$\frac{k_m\,d}{D} = K\left[\frac{d\,u\,\rho}{\mu}\right]^m\left[\frac{\mu}{\rho\,D}\right]^{m+r}$$

The dimensionless quantity $k_m\,d/D$ is known as the Sherwood number and is denoted by Sh. Likewise, $d\,u\,\rho/\mu$ is called the Reynolds number (Re) and $\mu/\rho\,D$, the Schmidt number (Sc).

Thus, the case of forced convective mass transfer in pipe flow, one has

$$\begin{aligned}\text{Sh} &= f(\text{Re}, \text{Sc})\\ &= K\,[\text{Re}]^m\,[\text{Sc}]^{m+r}\end{aligned}$$

On correlating with experimental data, it is found that $K = 0.023$, $m = 0.83$ and $m + r = 0.33$, so that

$$\mathrm{Sh} = 0.023\ [\mathrm{Re}]^{0.83}\ [\mathrm{Sc}]^{0.33}$$

Similar correlations are available with regard to other physical situations such as fluid flow over a flat plate, a sphere or a cylinder.

3.16.5
Fluid–Solid Reactions

From the point of view of chemical metallurgy, the class of heterogeneous reactions in which a fluid (gas or liquid) contacts a solid, reacts with it and transforms it into the product is very important and involves many of the principles pertaining to heterogeneous reactions. Fluid–solid reactions may essentially be represented in the following three ways:

$$\text{A (fluid)} + \text{B (solid)} \rightarrow \text{Fluid products}$$

$$\text{A (fluid)} + \text{B (solid)} \rightarrow \text{Solid products}$$

$$\text{A (fluid)} + \text{B (solid)} \rightarrow \text{Fluid and solid products}$$

There are numerous examples of fluid–solid reactions in chemical metallurgy. Examples in which the solid does not apparently change in size during the reaction include: (i) roasting of sulfide ores to yield metal oxides; (ii) preparation of metals from their oxides by reacting in a reducing atmosphere; and (iii) protective surface treatments of solids such as the plating of metals. There are also fluid–solid reactions in which the size of the solid changes. The most common examples of these are the reactions of carbonaceous materials with low ash contents, such as coal briquettes, wood, etc., to produce heat or heating fuels. Other examples of reaction in which the solid changes size include dissolution reactions, the attack on metal chips by acids and the rusting of iron.

Let a fluid–solid reaction of the following type be considered.

$$\text{A (fluid)} + b\,\text{B (solid)} \rightarrow c\,\text{C (fluid)} + d\,\text{D (solid)}$$

where b, c and d are stoichiometric coefficients.

Two simple examples of a reaction of this type are:

$$\mathrm{CuO\ (s)} + \mathrm{H_2\ (g)} \rightarrow \mathrm{Cu\ (s)} + \mathrm{H_2O\ (g)}$$

and

$$\mathrm{Fe_2O_3\ (s)} + \mathrm{CO\ (g)} \rightarrow 2\ \mathrm{FeO\ (s)} + \mathrm{CO_2\ (g)}$$

In general, the overall reaction process may comprise several individual steps, as shown in Figure 3.24. It could be seen that these steps pertain to (i) mass transfers of reactants and the products between the bulk of the fluid and the external surface of the solids; (ii) transport of reactants and the products within the pores of the solid; and (iii) chemical reaction between the reactants in the fluid and those in the solid. In order to be able to determine the rate-controlling step and to ascertain whether more than a single step should be consid-

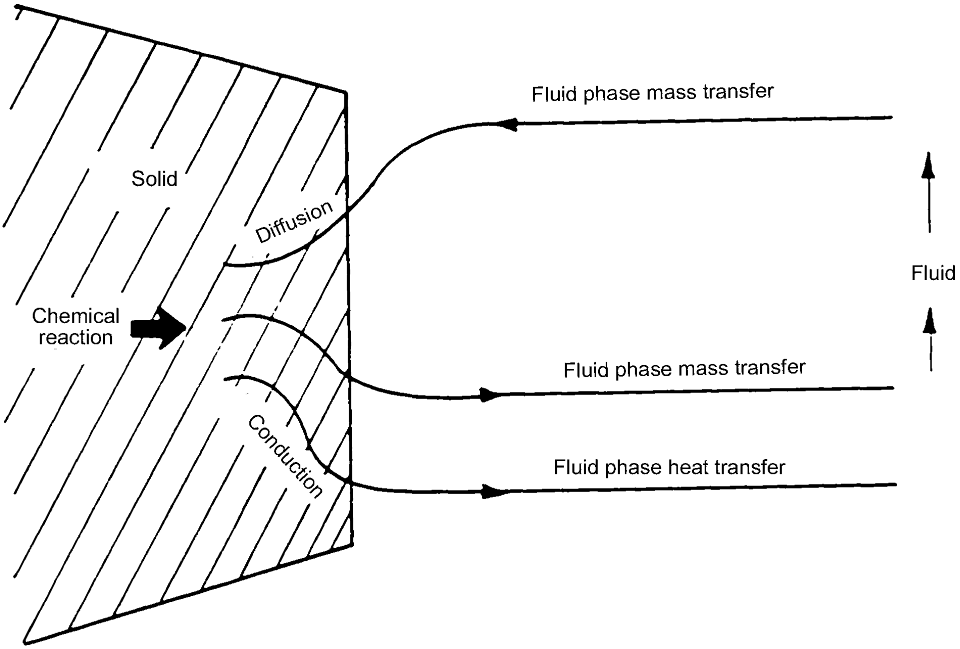


Figure 3.24 A sketch showing the overall reaction process involving individual steps.

ered while expressing the overall reaction rate, it is necessary to gain an understanding as to how the individual steps interact with each other. It must be borne in mind that a change in the reaction conditions may change the rate-controlling step and that there may not be a single rate-controlling step since several steps may have more or less equal effects on the overall reaction rate. The relative importance of these steps could also change as the reaction progresses.

Apart from the steps enumerated, two other factors could influence the overall reaction rate significantly. These are heat transfer and changes in the structure of the solid occurring during the reaction. Heat is either generated or consumed in many fluid–solid reactions. The heat of reaction must be transferred from where the reaction takes place to the surroundings, or from the surroundings to the location of the reaction. This heat transfer would involve conduction within the solid and convection and/or radiation between the solid surface and the surroundings. The chemical reaction itself and/or the heat may change the pore structure, and this could also affect the overall reaction rate.

3.16.6
Reactions of Nonporous Particles

In a situation where the solid participating in the reaction is nonporous to start with, the reaction occurs at a sharp interphase, either fluid–solid or solid–solid, depending as whether a solid product forms or not and if it does then whether it is porous or nonporous.

If no solid product forms (as in dissolution or gasification) or if the solid product is removed from the surface as soon as it forms, the solid reactant would always remain in contact with the fluid. If the solid is assumed to be a particle, its size will gradually decrease with the progress of the reaction. However, if a solid product is formed and if it persists as a coherent layer around the reactant particle, the reaction would occur at the interface separating the unreacted and the completely reacted zones. If the solid product is nonporous in nature, either the fluid reactant species has to diffuse through it by solid-state diffusion to reach the interface, or one (or more) of the constituent species of the solid reactant has to diffuse through the solid product layer to the surface to react with the fluid reactants. However, if the solid product is porous, the fluid reactant can reach the reaction interface by diffusing through the pores of the product. The variation in the size of the solid with the progress of the reaction would depend on whether the solid product formed has a larger or a smaller volume as compared with that of the reactant solid consumed. As the reaction progresses, the portion of the reactant solid which still remains unreacted becomes smaller and smaller. In other words, the unreacted core shrinks.

In some fluid–solid reactions, nucleation of the product constitutes an important step. With increasing size of the solid or with increasing reaction temperature, the time within which nucleation is important becomes small compared to the total reaction time, thereby making nucleation relatively less important.

It should be noted that in the case of the reaction of a fluid with a nonporous solid, the chemical reaction step and the mass transport step are connected in series. This makes the analysis much simpler as compared to the case of a porous solid. In reactions of nonporous particles there can essentially be two cases; one which shows absence of a solid product layer, and the other which shows its presence.

3.16.7
Reactions of Porous Particles

Strictly speaking, the validity of the shrinking unreacted core model is limited to those fluid–solid reactions where the reactant solid is nonporous and the reaction occurs at a well-defined, sharp reaction interface. Because of the simplicity of the model it is tempting to attempt to apply it to reactions involving porous solids also, but this can lead to incorrect analyses of experimental data. In a porous solid the chemical reaction occurs over a diffuse zone rather than at a sharp interface, and the model can be made use of only in the case of diffusion-controlled reactions.

If the reactant solid is porous, the reactant fluid would diffuse into it while reacting with it on its path; diffusion and chemical reaction would occur in parallel over a diffuse zone. The analysis of such a reaction system is normally more complex as compared to reaction systems involving nonporous solids. Here also it is important to assess the relative importance of chemical reaction kinetics and of mass and heat transport.

The dissolution of porous minerals, the combustion of porous carbon, the reaction between porous carbon and carbon dioxide, and the formation of nickel carbonyl from pure nickel are some examples of fluid–solid reactions where the reactant solid is porous and where no solid reaction product is formed. A reaction of this type can be represented as

A (fluid) + b B (porous solid) → Products (fluid)

A reaction in which a solid product layer is formed can be represented as

A (fluid) + b B (solid) → c C (fluid) + d D (solid)

The reactant solid B is porous and the reaction occurs in a diffuse zone. If the rate of the chemical reaction is much slower compared to the rate of diffusion in the pores, the concentration of the fluid reactant would be uniform throughout the pellet and the reaction would occur at a uniform rate. On the other hand, if the chemical reaction rate is much faster than the pore diffusion rate, the reaction occurs in a thin layer between the unreacted and the completely reacted regions. The thickness of the completely reacted layer would increase with the progress of the reaction and this layer would grow towards the interior of the pellet).

3.16.8
Reactions Among Solids Through Fluid Intermediates

Many reactions among solids are important with regard to pyrometallurgical processes. While some of these reactions are true solid–solid reactions, some others occur through fluid intermediates. For instance, the carbothermic reduction of many metal oxides proceeds through the gaseous intermediates CO and CO_2 in the following manner:

$$M_m O_n \text{ (s)} + CO \text{ (g)} \rightarrow M_m O_{n-1} \text{ (s)} + CO_2 \text{ (g)}$$

$$p\, CO_2 \text{ (g)} + p\, C \text{ (s)} \rightarrow 2\, p\, CO \text{ (g)}$$

Adding,

$$M_m O_n \text{ (s)} + p\, C \text{ (s)} \rightarrow M_n O_{n-1} \text{ (s)} + (2\, p - 1)\, CO \text{ (g)} + (1 - p)\, CO_2 \text{ (g)}$$

In these reactions there is a net generation of the gases CO and CO_2; this leads to a bulk flow of the gas mixture from the reaction zone. There are other types of reactions involving gaseous intermediates, in which there is no net gas generation. An example is the formation of a metal carbide from the metal and carbon:

$$C \text{ (s)} + 2\, H_2 \text{ (g)} \rightarrow CH_4 \text{ (g)}$$

$$M \text{ (s)} + CH_2 \text{ (g)} \rightarrow MC \text{ (s)} + 2\, H_2 \text{ (g)}$$

Adding,

$$C \text{ (s)} + M \text{ (s)} \rightarrow MC \text{ (s)}$$

Reactions among solids occurring through gaseous intermediates can be viewed as coupled gas–solid reactions, and thus can be analyzed in the light of the discussions presented in the preceding sections regarding fluid–solid reactions.

Apart from pyrometallurgy, the various ingredients of heterogeneous reaction kinetics are also very pertinent to several hydrometallurgical operations. This will be discussed in Chapter 5.

3.17
Elements of Process Reactor Design

It goes without saying that every process, whether chemical or metallurgical, is carried out in a reactor which implements the chemical treatment step that constitutes the heart of the process comprising a succession of steps to produce (economically) a desired product from a variety of starting materials. The design of the reactor, which was carried out mostly empirically in the early days, is no longer such a simple or routine exercise. This is because there are several alternatives available for each process. Each of these alternatives is strong in meeting certain requirements, and has limitations as regards some others. Hence, in a proper reactor design it is necessary to optimize with respect to a set of requirements. In such a situation the design of a reactor uses information, knowledge and experience from many areas such as thermodynamics, kinetics, fluid mechanics, heat and mass transfer, economics, energy consumption, and environmental impact. In reactor design there are two questions which must be answered: (i) what are the changes that are expected to take place; and (ii) how fast would these changes occur? The first question concerns thermodynamics, and the second the various rate processes – kinetics, heat transfer, etc. The following introduction provides an outline of the manner in which one approaches the subject of process reactor design.

The design of a reactor starts with the expression of material balance for any reactant (or product). The basis for all material balances is the law of conservation of matter, which states that matter cannot be created or destroyed in a given system (nuclear reactions are, of course, out of this dictum). Material balance is generally given as:

$$R_I = R_O + R_C + R_A$$

where R_I is the rate of reactant flow into the reactor; R_O is the rate of reactant flow out of the reactor; R_C is the rate of reactant loss due to chemical reaction within the reactor; and R_A is the rate of reactant accumulation in the reactor. In a situation where the composition within the reactor is uniform (independent of position), the accounting may be carried out over the whole reactor. In an another situation which is characterized by composition not being uniform, the accounting must be carried out over a differential element of volume and then integrated across the whole reactor for the appropriate flow and concentration conditions. For the various reactor types this equation simplifies in one way or another, and the resultant expression when integrated provides the basic performance equation for that type of unit. Since in batch reactor or operation, no stream is entering or leaving the reactor,

$$R_I = R_O = 0$$

the following relationship holds.

$$R_C = -R_A$$

A batch reactor is never a steady-state process operator, unlike a continuous process in which a steady state is defined as the state of a process in which there is no change with time of any condition of the process. This includes the amount and average composition of the material within the process, so that in a continuous process, there can be no accumulation or depletion. Notwithstanding an unsteady-operation where composition changes with time in the case of batch reactor, the accounting here is carried out for the whole reactor because at any instant the composition throughout the reactor is uniform.

When the process occurs nonisothermally in the reactor, energy balances must be used in conjunction with material balances. The general expression for energy balance is:

$$H_\mathrm{I} = H_\mathrm{O} + H_\mathrm{L} + H_\mathrm{A}$$

where H_I is the rate of heat flow into the reactor; H_O is the rate of heat outflow from the reactor; H_L is the rate of disappearance of heat within the reactor; and H_A is the rate of accumulation of heat within the reactor. Here also, the accounting is carried out by taking the reactor as a whole or by taking only a differential element, depending on circumstances. In a steady-state process, no heat is accumulated.

3.18
Temperature Effects

The effect of temperature on the rate of a typical heterogeneous reaction is shown in Figure 3.25. At low temperatures the reaction is chemically controlled and at high temperatures it is diffusion or mass transport controlled.

The activation energy of the chemical reaction step is much larger (a few hundred kilojoules per mole) than the activation energy for mass transport (a few tens of kilojoules per mole). As a result of this, even a relatively small change in temperature results in a large increase in the reaction rate when the reaction is controlled chemically, and thus this step ceases to be rate controlling at high temperatures. The activation energy for mass transport or diffu-

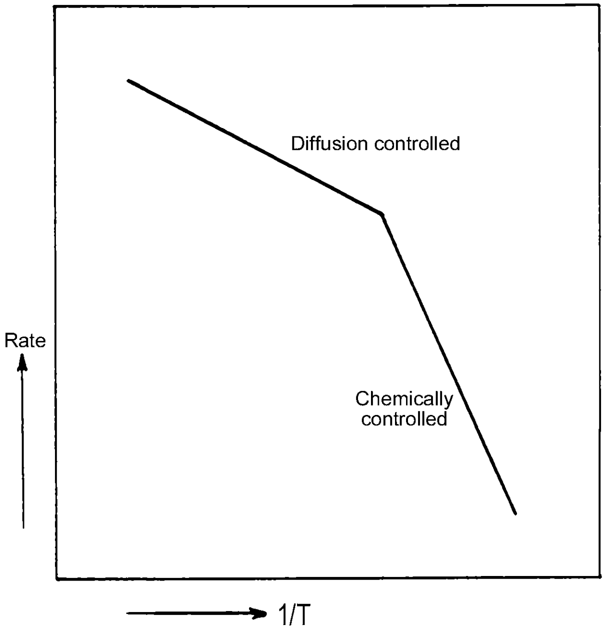


Figure 3.25 Influence of temperature on heterogeneous reaction.

sion is relatively small, and the increase in the mass transfer rate due to an increase in the temperature is less marked. Hence, the heterogeneous process remains diffusion controlled at high temperatures. As a result of this, high-temperature data points fall below the straight line that fits the data at low temperatures.

3.19
Catalysis

A catalyst is a substance which, by virtue of its being present, changes the rate of a reaction while itself remaining unchanged. If the presence of such a substance results in an increased reaction rate, then the substance is called a positive catalyst or simply a catalyst. However, if the substance decelerates the reaction rate, then it is called a negative catalyst or an inhibitor. Although catalytic reactions may be either homogeneous or heterogeneous, they have the following characteristics in common.

The first characteristic concerns the chemical stability of the catalyst. It refers to the fact that there is no alteration in the chemical nature of the catalyst used as well as the amount unused, with time. The physical nature of the catalyst, however, changes. For instance, when manganese dioxide lumps are used as a catalyst in the decomposition of potassium chlorate, they are found at the end of the decomposition process to have been converted into a fine powder. As another example, mention may be made of the reaction between oxygen and hydrogen in the presence of a platinum catalyst. In this case, if originally shiny metallic platinum is used as the catalyst, it is seen after a certain time to have a coating of fine particles of platinum. These two illustrations show that the surfaces of solid catalysts play a part in hastening the corresponding chemical reactions.

The second characteristic pertains to the fact that a very small amount of a catalyst may be able to maintain a high reaction rate over a long time. Although in practice some of the catalysts are extremely efficient for certain specific reactions, it is observed that in the majority of the cases of homogeneous catalysis, the enhancement in the reaction rate is proportional to the concentration of the catalyst used. In heterogeneous catalytic reactions involving reactant gases and solid surfaces, the total surface area of the solid may also affect the reaction rate.

The third characteristic refers to the fact that a catalyst does not influence the value of the equilibrium constant because it lowers the activation energy of the forward and backward reactions by the same amount and therefore changes the rates of the forward and backward reactions by the same amount. A catalyst only accelerates the attaining of equilibrium it does not exert any influence whatsoever on the quantitative yield of the products.

In a homogeneous catalytic reaction the catalyst is uniformly distributed throughout the system. The function of the catalyst is to decrease the activation energy of the given reaction, and thus to increase its rate, because more reactant molecules will then have the required energy for the reaction to occur. This is believed to be achieved by the formation of a compound between the reactants and the catalyst, which then decomposes to regenerate the catalyst and form the reaction products. A reaction in which the reactants X and Y react to yield a product XY can be represented in the absence of a catalyst as $X + Y \rightarrow XY$. When a catalyst Z is present, the reaction may be shown as involving in the following two steps:

$$X + Z \rightarrow XZ$$

$$XZ + Y \rightarrow XY + Z$$

If the intermediate compound XZ is very unstable, Z cannot serve as a catalyst, while if it is very stable then the reaction stops. The intermediate compound XZ must have the right degree of stability for the catalyst to be effective. It must be borne in mind that the catalyst will accelerate the forward as well as the reverse reactions to the same extent, so that the ratio of the specific rate constants for the forward (k_f) the backward (k_b) reactions will not be affected. As an example a gaseous reaction between sulfur dioxide and oxygen to yield sulfur trioxide may be considered. The reaction, which can be represented by the equation

$$2\ SO_2 + O_2 \rightarrow 2\ SO_3$$

proceeds very slowly in the absence of a catalyst. This reaction may be catalyzed by the addition of nitric oxide, in which case it is represented by the following equations:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

$$2\ SO_2 + 2\ NO_2 \rightarrow 2\ SO_3 + 2\ NO$$

In this example the XZ intermediate compound corresponds to the 2 NO_2 term, and the catalyst nitric oxide is regenerated continuously.

In a heterogeneous catalytic system the catalyst is not distributed uniformly throughout the system, but forms a separate phase. A number of examples are found of the use of solid heterogeneous catalysts in many gaseous reactions. The well-known Haber process for the synthesis of ammonia from a mixture of nitrogen and hydrogen gases, where the gas mixture is passed over a heated catalyst of either platinum or iron containing a promoter, is a good example. According to the adsorption theory of heterogeneous catalysis, the gaseous reactants are first adsorbed onto the surface of the catalyst. Then, after passing through a transition state, they form a compound with simultaneous desorption from the surface. If the binding forces between the adsorbed reactants and the catalyst surface are strong, formation of the transition state and removal of the product will be difficult and the catalyst may in such cases be said to have been “poisoned”. If, on the other hand, the reactants are adsorbed very weakly, they may not stay long enough on the surface for the reaction to take place.

The activity of a catalyst may sometimes be increased by adding an other substance or substances to it, which by themselves are not necessarily catalysts; these additions are called promoters.

It is worth mentioning that it is sometimes advantageous to retard a given chemical reaction by the presence of some suitable substances. As mentioned earlier, such substances are called negative catalysts and they can act in two ways. One is by changing the normal mechanism of the reaction. As example is the use of lead tetraethyl in petrol to inhibit a premature reaction between petrol vapour and oxygen on compression in an engine cylinder. The other way in which negative catalysts work is remove positive catalysts by combining with them. As an example, small amounts of urea are used to render nitrocellulose stable (and thus safe) by removing nitrogen oxides, which are positive catalysts for the decomposition of nitrocellulose.

It is useful here to recapitulate and place on record the different factors influencing reaction rate. These are:

- The chemical nature of the reactants: The reaction,

  $N_2 + 3\ H_2 = 2\ NH_3$

  may be considered as a representative example for the purpose of explanation. This reaction is quite slow at practical pressures (if a catalyst is absent) and temperatures. In contrast, the reaction,

  $O_2 + 2\ H_2 = 2\ H_2O$

  occurs very rapidly at relatively low temperatures of a few hundred degrees Celsius.

- Temperature: according to thermodynamics prediction, nickel oxide is reducible by hydrogen at all practical temperatures. However, this heterogeneous reaction,

  $NiO + H_2 = Ni + H_2O$

  is very slow at room temperatures. It is only above a temperature of about 250 °C that nickel oxide lumps with sizes not exceeding a few centimeters are found to completely reduce in a matter of a few minutes.

- Concentration of reactants: As an example of this factor, mention may be made of the dissolution reaction of cupric oxide in acids

  $CuO + 2\ H^+ = Cu^{2+} + H_2O$

  This reaction is found to depend very much on pH.

- Catalyst presence: as an example of this factor mention may be made of carbon gasification by water vapour:

  $H_2O + C = CO + H_2$ + other gaseous products

  This reaction accelerates very much in presence of the potassium hydroxide that serves as the catalyst.

- In the case of heterogeneous reactions, the transport of reactants and products plays a decisive role. As an example, reference may be drawn to the reaction:

  $FeO + H_2 = Fe + H_2O$

  If this reaction is implemented at temperatures where the iron yielded is a solid, a sectioned, fractionally reacted iron oxide might appear as shown in Figure 3.26. As shown, for the hydrogen to reach the iron oxide with which it reacts, it has to diffuse through a layer of iron (mostly porous). In addition, the water vapour produced as a consequence of the reaction must be transported away from the iron–iron oxide interface by diffusion. Failing this, there will be accumulation of water vapour at the interface which will permit equilibrium point to be attained and the reaction ceases from further occurring.

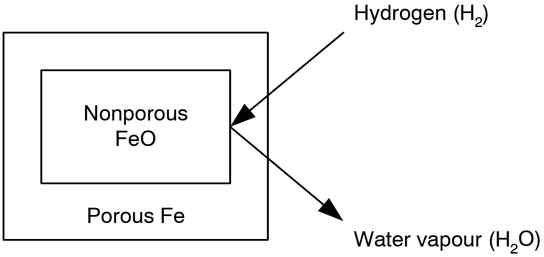


Figure 3.26 Iron oxide lump under reduction by hydrogen yielding porous iron and water vapour.

- The transport of heat: a fine example for this factor may be cited: thermal decomposition of limestone endothermically to lime. The heterogeneous reaction is chemically shown as:

  $CaCO_3 = CO_2 + CuO$

  An incompletely reacted and sectioned sample of limestone would appear as shown in Figure 3.27. For the reaction to sustain it is highly required that flow of heat occurs from outside the limestone sample particle to the reaction interface, which represents the shrinking core of limestone. This heat transport by conduction in the pores and solid body of the lime can affect the rate of reaction.

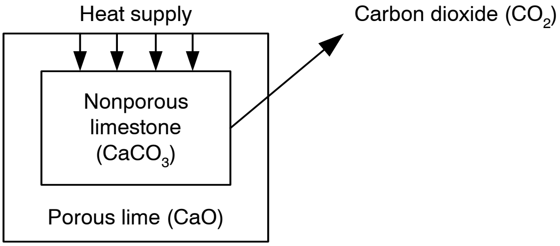


Figure 3.27 Endothermic thermal decomposition of limestone to lime, showing the need for transport of heat.

3.20
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4
Pyrometallurgy

4.1
Introduction

The term pyrometallurgy in chemical metallurgy refers to the use of high-temperature reactions and processes for the extraction and the refining of metals. The key parameters in pyrometallurgy are temperature and environment. The benefits derived from the use of high temperatures include favorable chemical equilibria and high reaction rates, and the possibility of producing the metal in molten or gaseous states which facilitates its ready separation from other reaction products. The environments in which pyrometallurgical reactions and processes can occur may be air, reducing gas mixtures, reactive atmospheres containing the halogens, inert gases or even vacuum. The use of special environments in pyrometallurgy has been greatly instrumental to lead to well-recognized and well-founded disciplines like halide metallurgy and vacuum metallurgy in their own rights. These particular areas of pyrometallurgy have, in fact, contributed phenomenally to the metallurgy of less-common metals. Were it not for the emergence of these processes less common metallurgy would not have traced the path of growth and development as it has registered today.

4.2
Drying

Materials containing water are often encountered at various stages in the conversion processes of ore to metal. Examples of such materials include ores, concentrates and compound intermediates. Water, if undesirably present in these initial source materials, has clearly to be removed prior to subjecting them to further processing. Some of the reasons for doing so may be cited as: (i) the elimination of water reduces the weight of the material handled; (ii) if the material is to be charged in an electric furnace where the operating temperature is high (~1700 °C), the sudden release of water can cause charge blow off; (iii) in some cases, the material becomes more reactive following water removal; and (iv) the presence of water can cause undesirable side reactions, leading to poor product quality and yield. This is not to be construed as an exhaustive listing but rather an illustrative and representative one.

Chemical Metallurgy: Principles and Practice. Chiranjib Kumar Gupta

ISBN: 3-527-30376-6

Water is present in the materials of interest as free water or water of crystallization, or as combined water. The process of dehydration refers to the removal of the water of crystallization, while the removal of combined water is called dehydroxylation because hydroxyl groups in the material are broken down to form water vapor. The dehydroxylation process is very often alternately described as calcination. The drying process used in the present text pertains to both dehydration and dehydroxylation. In the processing of ores for metal extraction, drying essentially implies the removal by evaporation of water which a material holds in it in various forms.

Drying, in general, may be expressed by the following equations:

$$MX_n \cdot m\,H_2O = m\,(H_2\,O) + MX_n \qquad \text{(dehydration)}$$

and

$$M(OH)_n = MO_{0.5\,n} + 0.5\,n\,H_2O \qquad \text{(dehydroxylation)}$$

The equilibrium constant, K_1, for the dehydration reaction is:

$$K_1 = P^m_{H_2O} \quad \text{so that} \quad P_{H_2O} = K_1^{1/m}$$

For the dehydroxylation reaction, the equilibrium constant, K_2, is given by:

$$K_2 = P^{n/2}_{H_2O} \quad \text{so that} \quad P_{H_2O} = K_2^{2/n}$$

In general, at temperatures normally required for drying the following condition apply:

$$K_1^{1/m} > K_2^{2/n}$$

The equilibrium water vapor pressure over the materials in hydrate forms is greater than that over the materials in hydroxide forms. Elimination of water vapor and hence drying of the material occurs when the ambient water vapor pressure in the system is lower than the equilibrium water vapor pressures given by the above equations. To effect drying, there are two options.

At a given ambient water vapor pressure (usually the level found in the open atmosphere), the temperature of the material is raised so that the equilibrium water vapor pressure over the hydrated material is higher than the ambient water vapour pressure. Generally, heating up to 400 °C is sufficient to remove all the water of crystallization from materials. This removal of water yields a material which may contain some more strongly bound water. To remove this water, the material requires to be heated to a higher temperature (400–600 °C) so that the equilibrium water vapour pressure exceeds the ambient water vapour pressure. For near-complete removal of the last traces of water, temperatures as high as 1000 °C may be required. In addition to the heat required to raise the temperature of the material, heat is also required for the evaporation of water, which is an endothermic process. The enthalpy of evaporation increases as the water content, and hence the equilibrium water vapor pressure, decreases.

The other option available for drying involves subjecting the material to reduced pressures. By decreasing the ambient pressure, for example, by evacuation, to a level lower than the equilibrium water vapor pressure over the material, drying can be implemented. This option is particularly important when heating affects the material, in addition to drying it.

Heating under reduced pressures is a useful technique. A similar effect is achievable by heating under a dry gas flow.

Drying is accomplished in a variety of equipment such as a rotary kiln, a fixed bed, a fluidized bed or a vacuum retort. In common metal flowsheet operations, drying can be effected by maintaining a continuous sweep of hot (a few hundred degrees) combustion gases until required through or above the material meant to be dried. These gases are usually available as by-products from metallurgical plants; if necessary they can, however, be separately generated. To cite a specific example, present reference may be drawn to rotary kiln drying which is commonly used for expelling water from the garnierite nickel ore which, in the as-mined condition, contains as much as 30% free water:

$$(\mathrm{Ni, Mg})_3(\mathrm{OH})_4 \cdot \mathrm{Si_2O_5} \cdot n\,\mathrm{H_2O} \rightarrow (\mathrm{Ni, Mg})_3\mathrm{O_2} \cdot \mathrm{Si_2O_5} + (n+2)\,\mathrm{H_2O}$$

Subsequently, the dried ore is reduced in an electric furnace to ferronickel. Drying of the ore ensures smooth operation in the reduction furnace. As another example, reference may be drawn to the processing of kaolinite, $Al_2(SiO_5)(OH)_4$, for the recovery of alumina. The mineral is leached with dilute sulfuric acid. In the hydrated form, the mineral is insoluble in dilute mineral acids, and on drying at 400 to 800 °C, kaolinite is converted to the amorphous form, metakaolin, $Al_2O_3 \cdot 2\,SiO_2$:

$$\mathrm{Al_2(Si_2O_5)(OH)_4} \rightarrow \mathrm{Al_2O_3} \cdot 2\,\mathrm{SiO_2} + 2\,\mathrm{H_2O}$$

from which up to 80% of the alumina present selectively dissolves in the acid, leaving behind silica (SiO_2). On drying at above 900 °C, metakaolin crystallizes to mullite, which is acid insoluble. These details lay emphasis on the need for control of temperature when drying of materials is carried out.

In the flowsheet of alumina production by the Bayer process, aluminum is precipitated from an aqueous solution as aluminum hydroxide. The hydroxide is dried in rotary furnaces. In recent times, fluidized-bed reactors have been deployed which yield practically nonhygroscopic alumina. The dissociation of aluminum hydroxide occurs in steps,

$$\mathrm{Al_2O_3} \cdot 3\,\mathrm{H_2O} \rightarrow \mathrm{Al_2O_3} \cdot \mathrm{H_2O} \rightarrow \gamma\text{-}\mathrm{Al_2O_3} \rightarrow \alpha\text{-}\mathrm{Al_2O_3}$$

forming alumina. The steps are characterized by progressively lesser number of water molecules and lower equilibrium dissociation pressures. For the removal of the last traces of water, temperatures in excess of 1000 °C are required. Drying of aluminum hydroxide at temperatures less than 950 °C results in the formation of γ-alumina which is fairly hygroscopic. To obtain anhydrous alumina, which contains approximately 70% γ-alumina and 30% α-alumina, the furnace temperature has to be raised to 1200 °C because in the temperature range of 950–1200 °C, a part of the γ-alumina transforms to the α-form.

In the drying of compound intermediates of refractory and reactive metals, particular attention is given to the environment and to the materials so that the compound does not pick up impurities during the process. A good example is the drying of zirconium hydroxide. After the solvent extraction separation from hafnium, which co-occurs with zirconium in the mineral zircon, the zirconium values are precipitated as zirconium hydroxide. The hydroxide is dried first at 250 °C for 12 h in air in stainless steel trays and then at 850 °C on the silicon carbide hearth of a muffle furnace.

4.3
Calcination

The term calcination is used to denote thermal decomposition of solids and is expressed by the general reaction

Solid 1 = Solid 2 + Gas

Calcination is a widely used unit operation in process metallurgy, and the compound represented as solid 1 is usually a carbonate and solid 2, an oxide. The decomposition of hydroxides, besides being termed as drying as indicated in the previous section, is also called calcination.

For example, consider decomposition of a carbonate, which can be shown chemically as:

MCO_3 (s) = MO (s) + CO_2 (g)

Assuming the solid phases as to be pure, the equilibrium pressure of carbon dioxide is then a function only of temperature:

$$p_{CO_2} = f(T) = K = \exp\left(\frac{-\Delta G^0}{R\,T}\right)$$

where K is the equilibrium constant and G^0 is the standard free energy change involved with the occurrence of above reaction. A plot of the equilibrium pressure of carbon dioxide as a function of temperature is shown in Figure 4.1. It is observed that as the temperature rises, the equilibrium pressure of carbon dioxide exhibits a rapid increase. The temperature at which the equilibrium pressure reaches 1 atmosphere differs from substance to substance, but all these temperatures are readily attainable in practice. To cite some examples, it may be mentioned that while the temperature required in the case of ferrous carbonate ($FeCO_3$) is only 200 °C, those required for magnesium carbonate ($MgCO_3$) and calcium carbonate ($CaCO_3$) are 400 °C and 900 °C respectively; the temperature requirements for strontium carbonate ($SrCO_3$), whilst some others (not shown) such as barium carbonate ($BaCO_3$) and sodium carbonate (Na_2CO_3) are even higher. In air, the dissociation of a carbonate can be considered to begin at the temperature at which the dissociation pressure (equilibrium pressure of carbon dioxide) of the carbonate exceeds the partial pressure of

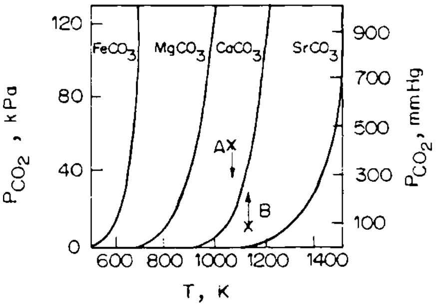


Figure 4.1 Effect of temperature on dissociation pressure of carbonates.

carbon dioxide in air (about 0.03%). However, vigorous decomposition of carbonates occurs at temperatures at which the dissociation pressure exceeds the atmospheric pressure. The decomposition point for carbonates thus refers to the temperature at which P_{CO_2} = 1 atm.

Let the points A and B in Figure 4.1 be considered for a description of calcination of limestone which occurs as shown below:

$$CaCO_3 = CaO + CO_2$$

Provided that the temperature and the carbon dioxide pressure conditions in the calcination furnace are such that they correspond to the point A, or to any point above the calcium carbonate line, no dissociation occurs because in such a situation,

$$P_{CO_{2(A)}} > P_{CO_{2(eq)}}$$

so that

$$\Delta G = R\,T\,(\ln P_{CO_{2(A)}} - \ln P_{CO_{2(eq)}})$$

is positive. On the other hand, if the conditions correspond to the point B, or to any point beneath the calcium carbonate line, then

$$P_{CO_{2(B)}} < P_{CO_{2(eq)}}$$

and

$$\Delta G = R\,T\,(\ln P_{CO_{2(B)}} - \ln P_{CO_{2(eq)}})$$

is negative. This condition is favorable for the dissociation to occur. The decomposition behavior of all the carbonates can be explained in a similar manner, and the conditions necessary for their decomposition are entirely desirable.

The presence of impurities can cause a shift in the dissociation point. It implies that the equilibrium temperature and pressure of the carbonate decomposition reaction are shifted. The effect of silica is particularly illustrative in the case of limestone. If silica is present as an impurity, it lowers the decomposition point of limestone. The acid anhydride silica slags combines with the basic calcium oxide according to following:

$$CaCO_3 + SiO_2 = CaO \cdot SiO_2 + CO_2$$

and the equilibrium constant becomes,

$$K = P_{CO_2} \cdot a_{CaO}$$

Since the value of K is fixed at a fixed temperature, and since a_{CaO} is less than unity, the value of the decomposition pressure P_{CO_2} for the calcium carbonate decomposition reaction at a given temperature is greater in the presence of silica than in its absence in limestone. The occurrence of silica thus makes the decomposition of calcium carbonate far easier. In the calcination of limestone, environmental factors (including the temperature) are adjusted in such a manner that the desired product is obtained. Soft burnt lime, which is more porous, with a large surface area and enhanced reactivity, is obtained by calcining limestone at 750–850 °C. Calcination at 1200–1300 °C results in a less reactive product in which the particles are found to have undergone sintering.

The calcination of magnesite ($MgCO_3$) to magnesia proceeds in essentially the same manner as in the case of limestone, but occurs at a lower temperature. This fact readily ensues from a reference to Figure 4.1. The raw material for the production of magnesium by the pyrometallurgical route is dolomite. Dolomite is calcium magnesium carbonate ($Ca_xMg_{1-x}(CO_3)$). The dissociation of dolomite can be expected to occur in two stages, involving the decomposition of calcium magnesium carbonate, followed by that of the more stable calcium carbonate:

$$Ca_xMg_{1-x}CO_3 \rightarrow x\ CaCO_3 + (1-x)\ MgO + (1-x)\ CO_2$$

$$x\ CaCO_3 = x\ CaO + x\ CO_2$$

The first step (namely, the decomposition of calcium magnesium carbonate) occurs at 720–750 °C-temperatures that are higher than the decomposition temperature range (640–660 °C) of pure magnesium carbonate. This upward shift in temperature can be explained in terms of the higher stability of the double carbonate as compared to the plain carbonate. The activity of magnesium carbonate in dolomite is less than unity (dolomite is not just a physical mixture of calcium carbonate and magnesium carbonate) and hence the dissociation pressure of magnesium carbonate in dolomite is

$$P_{CO_2} = a_{MgCO_3} \cdot K$$

where K, the equilibrium constant, is less than that associated with pure or unadulterated, so to say, magnesium carbonate. Calcium carbonate decomposes at 850 °C. Even though the decomposition of the constituent carbonates in dolomite is expected to be complete at 900 °C, in pyrometallurgical practice dolomite is actually calcined at temperatures as high as 1200 °C.

Three different types of furnaces are generally in use for calcination. The shaft furnace is considered to be the most suited for calcining coarse limestone. Furnaces of the rotary kiln type are used for handling materials of mixed particle sizes and lumps which disintegrate during the process. Calcination can be carried out in a fluidized bed-reactor for materials of small and uniform particle size. These furnaces are usually fired with gas, oil or coke; in some cases electric heating is resorted to.

4.4
Roasting

The roasting process mostly used for sulfidic sources of metals is one of the most important and the most complex of all the pyrometallurgical unit operations. This process is carried out by heating the sulfides in air or in oxygen. A sulfide ore or concentrate is subjected to roasting in order to achieve one or more of the following objectives: (i) partial oxidation causing loss of part of the sulfur content; (ii) oxidation to sulfates, which is essentially called sulphation roasting; and (iii) complete removal of sulfur, i.e., conversion to oxides, which is essentially called dead roasting. The conditions to be used for achieving each of these objectives are different and are determined by the thermodynamic properties of the pertinent metal–sulfur–oxygen (M–S–O) systems.

4.4.1
Thermodynamics

Before focusing attention on the application of thermodynamics to roasting it will be instructive to start this presentation on a wider and broader premise. The Ellingham diagrams are very well known among the different well-founded graphical portrayals of thermodynamic data. From their treatment given in the chapter on thermodynamics and kinetics it will be readily recognized that they are drawn using standard state data (this implies that they apply to atmospheric pressure). The question may naturally arise (and readily does) as to what would be the consequence if change were to occur to some other total pressure. It order to answer or understand these important issues, present attention to directed to the following reaction:

$2\ C + O_2 = 2\ CO$

In the reaction shown above, the volume of the reaction products (2 mol CO) is seen to be much greater than that of the reactants (2 mol of solid carbon plus 1 mol of oxygen). The effect of pressure on the free energy of formation of an oxide associated with an increase in the number of gas molecules which is representative of the type of reaction in the present illustration is shown in Figure 4.2 (A). Applying the criterion of volume increase per mole accompanying reaction at standard state to the case of metal oxidation such as

$2\ M + O_2 = 2\ MO$

it is observed that free energy of the reaction would be lowered, or in other words made more negative by an increase in O_2 pressure, as shown in Figure 4.2 (B). Superimposing these two plots as in Figure 4.2 (C) in order to examine the reduction reaction

$2\ MO + C = 2\ M + 2\ CO$

it is observed that at higher pressure the reaction temperature (the temperature at which free energy of the reaction becomes zero) is higher. The two intersecting points on Figure 4.2 (C) can be regarded as two points on a plot of reaction temperature against pressure. Such a presentation or plot appears in Figure 4.2 (D), and normally called a plot is predominance diagram. This nomenclature arises because it relates to the chemical species that will be dominant, when equilibrium is attained, if the temperature and pressure in the reactor are kept fixed. In the present example, if the point representing the temperature and pressure is above the curve, MO and C will be dominant at equilibrium; below the curve M and CO will dominate.

There is, of course, no compulsion to have restriction only on temperature and pressure as manipulated variables in producing predominance diagrams; one is fully at liberty to fix the temperature and pressure and manipulate the partial pressures (composition) of a gas in contact with a solid. Figure 4.3 provides a fine example of this, and illustrates a metal–sulfur–oxygen (M–S–O) system. This diagram shows the ranges of gas compositions (partial pressures of sulfur dioxide and oxygen) over which each phase (M, MS, MO, MSO_4) exists singly, or in equilibrium with another phase or phases. Application of the phase rule to the three-component (ternary) system M–S–O shows that at a fixed temperature and a given total pressure of the gas phase, a maximum of three condensed phases can co-exist.

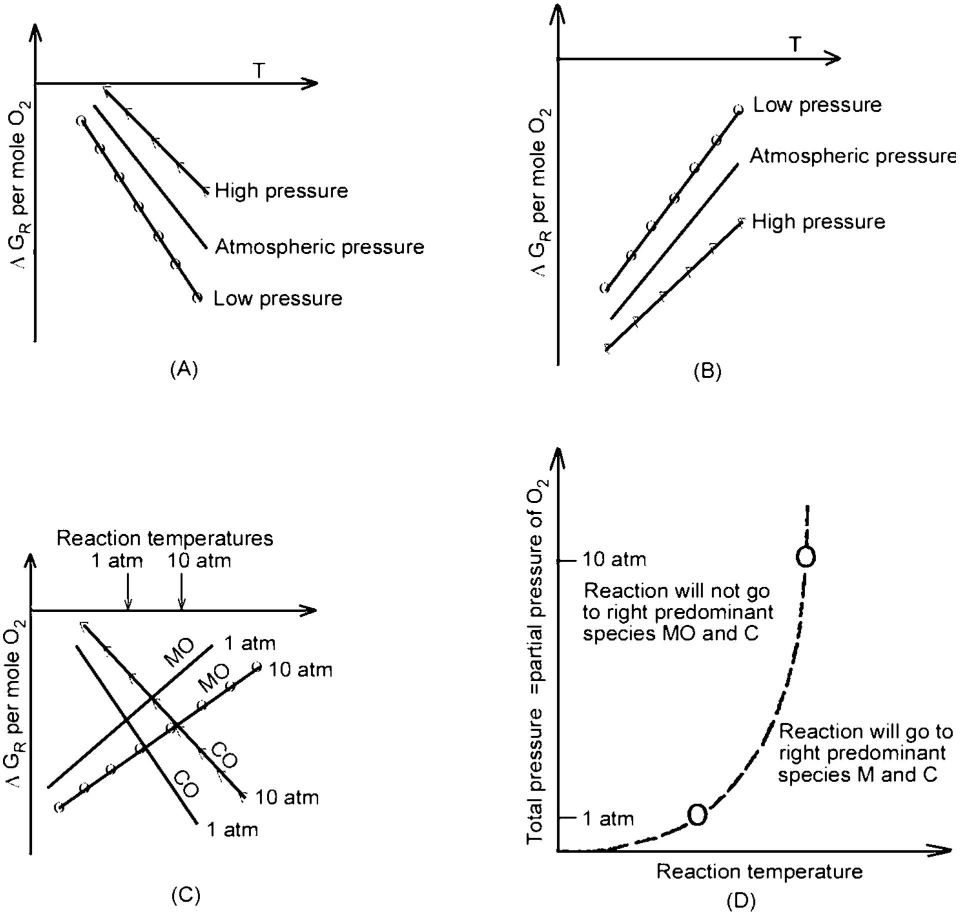


Figure 4.2 (A) Effect of pressure on free energy formation of an oxide produced with an increase in the number of gas molecules; (B) effect of pressure on free energy formation of an oxide produced with a decrease in the number of gas molecules; (C) superimposition of (A) and (B), displaying the enhancement of temperature at which reaction becomes significant with increasing pressures; (D) predominance diagram for M–O–C.

This situation is indicated by the point of co-existence of M, MO and MS, as well as by the point at which MS, MO and MSO_4 co-exist in the figure. At the fixed temperature, the values of P_{O_2} and P_{SO_2} necessary for the maintenance of equilibrium between any two condensed phases are represented by the lines. The areas bounded by the lines represent the P_{SO_2} and P_{O_2} values over which only a single condensed phase is stable. For example, if the conditions of roasting correspond to any point in the region marked MO in the figure, the end product will be an oxide; if the conditions correspond to a point on the line separating the MO and the MSO_4 regions, then a mixture of the sulfate and the oxide will be obtained by roasting. The metal will be the end product of roasting if at the temperature T the values of P_{SO_2} and P_{O_2} are maintained within the M region.

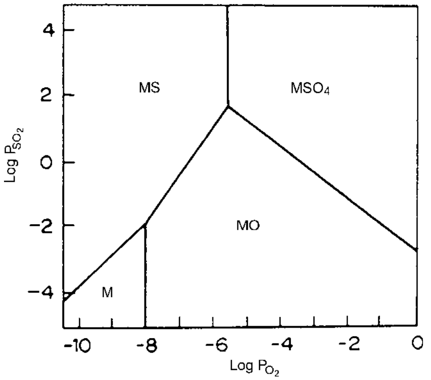


Figure 4.3 A stability diagram for a metal (M) – sulfur (S) – oxygen (O) system at a fixed temperature.

As an additional example, reference is drawn to oxide systems in which one of the peer examples is shown in Figure 4.4 (A) which depicts the predominance diagram for oxides of iron in contact with CO/CO_2 mixture. It can be well used to obtain the answer of: (i) consequence of contacting Fe_2O_3 with a gas mixture such that the composition and temperature correspond to the point of *X*; (ii) the minimum temperature required at which reduction of Fe_3O_4 with CO/CO_2 mixtures causes wustite (FeO) to form; and (iii) the reaction product expected to form first as a result of oxidation of iron with CO_2 at 1200 K. The Figure 4.4 (A) is very often studied with a line superimposed to indicate the equilibrium in reaction

$$C + O_2 = 2\,CO$$

at 1 atm, as is carried out in Figure 4.4 (B) by a dashed line. This particular line provides the gas composition in equilibrium with solid carbon at the temperature in question. So, any point away from the dashed line will represent a composition that is not in equilibrium, and the reaction,

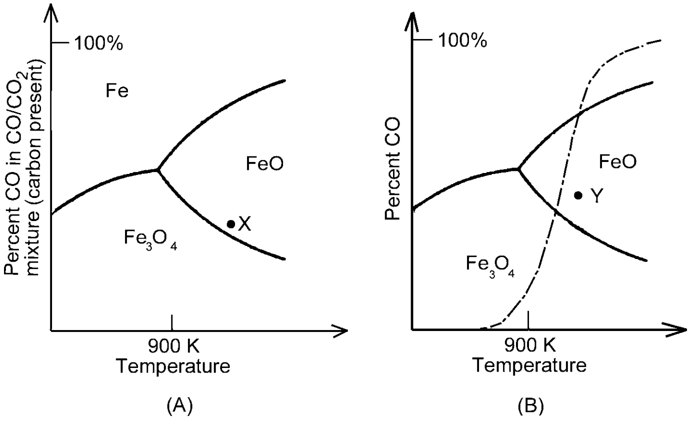


Figure 4.4 (A) Predominance diagram of iron and its oxides in contact with carbon monoxide/dioxide mixtures; (B) predominance diagram of (A) with the equilibrium line for carbon in contact with its oxides superimposed.

$C + O_2 = 2\ CO$

would occur, in the forward or backward direction. In a closed reactor vessel and with no other reactions occurring, the composition of the gas would go down (or up) toward the dashed line. However, if iron and its oxides are present, there are a number of other reactions that can accompany:

$C + O_2 = 2\ CO$

A gas of composition and temperature corresponding to the point Y in Figure 4.4 (B) is considered to have established a contact with carbon in a reactor containing Fe_3O_4 inside. It is clear that the stable oxide at this point *Y* is FeO and the reaction

$Fe_3O_4 + CO = 3\ FeO + CO_2$

occurs using CO and propelling the gas composition down from point *Y*. Simultaneously, reaction,

$C + O_2 = 2\ CO$

takes place, producing CO and propelling to move the gas composition upwards from the point *Y*. In actuality, some change of the composition will occur and that, of course, depends on the rates of the different reactions, and reactions,

$Fe_3O_4 + CO = 3\ FeO + CO_2$

and

$C + O_2 = 2\ CO$

occur until consumption of either all the Fe_3O_4 or all the carbon. Considerations such as this point to the conclusion that only at the two points identified by intersection of solid and dashed lines is carbon in equilibrium with more than one solid phase. The situations are: below the lower temperature intersection, carbon is in equilibrium with Fe_3O_4, above the higher temperature one, it is in equilibrium with Fe (this statement for the time being ignores the solubility of carbon in iron), and between the two intersections it is in equilibrium with FeO. The lower intersection therefore provides the minimum temperature for reduction of Fe_3O_4 to FeO by C (at 1 atm), and the upper one the minimum temperature for reduction of FeO to Fe.

The roasting process mostly applied to sulfidic sources is carried out in appliances of different types with different design features. Without describing their features and constructional details, it may simply be mentioned here that some of the widely acclaimed roasting units are traveling grate furnaces, multiple hearth furnace, rotary kilns, and fluidized-bed roasters.

The one common feature among the roasting units is that they are all intended for continuous operation. The solids on the traveling grate and within the multiple hearth furnaces or in the rotary kiln are approximately in plug flow, while the solids in a fluidized bed or a flash roaster are nearly perfectly mixed. This might suggest that the first three types of roasters would provide a greater conversion than the last two for a comparable residence time. However, mass transfer in a fluidized bed is so rapid that currently the fluidized-bed roaster is the unit of choice for the roasting of sulfide concentrates. The multiple hearth furnace and the rotary kiln generally have countercurrent flow of gas and solid. The traveling grate furnace provides for a crosscurrent flow of gas and solid. The multiple hearth furnace has many moving parts and its throughputs are limited. All the units generate a great deal of hot waste gas which can be passed through a boiler to raise steam. In this way part of the heat of the waste gases can be recovered. This philosophy of waste heat utilization in this or in many other variants figures prominently in Chapter 7 on energy and environment.

4.5
Smelting

Smelting is essentially a melting operation in which the constituents of the charge, in the molten condition, partition into two or more phases which may be slag, matte, speiss or metal. The charge often contains fluxes to facilitate formation of a low-melting slag phase. Smelting does not necessarily involve refining. It is, however, usual to take a variety of measures, such as adjustments of slag composition, oxygen potential and temperature in order that the undesirable constituents separate from the metallic phase and enter the slag, the speiss, or the vapor phases. As examples, mention may be made of sulfur going into the slag in iron smelting, of copper into the matte in lead smelting, and of cobalt into the speiss in copper smelting. The different types of smelting are: (i) reduction smelting; (ii) matte smelting; and (iii) flash smelting.

The reduction smelting process involves the reduction of oxidic sources of metals with carbon in the presence of a flux. The process can generally be represented as:

mineral + reducing agent + flux = metal + slag + gases

The blast furnace is the most popular of the furnaces used for carrying out reduction smelting operations. An illustrious example of a blast furnace smelting product is iron.

The matte smelting process involves the fusion of sulfidic sources of metals with a flux without the use of any reducing agent. This results in the production of a molten mixture of sulfides, known as the matte, the gangue associated with the starting sources passing into the slag. The reaction can generally be represented as:

sulfidic source concentrate + flux = matte + slag + gases

The term matte smelting has come being almost synonymous with the pyro way of extraction of copper. It will be pertinent to add here that, in principle, the sulfidic source of copper can be oxidized and subsequently subjected to blast furnace smelting, using carbon as a reductant, to yield metallic copper. However, it so happens that the iron sulfide associated with copper sulfide fully oxidizes to ferric oxide first, and only then can the oxidation of copper sulfide takes place. This ferric oxide is not easily removed by slagging. In the normally used process in copper metallurgy, the roasting operation removes sulfur to a desired extent, during which the associated iron sulfides (FeS and FeS_2) convert to ferrous oxide, which passes into the slag more easily than the higher oxides of iron (Fe_2O_3 and Fe_3O_4). Matte smelting has traditionally been carried out in reverberatory furnaces. The blast furnace smelting process is suitable when somewhat strong reducing conditions are required.

The reverberatory furnace smelting, on the other hand, is reserved particularly for those situations where reducing conditions are either not necessary or are not desirable.

The flash smelting process combines into one the flash roasting and the smelting operations. The sulfide concentrate fines react with oxygen at high temperatures. The oxidation process itself generates sufficient heat for the smelting process to occur simultaneously. The combustion rate in the furnace is conducive for rendering the gases that come out enriched with sulfur dioxide; a gaseous output of such quality that can be economically processed to sulfuric acid.

4.5.1
Slags

In the smelting processes described, slags may appear simply to be thrown away after having been separated from the matte or metal. This is not correct. There are instances, however, wherein the slag by design is made the economic product and the reduced metal the byproduct. For example, ore from one of the world's largest deposits of ilmenite is admixed with coal and then arc smelted to produce a pig iron byproduct and a high-titania slag main product; the latter subsequently serves as the principal raw material for the production of the pigment-grade titania. To cite other examples of utilities, reference may be drawn to iron blast furnace slags and to lead blast furnace slags. The former may be used for cement manufacture and as concrete aggregate. The latter may be used for zinc recovery prior to discarding. Most nonferrous smelting slags are of no value and are discarded.

To provide a short account of copper resource it may at the very outset be stated that most copper-bearing mineral is chalcopyrite, $CuFeS_2$. Where chalcopyrite deposits are close to the Earth's surface, weathering processes can take place which chemically change chalcopyrite, over geological times, into other copper-containing minerals. Closest to the surface, so-called oxide minerals are formed. These include tenorite (CuO), malachite and azurite (copper carbonate), and chrysocolla (copper silicate). At lower depths, secondary copper sulfides are formed, including chalcosite (Cu_2S), and bronite (Cu_5FeS_4), while below these, the primary, unchanged chalcopyrite is found. The oxide minerals found in the weathered zone of copper deposits are not amenable to concentration by flotation or any other physical methods, but both the primary and secondary copper sulfide minerals are readily concentrated by flotation. A typical run-of-mine copper sulfidic source will usually contain less than 2% copper and following concentration by froth flotation, the resulting copper concentrate containing 20 to 30% copper form the typical starting point for a pyrometallurgical smelting process. The following are the major pyrometallurgical processes available for the production of copper from sulfide sources: (1) conventional process (using a reverberatory furnace); (2) Outokumpu flash smelting process; (3) Inco flash smelting process; (4) Noranda process; (5) Worcra process; (6) Mitsubishi process.

The conventional process of copper making involves carrying out three steps that involve roasting, smelting, and converting in separate operations. Roasting is often done prior to smelting with the objective of using the released heat to dry and heat the charge before it forms the smelting furnace charge. This step will give rise to fuel saving and also enhance smelting furnace capability. The tradition has been to use reverberatory furnaces for smelting of the mixture of copper concentrate/calcine and the silica flux. Combustion of oil, natural gas, or pulverized coal provides the heat needed to maintain a temperature at about 1200 °C of the two-phase liquid system of matte and slag. The hot combustion gases sweep and pass over the charge. This system as such suffers from several disadvantages. Fuel consumption is considerable, and the oxidation of sulfides in the furnace gives rise to pollution problems because the sulfur dioxide in the smelter effluent gases is too dilute (1–2%) for recovery as sulfuric acid. In modern reverberatory installations which usually are provided with fluid bed roaster it is possible to attain 90% sulfur recovery without treatment of exhaust gas from the smelter. However, reverberatory smelting installations which once dominated in copper metallurgy have fallen into insignificance, and it is unlikely that any new reverberatory will ever be built.

The emission problem associated with the reverberatory smelting may be solved by electric furnace smelting. In the electric smelting process the quantity of effluent gas can be rather small and the sulfur dioxide concentration can readily be controlled by adjusting the air entrainment into the electric furnace.

The copper content of the slag phase is an important point in the matte smelting stage. The copper concentration in the discarded slag ranges from 0.2 and 1%, depending purely upon the operational conditions. The concentration of silica in the slag close to saturation is conducive. It results in: (i) minimum solubility of copper in the slag; and (ii) minimum miscibility between matte and slag. Avoidance of excessive oxidizing conditions is an additional conducive point. This inhibits formation of magnetite (Fe_3O_4) which, if present in excess, makes the slag viscous such that separation of the two phases becomes more difficult. The crux of the matter is that if the slag is taken care of, the product, the matte or the metal, takes care of itself.

The conversion process for the copper matte removes iron, sulfur and other impurities from matte, thereby yielding liquid metallic copper of about 99% purity (blister copper). The slags which come out of converters contain from 2 to 15% copper and must go through treatment for copper recovery, usually by froth flotation of the copper from solidified and slowly cooled slag.

The story of copper remains very much incomplete if the text does not include the modern processes for copper smelting. Trends are to make full use of the energy source obtainable by complete oxidation of the sulfide charge and to make processes suitable for continuous operation. The first development in this direction was the introduction of flash smelting which utilizes considerable sulfide combustion energy for the melting of matte and slag. The flash smelting technique has been developed along two different lines: (i) The Inco process which is made completely autogeneous by use of oxygen; and (ii) The Outokumpu process which uses preheated air, in some cases with oxygen enrichment. There is a need to add in hydrocarbon fuel in the Outokumpu process for making up its thermal deficiency. Advantages of the Inco over the Outokumpu process are shown in Table 4.1.

Later developments which have had more impact on copper smelting relate to an approach which combines roasting, smelting and converting steps in one reactor, thereby making the copper production process continuous. The three unique continuous processes tried in operation are: (i) the Worcra process, (ii) the Noranda process; and (iii) the Mitsubishi process. The principles of the processes are respectively shown in Figures 4.5 to 4.7.

In conclusion of the story of copper, reference is drawn to Figure 4.8 which depicts an outline flowsheet for pyro-way of making copper sulfide concentrate by the traditional route,

Table 4.1 Comparison between Inco and Outokumpu processes for copper smelting.

	Inco process	*Outokumpu process*
Energy	Lower energy requirement	Higher energy requirement
Volume of effluent gas	Small volume because of absence of nitrogen and hydrocarbon combustion products	Large volume because of presence of air and fuel combustion products
Concentration of sulfur dioxide in the combustion gases	As high as 80% – very well suited for processing to sulfuric acid or sulfur or liquid sulfur dioxide	Not as high as Inco process
Dust losses	Low (due to modest volumetric flow of gas)	Not low
Throughput (equipment size same)	30% higher than Outokumpu process	30% lower than Inco process

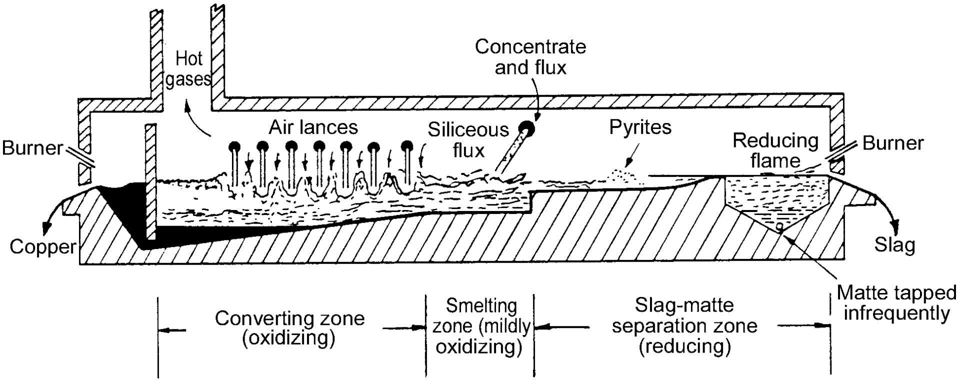


Figure 4.5 Worcra furnace for the continuous production of copper.

and by the newer route. It may be summarized that the copper pyro process in the traditional route involves the three main stages: smelting, converting, and refining. Modern flash smelting furnaces have replaced the reverberatory furnaces. They are efficient, environmentally friendly units, and operate continuously. The furnace gases are quite rich in sulfur dioxide, which permits efficient and almost complete conversion to sulfuric acid. The matte and slag formations in flash smelting may be shown chemically as:

$$4\ \mathrm{CuFeS_2} + 5\ \mathrm{O_2} = 2\ (\mathrm{CuS} \cdot \mathrm{FeS})_{\mathrm{matte}} + 2\ \mathrm{FeO} + 4\ \mathrm{SO_2}$$

$$2\ \mathrm{FeS_2} + 5\ \mathrm{O_2} = 2\ \mathrm{FeO} + 4\ \mathrm{SO_2}$$

$$2\ \mathrm{FeO} + \mathrm{SiO_2} = 2\ (\mathrm{FeO} \cdot \mathrm{SiO_2})_{\mathrm{slag}}$$

Converting involves blowing air through molten matte. Two stages of oxidation occur: (i) slag formation, and (ii) copper production. In the slag formation stage, FeS is oxidized to FeO, Fe_3O_4 and SO_2 and the iron oxides joins the slag phase. Copper remains as cuprous sulfide in the matte phase, which is known as "white metal" at the end of slagging stage:

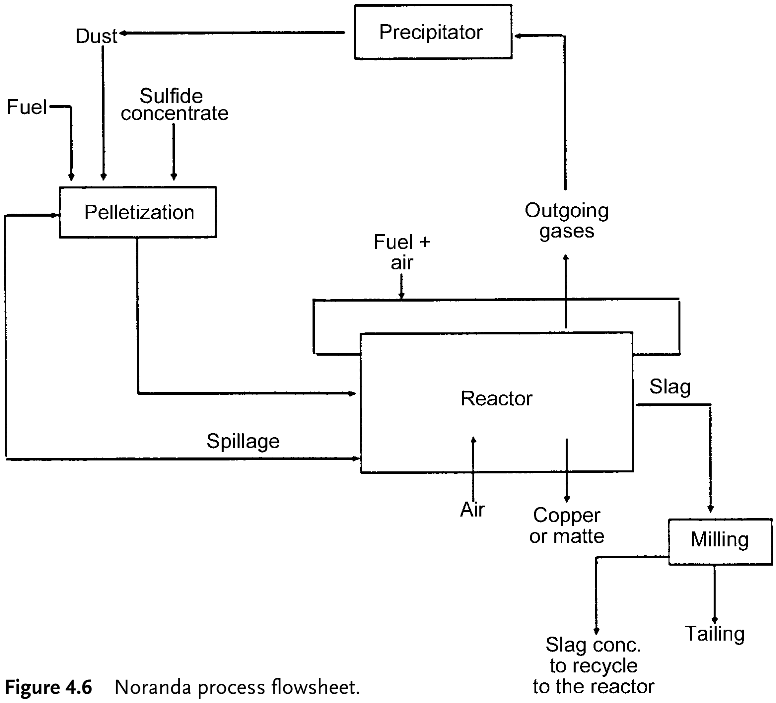


Figure 4.6 Noranda process flowsheet.

$$2\ Cu_2S \cdot FeS_{(matte)} + 3\ O_2 \rightarrow 2\ Cu_2S_{(white\ metal)} + 2\ FeO_{(slag)} + 2\ SO_2$$

In the copper production stage, copper sulfide is oxidized to molten copper metal, known as "blister copper" and so named because when liquid copper cools, the evolution of the residual sulfur and oxygen from the metal as sulfur dioxide gas causes blisters to form on the surface of the metal. The conversion reaction may be shown as:

$$2\ Cu_2S_{(white\ metal)} + 2\ O_2 = 4\ Cu + 2\ SO_2$$

The conversion process is carried out in converters. The liquid copper formed in the process sinks to the bottom of the converter, while the top layer is of white metal. For this reason, it is essential that the converter is side-blown and not bottom-blown. The cold air blast generates a large amount of heat when it meets and oxidizes the sulfide. This heat is sufficient to melt the phases, and also to heat the gas to the process temperature. If the incoming cold air were to meet the liquid copper containing only about 2 at-% sulfur, as would happen in a bottom-blown converter, not enough heat would be generated. As a result, the liquid surrounding the tuyere would freeze. The newer pyro way of making copper combines roasting, smelting and converting into one and continuous in operation. These, of course, have not yet replaced the traditional route in the same way as the reverberatory furnace smelting process may rightly be said as having been completely taken over by flash smelting in copper metallurgy. The engineering and design of reactor are of utmost importance in continuous operation. The processes for refining blister copper have been covered in later text.

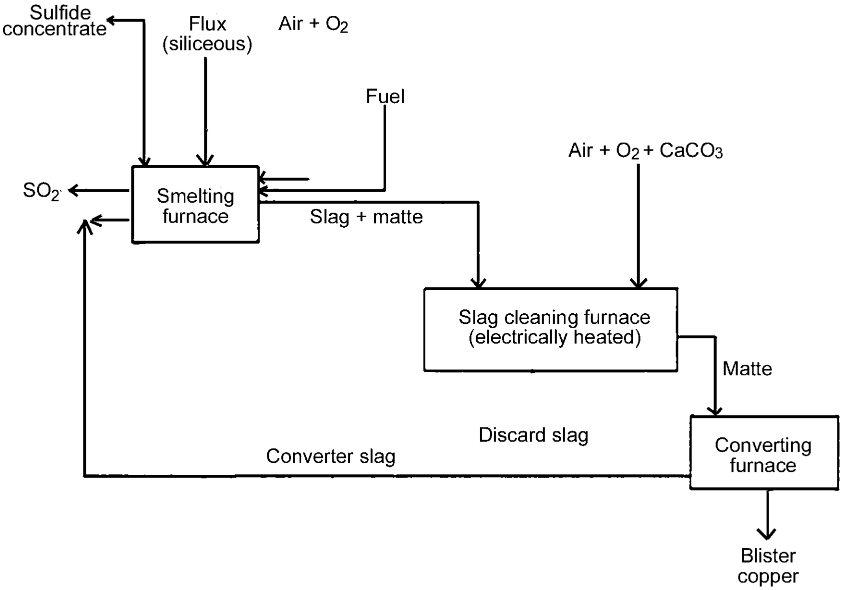


Figure 4.7 Principle of the Mitsubishi continuous smelting process.

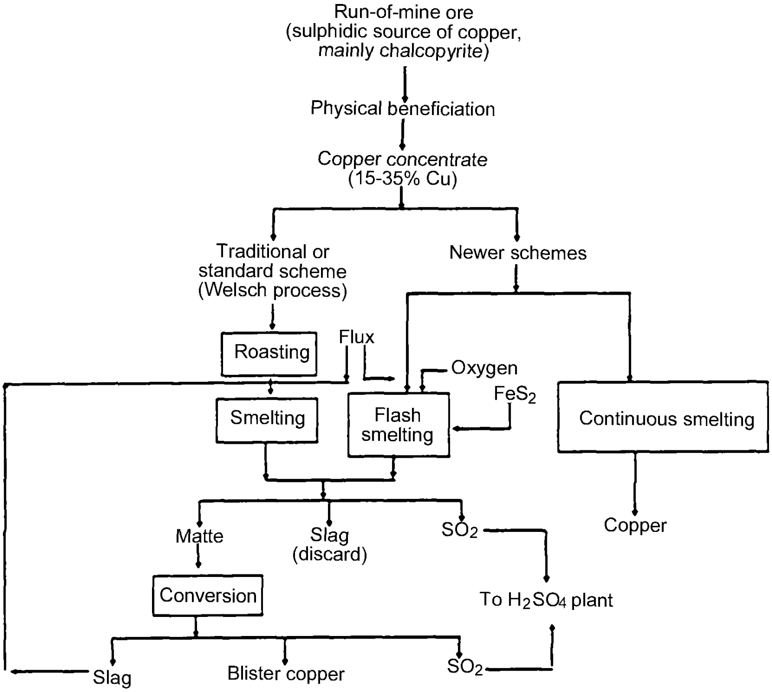


Figure 4.8 Flowsheet for copper extraction from sulphide concentrates.

4.6
Oxide Reduction

Among the wide and varied types of compounds that are reduced to metals, the oxides are by far the most extensively encountered entities. Metal oxides, in forms amenable to reduction, occur either as principal compounds in ores or can be readily obtained from other compounds that occur in the ores. Many reducing agents are available for converting the oxides to the metal.

The Ellingham diagram, given in Figure 4.9, is the logical starting point for considering metal preparation by oxide reduction. The less-stable metal oxides appear in the top region of the diagram; oxides of moderate stability occupy the middle region; and very stable ones occupy the bottom region of the diagram. Even among the least stable oxides, only those of the more noble metals (e.g., silver, platinum, palladium) can be converted to the metals merely by simple thermal decomposition; all other oxides can be converted to metals only by the use of reducing agents.

In principle, any element whose Ellingham line lies below the Ellingham line of a specified element, is capable of reducing the oxide of the specified element to the elemental state. In practice, however, only the nonmetals, carbon, hydrogen and silicon, and the met-

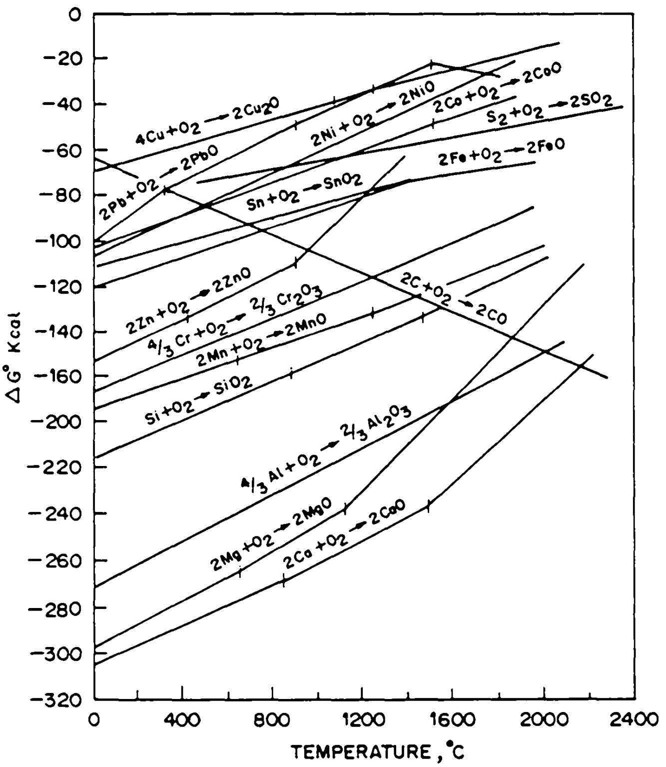


Figure 4.9 Ellingham diagram for the free energy of formation of metallic oxides.

als, calcium, magnesium and aluminum, have been used as reducing agents for preparing metals from their oxides. Obviously, the ability to reduce is only one of the several qualifications which an element should possess in order to be useful as a reducing agent. The desirable characteristics of a good reducing agent and the relevance of these characteristics in any reduction process are best appreciated by examining the actual processes in which these reducing agents are used.

4.6.1
Carbothermy

The term "carbothermy" implies the use of both carbon and high temperatures to influence a reduction. Carbon needs no introduction as the cheapest reductant known to metallurgists. The ability of carbon to function as an effective reducing agent is based on its unique property that it forms two gaseous oxides, carbon monoxide and carbon dioxide, both of which have excellent thermodynamic stability. The positions of the Ellingham lines of carbon dioxide and carbon monoxide are of considerable significance in oxide reduction processes. The Ellingham line of carbon dioxide is almost parallel to the temperature axis, implying little change in its stability with changes in temperature. The Ellingham line of carbon monoxide, on the other hand, has a large negative slope, indicating that the stability of carbon monoxide increases markedly with increasing temperature. Thus, although carbon dioxide is more stable than carbon monoxide at lower temperatures, the reverse becomes true at higher temperatures. The gas phase in equilibrium with carbon at any temperature is a carbon monoxide–carbon dioxide mixture. For the reasons just noted, the ratio of partial pressures, P_{CO}/P_{CO_2}, increases with increasing temperature. For $P_{CO} + P_{CO_2} =$ 1 atmosphere, the equilibrium gas contains less than 1% carbon monoxide at temperatures below 400 °C, and less than 1% carbon dioxide at temperatures above 980 °C. The mixture is equimolar at 674 °C. The carbon line is a continuum of states in which carbon is in equilibrium with a carbon monoxide-carbon dioxide mixture at 1 atmosphere pressure. This carbon line, marked abcd in Figure 4.10, follows the carbon dioxide Ellingham line up to 400 °C, and then curves down gently to tangentially meet and join the Ellingham line for carbon monoxide at about 1000 °C. The ratio, P_{CO}/P_{CO_2}, is fixed along the carbon line by the equilibria:

$$C + CO_2 = 2\ CO$$

and

$$CO + 0.5\ O_2 = CO_2$$

The oxygen pressure is also fixed along this line. It is, therefore, possible to divide all the oxides into two groups, depending on whether the associated Ellingham line lies above the carbon line or below it. For an oxide belonging to the former group, the carbon line is in the stability field of the metal and so carbon can, in principle, reduce the oxide to the metal. It may be noticed that in the Ellingham diagram the lines associated with oxides such as cupric oxide, nickel oxide and many others lie above the carbon line at all temperatures. In such cases the minimum temperature required for reduction is decided by the reaction kinetics. For oxides belonging to the second group (i.e., oxides whose Ellingham lines are

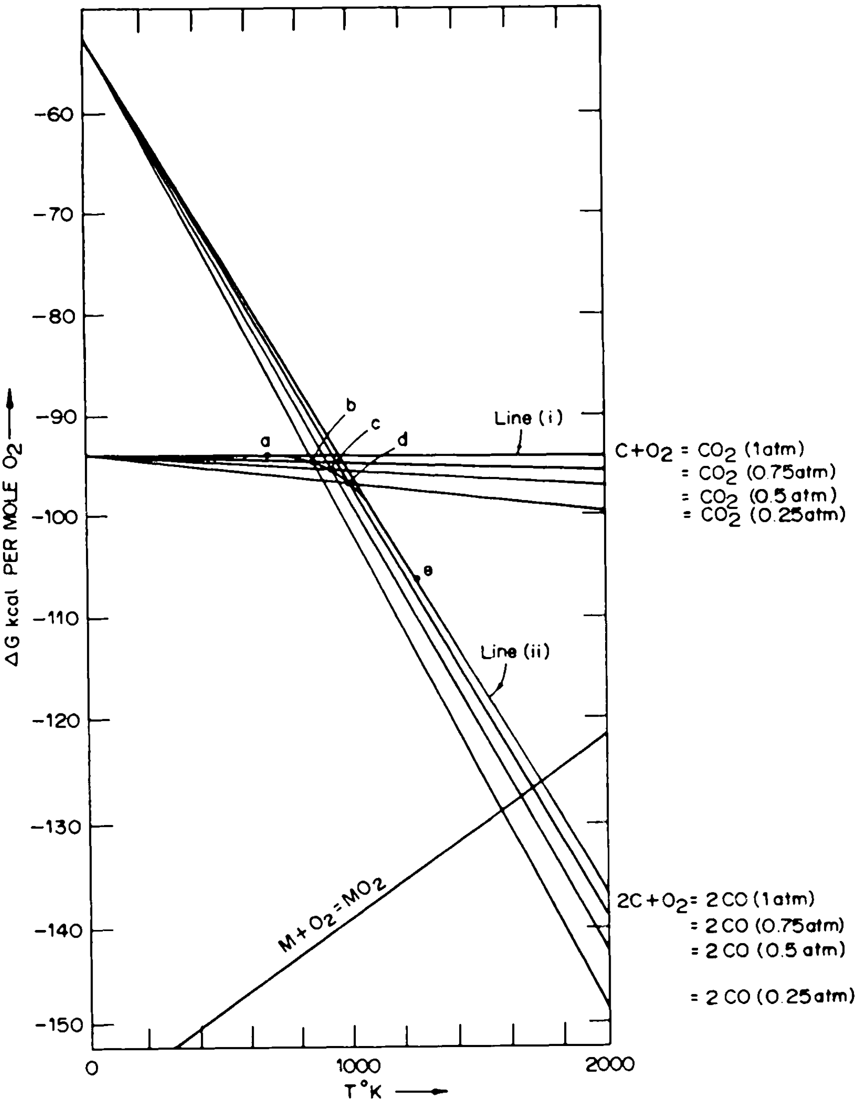


Figure 4.10 The effect of varying the pressures of the product gases of the reactions.

located below the carbon line), the carbon line lies in the oxide stability field. Carbon, therefore, can not reduce these oxides. When the Ellingham line associated with an oxide intersects the carbon line, the temperature of intersection represents the minimum temperature at which the oxide may be reduced by carbon. Ferrous oxide, for example, can be reduced by carbon only above 675 °C. It can similarly be seen that several important nonferrous metal oxides can be reduced by carbon at temperatures around 1000 °C. These include oxides of tin, lead, copper, nickel, and zinc.

The general reaction representing the reduction of a metal oxide by carbon can be written as

$$(x + 2\,y)\ \mathrm{MO} + (x + y)\ \mathrm{C} = (x + 2\,y)\ \mathrm{M} + x\ \mathrm{CO} + y\ \mathrm{CO_2}$$

This equation simplifies to

$$2\ \mathrm{MO} + \mathrm{C} = 2\ \mathrm{M} + \mathrm{CO_2}$$

$$\mathrm{C_{(gr)}} + \mathrm{O_{2(g,\ \mathit{P}=1)}} = \mathrm{CO_2} \text{ and } 2\ \mathrm{C_{(gr)}} + \mathrm{O_{2(g,\ \mathit{P}=1)}} = 2\ \mathrm{CO_{(g)}}$$

on the $\Delta G - T$ variations for the two reactions. The line a, b, c, d, e represents the carbon line at temperatures below 400 °C, and to

$$\mathrm{MO} + \mathrm{C} = \mathrm{M} + \mathrm{CO}$$

at temperatures above 980 °C. Carbothermic reduction, usually represented as a solid–solid reaction by the general equation

$$2\ \mathrm{MO} + \mathrm{C} = 2\ \mathrm{M} + \mathrm{CO_2}$$

probably involves the following sequence of gas-solid reactions:

$$\mathrm{CO} + 0.5\ \mathrm{O_2} = \mathrm{CO_2}$$

$$\mathrm{CO_2} + \mathrm{C} = 2\ \mathrm{CO}$$

$$\mathrm{CO} + \mathrm{MO} = \mathrm{M} + \mathrm{CO_2}$$

The reaction involving only carbon dioxide, carbon and carbon monoxide is popularly known as the Boudouard reaction. Its occurrence in the forward direction is favored at high temperatures. The reverse reaction, namely, carbon precipitation, occurs at lower temperatures. The precipitation of carbon is, however, known to occur only slowly at temperatures below 700 °C in the absence of a catalyst.

The carbothermic reduction processes outlined so far apply to relatively unstable oxides of those metals which do not react with the carbon used as the reductant to form stable carbides. There are several metal oxides which are intermediate in stability. These oxides are less stable than carbon monoxide at temperatures above 1000 °C, but the metals form stable carbides. Examples are metals such as vanadium, chromium, niobium, and tantalum. Carbothermic reduction becomes complicated in such cases and was not preferred as a method of metal production earlier. However, the scenario changed when vacuum began to be used along with high temperatures for metal reduction. Carbothermic reduction under pyrovacuum conditions (high temperature and vacuum) emerged as a very useful commercial process for the production of the refractory metals, as for example, niobium and tantalum, and to a very limited extent, of vanadium.

In order to gain an appreciation of the variation of the carbothermy in implementing it under pyrovacuum conditions (as pointed out in the preceding paragraph), the general reaction for the carbothermic reduction of a metal oxide be once again considered:

$$\mathrm{MO} + \mathrm{C} = \mathrm{M} + \mathrm{CO}$$

The temperature at which the Ellingham lines of the metal oxide (MO) and of carbon monoxide (CO) intersect is the minimum temperature, T_R, at which this reaction can take place, yielding the metal and carbon monoxide (all at 1 atm pressure). If the carbon monoxide pressure in the system is maintained at a value P_2 atm which is different from 1 atm, then the minimum temperature for the reaction would be either greater than T_R or less than T_R, depending on whether P_2 is more than 1 atm or less. This happens because the free energy change due to the change in the carbon monoxide pressure from 1 atm to P_2, given by the expression

$$\Delta G = R\,T \ln \frac{P_2}{l} = R\,T \ln P_2$$

has to be added to the standard free energy change for the reaction, to obtain the free energy change associated with the reaction in a situation where carbon monoxide is obtained at a pressure P_2. Thus

$$\Delta G = \Delta G^0 + R\,T \ln P_2$$

At any given temperature T, ΔG assumes a more negative value than G^0 if P_2 is less than 1.

In Figure 4.10 are shown the lines corresponding to the standard free energies of formation of a metal oxide and of carbon monoxide; also shown is the line for the free energy change associated with the reaction

$$2\,\mathrm{C} + \mathrm{O}_2 = 2\,\mathrm{CO}\ (P\ \mathrm{atm}), \quad P < 1$$

The last-mentioned line intersects the metal oxide line at a lower temperature than the line corresponding to the formation of carbon monoxide at 1 atm. It is, therefore, clear that the minimum temperature required for the carbothermic reduction of the metal oxide under vacuum is less than the minimum temperature for the same reaction at atmospheric pressure. Thus, by increasing the temperature and decreasing the pressure of carbon monoxide, it may be possible to reduce carbothermically virtually all the oxides. This possibility has been summarized by Kruger in the statement that at about 1750 °C and at a carbon monoxide pressure below 10^{-3} atm, carbon is the most efficient reducing agent for oxides.

When the metal can form a stable carbide, the product of the carbothermic reduction of its oxide may be a carbide instead of the metal itself. The question as to whether a carbide or the metal forms under standard conditions when the oxide is reduced by carbon is not answered by the Ellingham diagram. To obtain an answer to this question, a more detailed consideration of the thermodynamic properties of the system is necessary.

For the ternary system metal–carbon–oxygen (M–C–O), the fixing of its thermodynamic state requires the specification of the values of three of the four variables T, a_M, a_C, and P_{O_2}. The terms a_C and a_M refer respectively to the activity of carbon and the activity of the metal in the system. A graphical representation of the equilibria in the system, spanning all the states in which it can exist, would involve the construction of a three-dimensional diagram. When one of the above variables (e.g., temperature) is fixed, the equilibria can be described in a two-dimensional diagram. Such a diagram, for the system chromium–carbon–oxygen at 1245 °C is shown in Figure 4.11. In the areas bounded by the solid lines a condensed phase is in equilibrium with the carbon monoxide–carbon dioxide gas phase. Along the solid lines two condensed phases (i.e., those lying on either side of the line) and this gas phase are in equilibrium while at the points of intersection of the solid lines three condensed phases and the gas phase are in equilibrium. There are two types of broken lines

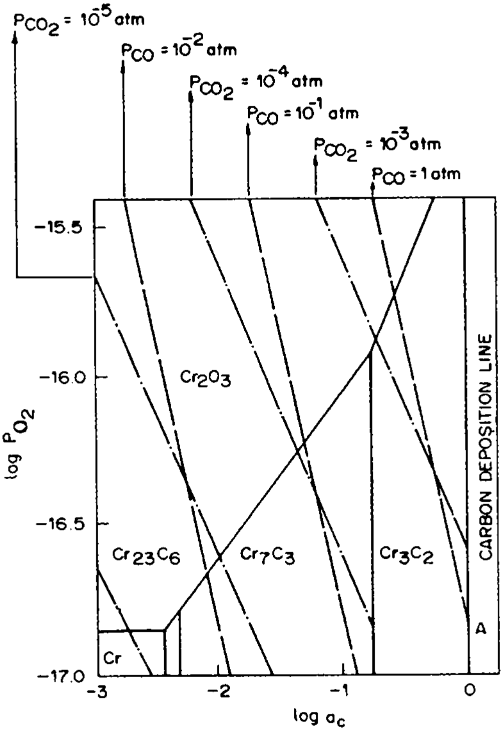


Figure 4.11 The stability diagram for the chromium-oxygen-carbon system at 1245 °C.

appearing in the figure: one giving the partial pressure of carbon monoxide in the gas phase; and the other the partial pressure of carbon dioxide. At specified values of a_C and P_{O_2} the individual values of P_{CO} and P_{CO_2} are fixed. Thus, by calculating P_{CO} at different a_C and P_{O_2} values, the carbon monoxide line can be drawn. Similarly, the P_{CO_2} line can also be drawn.

Figure 4.11 corresponds to a temperature of 1245 °C, which is a very important temperature for this system. At this temperature the Ellingham lines for chromium oxide (Cr_2O_3) and carbon monoxide intersect. From the P_{O_2} nanographic scale given in the Ellingham diagram it can be inferred that the decomposition pressure, P_{O_2}, of chromium oxide at 1245 °C is $1.4 \cdot 10^{-17}$ atm ($\log P_{O_2} = -16.86$). Thus, decreasing P_{O_2} below this value in the system should lead to the reduction of pure chromium oxide to pure chromium. This, however, is only a part of the story. The complete story is that when carbon is used to affect the decrease in the oxygen pressure in the system to below the decomposition pressure of chromium oxide at 1245 °C, chromium metal can be the product only when the activity of carbon in the system is less than $3.6 \cdot 10^{-3}$ ($\log a_C = -2.44$). In the Ellingham diagram, at the point where chromium oxide and carbon lines intersect, $P_{O_2} = 1.4 \cdot 10^{-17}$ and $a_C = 1$. In Figure 4.11, this corresponds to the point A and the stable state of the system is the mixture: carbon + chromium oxide. In other words, under the conditions prevailing at the intersection of the chromium oxide and the carbon lines in the Ellingham diagram, carbon reduces chromium oxide to chromium carbide (Cr_3C_2). This is the status practically with all the elements which form not only stable oxides but also stable carbides.

It is now worthwhile to focus attention on the carbide–oxide reactions which may be identified as the specific variant of the carbothermy under pyrovacuum conditions for some metals. Such reactions can be represented as:

$$\frac{1}{y}\mathrm{M}_x\mathrm{O}_y + \frac{x+y}{y}\mathrm{C} = \frac{x}{y}\mathrm{MC} + \mathrm{CO}$$

and

$$\mathrm{MC} + \frac{1}{y}\mathrm{M}_x O_y = \frac{x+y}{Y}\mathrm{M} + \mathrm{CO}$$

This sequence emphasizes the fact that the oxide is first converted to the carbide and metal formation occurs subsequently by a reaction between the oxide and the carbide.

The metals vanadium, niobium, tantalum, and chromium are examples of elements which form more than one oxide and carbide. Carbothermic reduction would then involve more steps than the two indicated above. Reactions pertaining to the formation and conversion of lower oxides and/or carbides (and in some cases oxycarbides) would occur before the metal is ultimately formed. This information is presented in a systematic and useful format in Pourbaix–Ellingham (*P–E*) diagrams. In these diagrams the equilibria pertaining to various reactions steps are shown by plotting the two variables: $R\,T\ln\,P_{\mathrm{O}_2}$; and T, where P_{O_2} is the oxygen pressure in equilibrium with the metal and oxide and T is the temperature at which the equilibria is considered. The plot is thus a two-dimensional diagram giving an overall picture of the thermodynamically stable regions in the metal–carbon–oxygen system. Pourbaix–Ellingham diagrams are useful in estimating the minimum temperature necessary to obtain the metal by carbothermic reduction under reduced pressure. These diagrams indicate that it is not possible to obtain a solid metal if the reduction pressure is 1 or even 10^{-2} atm; still lower pressures are required.

The study on carbothermy discussed so far in the present text has among various matters brought out two general pathways by which the process can be carried out. This basis permits a categorization of metals. One category of metals lends to extraction by applying carbothermy at or near-ambient pressures. There may be another category of metals which display applicability of carbothermy under reduced pressures. Iron, is an important example that may be cited as belonging to the former category, and niobium to the latter category. The following description pertains to extractive principles and practice of carbothermy for these two metals.

4.6.1.1 **Iron**

The iron blast furnace, so named because its working involves the introduction of an air blast, is depicted in Figure 4.12. The main reactions occurring in the furnace are also indicated in the figure. The furnace is constructed of steel with a refractory lining. The various raw materials constituting the blast furnace burden are: (i) iron ore: the world's main supply of iron is derived from hematite ore; other minor iron-bearing materials that may go into the furnace are mill scale, blast furnace flue dust (which is sintered and fed) and open hearth slag; (ii) coke: this produces the heat required for the reduction and for melting iron, and also supplies the reducing agent (mainly carbon monoxide); (iii) limestone: this renders

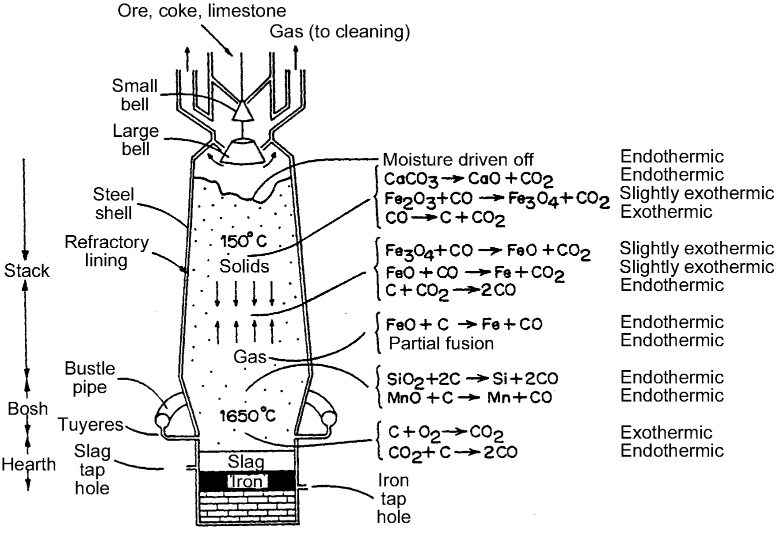


Figure 4.12 Iron blast furnace, showing chemical reactions.

the gangue of the ore and the ash of the coke (mainly silica and alumina) easily fusible; and (iv) air: it is used under preheated (500–1000 °C) and compressed (2–3 atm) conditions to burn coke for producing carbon monoxide. The operation of the furnace is semi continuous in the sense that coke, ore, and limestone are introduced into the furnace batchwise, while preheated air is blown continuously through the tuyeres (derived from the French word for “tubes”) located near the furnace bottom. The furnace load descends and the gases flow upwards through the interstices between the lumps of solids in the furnace load, making this a countercurrent operation. The gases coming out of the top of the bed are nitrogen, carbon monoxide and carbon dioxide, water vapor, and hydrogen. This off-gas is frequently used as a low-grade fuel.

The materials entering the iron blast furnace consist of the iron ore, the flux (limestone), and the fuel (nearly always coke), fed together at the top, and the air blown in the bottom through the tuyeres. The term “charge” in common usage refers to the materials fed at the top and therefore includes the fuel; the ore and flux without the fuel is sometimes termed the “burden”. The ore is an oxide of an iron, and the process is essentially one of reduction of the oxide to metal by ascending CO formed by combustion of coke in the tuyere zone. Since the reaction is a reversible one, a strong reducing atmosphere must be maintained by having an excess of CO, in order that the reaction may proceed rapidly in the right direction. The equation $Fe_2O_3 + 3\ CO = 2\ Fe + 3\ CO_2$ expresses the reduction of Fe_2O_3 by CO. To both sides of this equation a proper amount of CO should be added to represent the excess required.

It is to be noted that in the above reaction it is assumed that the reduction of Fe_2O_3 is performed by CO, not by C, this being supplied by combustion of C of the coke in the tuyere zone. Some of the carbon of the coke is consumed in reduction of silicon, manganese, and phosphorus in the smelting zone, and some by contact with iron oxides farther up in the furnace, for example:

$SiO_2 + 2\ C = Si + 2\ CO$

$MnO + C = Mn + CO$

$P_2O_5 + 5\ C = 2\ P + 5\ CO$

$FeO + C = Fe + CO$

$2\ FeO + C = 2\ Fe + CO_2$

The reduction of iron is completed before the descending charge reaches the smelting zone. The reduction of the impurities takes place almost entirely in the smelting zone, the proportion of each reduced depending on its chemical strength at the smelting temperature. Thus most of the phosphorus on the charge is reduced, possibly half of the manganese, and perhaps a fifth of the silica, the exact proportion varying with conditions, chiefly the temperature attained. No alumina or other oxide stronger than silica is reduced.

The oxygen in the blast penetrates but a short distance above the tuyere level. It is all consumed in burning the carbon of the coke to CO. Most of the carbon in the coke descends through the shaft of the furnace until it reaches the tuyere zone, where it is met by the blast and burned to carbon monoxide. The high temperature precludes the formation of carbon dioxide. Some of the carbon, however, through actual contact with iron oxide, is oxidized (either to CO or CO_2) in the upper part of the furnace. This oxidation, of course, liberates heat above, instead of in, the smelting zone where it is most needed and likewise tends to decrease the proportion of carbon fully oxidized to CO_2 in the furnace and thereby the quantity of heat developed in the furnace.

With respect to the combustion of its fuel and the resultant formation of gases, the iron blast furnace is like a huge gas producer. There is always an excess of carbon in the combustion zone, and the product formed from it is CO. There is, of course, no steam blown in as such, but whatever moisture is present in the blast is decomposed by carbon as in the gas producer:

$H_2O + C = CO + H_2$

Added to this hydrogen are any hydrogen and other volatile matter expelled from the coke, these two sources accounting for the small percentage of hydrogen and CH_4 found in blast furnace gas. It must be noted that the furnace charge enters at the top and undergoes a gradual heating as it descends slowly in the furnace, while the blast enters directly the hottest part. Moisture in the ore, flux, and coke is evaporated in the upper part of the furnace and enters the gas as H_2O vapor.

Blast furnace gas is accordingly combustible, though of much lower heating value than producer gas. The high temperature required in the blast furnace necessitates using preheated blast. Burning a portion of the blast furnace gas in “hot blast stoves” constitutes a convenient and cheap method of heating the blast. The stove receives a portion of the gas and burns it, thus heating the refractory material of which the interior of the stove is constructed.

The chemical processes occurring inside the blast furnace can be stated to start basically from the hot air coming into contact with the white-hot coke. The coke burns to form carbon dioxide. This reaction generates a very large quantity of heat, and it is this heat which maintains the high temperature necessary for the reduction process. As the gas is forced high up the furnace, the supply of oxygen (from the air) diminishes and the carbon dioxide coming into contact with white-hot coke is reduced to carbon monoxide. This carbon monoxide, at the prevailing high temperatures, reduces iron oxide to metallic iron, and becomes converted to carbon dioxide. The limestone, introduced together with the ores, decomposes at these high temperatures to form calcium oxide. The gangue, present in the lump ore, sinter or pellets fed to the furnace, forms a molten, fluid slag with the calcium oxide so produced. Some constituents of the gangue, such as the oxides of silicon, manganese, sulfur, and phosphorus, are partly reduced at the high temperatures and the reducing conditions prevailing at the bottom of the furnace, leading to the formation of elemental silicon, manganese, sulfur, and phosphorus; these, along with carbon, end up in the iron produced and act as contaminants. Molten iron dissolves up to 4% carbon and this dissolved carbon decreases the melting temperature of iron. The iron tapped from the blast furnace is, therefore, quite impure and is known as pig iron or hot metal. A major fraction of blast furnace-produced iron is processed while still in the molten form, to remove the impurities and to produce steel. A significant amount of pig iron finds use in the production of cast irons. Cast irons are produced in a foundry, which may be at a location different from that of the blast furnace. In such a case the pig iron is poured from a ladle into steel molds and solidified. The solidified "pigs" are then transferred to the foundry for manufacturing cast irons in cupola furnaces, which resemble miniature blast furnaces.

Over the past few decades significant improvements have been made in blast furnace technology, resulting in the installation of furnaces which are more productive and consume less coke. These improvements include higher blast temperatures, oxygen enrichment of the blast, fuel injection, higher top pressures, and better feeding of the furnace charge.

The advantage of a higher blast temperature is that it provides for more heat for the endothermic reactions that occur within the furnace. The productivity can, therefore, be increased and/or the coke rate decreased. A limit on this improvement is imposed by the fact that enhanced blast temperatures tend to result in enhanced temperatures near the bosh region of the furnace. It is in this region that the highly endothermic reduction of the oxides of silicon, manganese, phosphorus, and sulfur occurs. By the Le Chatelier principle, these impurity-producing reactions are promoted by high bosh temperatures. One way of controlling an excessive rise in the blast temperature is to increase the humidity of the blast (by injecting steam). The endothermic reaction

$$H_2O + C = H_2 + CO$$

prevents excessive bosh temperatures. The hydrogen produced in the reaction can act as a reducing agent in the upper region of the furnace.

The nitrogen component of the air blast does no useful job, but goes through the furnace, imposing a heat load that it would be desirable to avoid. This objective can be partially achieved by replacing a part of the nitrogen with oxygen, that is, by using an oxygen-enriched air rather than ordinary air, as the blast. The nitrogen in the blast air imposes a heat load mainly in the bosh region, and an oxygen enrichment of the blast tends to increase the bosh temperature, with a concomitant increase in the impurity levels in the pig iron produced. This deleterious effect can be minimized by increasing the blast humidity.

Carbon (coke) consumption, as a fuel and as a producer of the gaseous reductant, carbon monoxide, takes place in the blast furnace. An alternative source of such carbon, along with hydrogen, would be fuel oil or other hydrocarbons, injected at the tuyeres. These hydrocarbons undergo cracking in the bosh region by the highly endothermic reaction

$$C_xH_2\,y = x\,C + y\,H_2$$

It is, therefore, advisable to combine hydrocarbon injection with higher blast temperatures, reduced humidity, and greater oxygen enrichment. The injection of hydrocarbons is quite effective in reducing the coke consumption rate. The hydrocarbons are, however, somewhat costly.

A high top pressure implies a throttling of the gas flow out of the furnace so that the gas pressure at the top of the furnace increases. In such a situation, the pressure throughout the furnace increases. The overall reaction in the furnace

$$\text{coke} + \text{iron oxides} = \text{iron} + \text{gases}$$

shows that there is gas generation. According to Le Chatelier's principle, this would imply that an increase in gas pressure in the furnace would inhibit the reaction. However, from the Ellingham diagram for oxides, one can see that the oxide reduction reactions that produce gas (e.g., $C + FeO = Fe + CO$) are associated with large negative free energies at 1200 °C. This means that these reactions are essentially not reversible, and an increased pressure to the tune of about one atmosphere or so achievable in blast furnaces, would not have a significant influence on the chemical equilibrium.

The productivity of a blast furnace can be increased by supplying the feed materials to it more rapidly. Only a negligible decrease in the conversion of the reactants to the products in the furnace occurs if the residence time is reduced by increasing the feed rate. Since the production rate is simply the feed rate × the fraction converted to the products, substantial advantages can be gained by increasing the feed rate. In the case of iron blast furnaces, increasing the feed rate implies increasing the feed rate of ore, coke, and limestone as well as the feed rate of air. Enhancing the feed rate of air poses difficulties, because as one increases the volumetric flow rate of the blast, the pressure drop necessary to drive this flow though the bed of solids filling the furnace is also increased. The electrical power required to drive the air compressor that injects the air is dependent on the product of the volumetric flow rate and the pressure drop. As a result, beyond a certain limit it becomes uneconomical to increase the volumetric flow rate of the air any further. Moreover, if the volumetric flow rate is increased beyond a point, it may interfere with the downward flow of liquid iron and slag at the bottom of the furnace. Therefore, if the point of the maximum permissible volumetric flow of the blast has been attained, there is only one way of increasing the mass flow rate of the air in order to effect a further increase in the productivity: to raise the density of the air by increasing the pressure throughout the furnace. A high top pressure can thus lead to a greater mass throughput of the reactants and, therefore, to an increased output of iron, without entailing excessive penalties in terms of compressor costs and interference with the downflow of iron and slag.

4.6.1.2 **Niobium**

Among the metals considered for carbothermic reduction under reduced pressure, an important example is the reduction of niobium oxides. The possibilities and the conditions for the carbothermic reduction of niobium oxides can be examined on the basis of the Pourbaix–

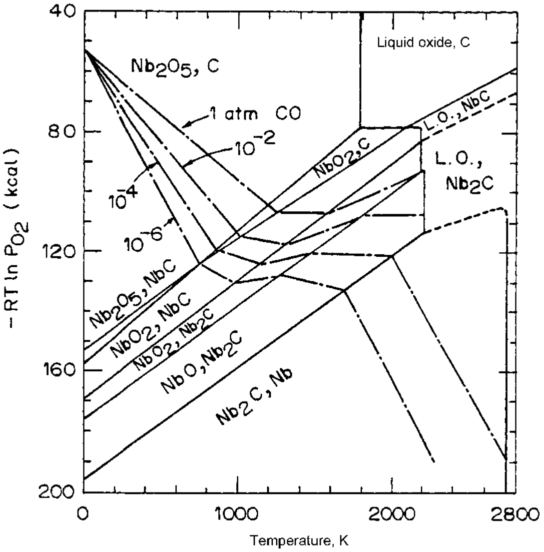


Figure 4.13 Pourbaix–Ellingham for the Nb-C-O system.

Ellingham diagram for the niobium–carbon–oxygen (Nb–O–C) system, given in Figure 4.13. The diagram has been constructed to represent initial charges in which the amount of carbon is more than sufficient to react with all the oxygen in the charge but is not enough to convert all the metal in the charge to carbides. The beginning of the reduction process is represented by the uppermost area which shows the occurrence of an oxide–carbon mixture in the condensed phase. The end of the reduction process is represented by the lowermost area in which a metal and metal carbide mixture exists in the condensed phase. Above 1027 °C, the vapor pressure over the condensed phases is equivalent to the carbon monoxide pressure, and the reduction paths are indicated by the carbon monoxide pressure lines. If it is assumed that no other phases exist, then the carbothermic reduction of niobium pentoxide to niobium occurs, according to the Pourbaix-Ellingham diagram, through the following sequence of reactions:

$Nb_2O_5 + C = 2\ NbO_2 + CO$

$Nb_2O_5 + 7\ C = 2\ NbC + 5\ CO$

$3\ Nb_2O_5 + NbC = 7\ NbO_2 + CO$

$2\ NbO_2 + 10\ NbC = 6\ Nb_2C + 4\ CO$

$3\ NbO_2 + Nb_2C = 5\ NbO + CO$

$NbO + Nb_2C = 3\ Nb + CO$

The higher oxides and carbides should first be converted to NbO and Nb_2C before these two react to form the metal.

The minimum temperature necessary for the formation of the metal under a particular reduction pressure is that temperature at which the corresponding carbon monoxide pressure line intersects the Nb_2C–NbO–Nb equilibrium line in the Pourbaix–Ellingham diagram.

For a reduction pressure of 10^{-4} atm, NbO and Nb_2C react to form niobium and carbon monoxide at 1687 °C. When the carbon monoxide pressure is kept at 10^{-6} atm, the reaction resulting in the formation of the metal would occur, according to the diagram, at 1382 °C.

Having established the feasibility of niobium metal production by the carbothermic reduction of niobium pentoxide under temperature and pressure conditions readily attainable in the laboratory and in industry, the principles of efficient process execution may now be examined. In a high-temperature vacuum furnace operation, the quantity of gas that is to be pumped off can influence the choice of the vacuum process. When the reduction of niobium pentoxide with either carbon or niobium carbide is attempted according to the following overall equations:

$$Nb_2O_5 + 5\ C = 2\ Nb + 5\ CO$$

$$Nb_2O_5 + 5\ NbC = 7\ Nb + 5\ CO$$

and when the temperature of the gases is assumed to be 200 °C at the pumps, the amount of carbon monoxide that must be pumped out per kg of niobium produced is 798 m^3 for the first reaction, if a pressure of 1 torr prevails in the furnace. If the second reaction is considered under identical conditions, 228 m^3 of carbon monoxide must be pumped out. The volume of the gas to be pumped out increases dramatically to 798,000 and 228,000 m^3 respectively for the above reactions if the pressure in the furnace is 10^{-3} torr. The process must, therefore, be divided into individual steps so that most of the gas load is pumped out at the highest permissible pressure and only a relatively small quantity of gas has to be removed under high-vacuum conditions. Thus, the carbothermic reduction of niobium pentoxide is carried out in two major stages. In the first stage, niobium carbide is prepared according to the following overall reaction:

$$Nb_2O_5 + 7\ C = 2\ NbC + 5\ CO$$

In the second stage, the carbide is reacted with the oxide to prepare the metal:

$$Nb_2O_5 + 5\ NbC = 7\ Nb + 5\ CO$$

The first step in the procedure for the preparation of niobium carbide consists of mixing stoichiometric amounts of the oxide and carbon (preferably in the form of carbon black), pelletizing the charge at about 10 tsi pressure using a suitable binder (camphor, sugar etc.), charging the oxide–carbon pellets in a graphite crucible and heating this charge in a vacuum furnace (resistance or induction heating) gradually to 1800 °C under a dynamic vacuum of 10^{-3} torr. After the completion of the reaction the charge is cooled under vacuum and removed for analysis and further treatment.

In the second step, niobium carbide is powdered and mixed with niobium pentoxide such that the oxygen to carbon molar ratio (O/C ratio) in the mixture is about 1.15. The mixture is pelletized, the pellets are loaded in a graphite crucible and the charge is then treated in a resistance or induction-heated vacuum furnace which is connected to a pumping system of high pumping speed. The working conditions and products obtained in this process are summarized in Table 4.2. The metal product obtained after treatment at 2100 °C under 10^{-4} torr pressure is about 99.7% pure niobium, the principal impurities being residual carbon (< 0.2%) and oxygen (< 0.1%).

Table 4.2 Reduction of Nb_2O_5 by NbC to Nb in a vacuum.
Starting mixture containing 10 wt-% oxygen and 7 wt-% carbon.

Temperature (°C)	*Final pressure (torr)*	*Time (min)*	*Analysis (wt-%)*		
			O	*C*	*N*
1500	10^{-3}	80	6	2	0.39
1800	10^{-2}	100	2.5	1.1	0.41
2100	10^{-4}	140	< 0.1	< 0.2	0.02

Oxygen and carbon have substantial solid solubilities in niobium at the temperatures normally required for reduction. As the activity coefficients of both carbon and oxygen in niobium are low, their retention in the niobium metal produced by the carbothermic reduction of niobium oxide is expected. It is, however, possible (as explained later) to remove these residual impurities by extending the pyrovacuum treatment to still higher temperatures and lower pressures.

4.6.1.3 Tantalum

The principles of tantalum metal formation by the carbothermic reduction of tantalum pentoxide and the technology of tantalum metal production by this method are similar to those pertaining to niobium metal production by carbothermy.

The Pourbaix–Ellingham diagram of the tantalum–carbon–oxygen (Ta–C–O) system indicates fewer sequential steps between the oxide and the metal as compared to the niobium–carbon–oxygen system:

$$Ta_2O + 7\,C = 2\,TaC + 5\,CO$$

$$Ta_2O_5 + 12\,TaC = 7\,Ta_2C + 5\,CO$$

$$Ta_2O_5 + 5\,Ta_5C = 12\,Ta + 5\,CO$$

The temperature required for reduction depends on the carbon monoxide pressure maintained in the system. It is 2130 °C when the pressure is 1 torr, and 1705 °C when the pressure is 10^{-3} torr. Because of the high melting point of tantalum (3020 °C), it may be possible to obtain the metal in the solid state even at 1 atm carbon monoxide pressure since the temperature required in this case is 2860 °C.

The industrial practice for the production of tantalum consists of two steps. In the first, the carbide is made by charging a graphite crucible with an intimate, pelletized mixture of lamp black and tantalum pentoxide and heating it in a high-frequency furnace under a dynamic vacuum (10^{-3} torr). In the next step, the ground carbide and the requisite amount of tantalum pentoxide are mixed, palletized, and fed to a reduction furnace where the reduction to the metal occurs. The formation of tantalum carbide as well as the reduction to the metal occur at about 2000 °C. The product leaving the reduction furnace is in the form of pellets or roundels (small cylinders) of porous metal, usually sintered together.

Tantalum obtained by carbothermic reduction at 2000 °C and 10^{-4} torr is more than 99.8% pure. The levels of the principal impurities, carbon and oxygen, are less than 0.1% each.

4.6.1.4 Magnesium

Carbothermic reduction, as a method of metal production, becomes more versatile when a metal product generated in the vapor form is acceptable. Vaporization of the metal product is considered to be an undesirable phenomenon in the carbothermic reduction of refractory metals. In the production of common metals, however, this phenomenon can be accommodated (e.g., in the process for the production of zinc). Another important example in this regard is the production of magnesium.

Magnesium is not a carbide former, and its reduction conditions can be readily estimated by using the Ellingham diagram, without having to consider the Pourbaix–Ellingham diagram. According to the Ellingham diagram the minimum temperature for the reduction reaction

$$MgO\ (s) + C\ (s) = Mg\ (g) + CO\ (g)$$

is 1850 °C, corresponding to $P_{Mg} = P_{CO} = 1$ atm. On slow cooling of the product gas mixture, magnesium vapor is reoxidized to magnesium oxide by carbon monoxide. Reoxidation can be prevented by rapid cooling of the product gas mixture to temperatures below the boiling point of magnesium. Considering the fact that the reduction temperature is about 750 °C above the boiling point of magnesium, quenching of the product gas mixture to the required temperature appears to be a more severe problem than that encountered in zinc extraction where the reduction temperature is only about 50 °C above the boiling point of zinc.

In an industrial process operated at Permanente in California during the second world war, the carbothermic reduction of magnesium oxide was carried out in a carbon lined furnace. The charge was introduced into the furnace in the form of magnesium oxide and carbon briquettes and was heated to the reduction temperature (above 1850 °C) by an electric arc struck between a graphite electrode and a coke bed. The product gas mixture, consisting of magnesium vapor and carbon monoxide from the furnace, was quenched to below 250 °C by means of an inert gas. Natural gas was used as the inert gas in the Permanente plant; hydrogen also could be used in its place. For shock cooling one mole of magnesium, about 50 moles of the coolant gas were needed. In spite of the fast cooling, partial reoxidation did occur and magnesium condensed in the form of solid particles covered with oxide and soot. This magnesium dust was collected in bag filters. The dust was pyrophoric and, owing to its oxide layer, would not coalesce to bulk liquid on melting. It was therefore, briquetted under an inert atmosphere and purified to the bulk metal by sublimation under vacuum.

4.6.2
Hydrogen Reduction

According to the Ellingham diagram of oxides, water or steam (H_2O) is stabler than many metal oxides over a wide and useful range of temperatures, and hydrogen can reduce many metal oxides by reactions of the type

$$MO + H_2 = M + H_2O$$

under standard conditions.

The reducibility of an oxide by hydrogen is decided by the partial pressure, P'_{H_2O} of steam in the reducing gas, hydrogen. At a given temperature, if the ratio P'_{H_2} / P_{H_2} in the hydrogen used for reduction is lower than the value of the ratio, P_{H_2O}/P_{H_2}, given by the equilibrium constant for the reduction reaction, then the oxide will be reduced to the metal. It follows, therefore, that many metal oxides for which the standard free energy change, ΔG^0_R, for hydrogen reduction is positive could be reduced to the corresponding metals in a flow system where dry hydrogen, flowing at a high flow rate, is used. This ensures a small value for P_{H_2O}/P_{H_2} and hence a high hydrogen reduction efficiency. In a way this situation is analogous to using vacuum in a carbothermic reduction reaction.

Many of the metal oxides that are reducible by hydrogen can also be reduced by cheaper reductants such as carbon or carbon monoxide; and this has made hydrogen industrially less important as a reductant. However, when the use of carbon can cause carburization of the reduced metal, and when hydrogen can also be used, the use of hydrogen is obviously preferred. This is the case with tungsten and molybdenum. The gaseous form of the reducing agent, hydrogen, is also an advantage.

Apart from playing an important role in reducing many metal oxides (in some cases its use has been incorporated in commercial practice), hydrogen has also been exploited as a reductant for metal sulfides. However, the hydrogen reduction route for metal sulfides has not yet passed the laboratory development stage as the process involves interesting phyiscochemical principles.

The hydrogen reduction of a metal sulfide (MS) can be represented in a simplified manner as

$$MS + H_2 \rightarrow M + H_2S$$

The above reaction can be driven in the forward direction by continuously removing hydrogen sulfide from the system. This is accomplished in the sulfide reduction process by incorporating lime, which acts as a scavenger for hydrogen sulfide in accordance with the reaction

$$CaO + H_2S \rightarrow CaS + H_2O$$

This reaction is characterized by a high value of the equilibrium constant ($1.7 \cdot 10^6$), pointing thereby to the efficacy of lime in scavenging hydrogen sulfide. With lime incorporated, the final reaction is given by

$$MS + H_2 + CaO \rightarrow M + CaS + H_2O$$

4.6.2.1 **Tungsten**

Tungsten forms several oxides, and the reactions pertinent to the reduction of tungsten oxide to tungsten metal are expressed by the following equations:

$$4\ WO_3 + H_2 = W_4O_{11} + H_2O$$

$$W_4O_{11} + 3\ H_2 = 4\ WO_2 + 3\ H_2O$$

$$WO_2 + 2\ H_2 = W + 2\ H_2O$$

Tungsten metal can be obtained by exposing tungsten oxides to dry hydrogen in a flow system maintained above about 500 °C. An increase in the temperature shifts the reaction towards metal formation. For the first two stages of reduction, corresponding to the formation of W_4O_{11} and WO_2, the permissible steam content in the hydrogen used is fairly high. Even for the last stage of reduction, i.e., for the conversion of tungsten dioxide (WO_2) to tungsten metal at 850 °C, the value of $K = P' P_{H_2O} / P_{H_2}$ is about 45%. This means that the reduction of the oxide to the metal can occur even with a significant concentration of moisture in the gas phase. However, the concentration of moisture in hydrogen has to be kept low for another reason: the reduction of tungsten dioxide by hydrogen is catalyzed by tungsten metal, and this catalytic effect is strongly inhibited by the presence of moisture.

The hydrogen reduction of tungsten trioxide yields tungsten metal in a powder form. The particle size of the powder obtained is strongly affected by the steam content of the reaction gas. Factors such as the temperature, the flow rate and the manner in which the oxide charge is loaded in the furnace affect the moisture content of the hydrogen used, and hence the particle size of the powder. Moisture plays this role though a chain of events. It reoxidizes the reduced product, forming tungsten trioxide. This oxide is fairly volatile at the reduction temperature, and its vapor pressure is higher over finer particles than over coarser particles. So the coarser oxide particles grow at the expense of the finer oxide particles by evaporation and condensation. The tungsten particles produced from the oxide are also coarser.

During the conversion of tungsten trioxide to tungsten, the density of the material changes drastically, from 7.2 g/cm^{-3} for tungsten trioxide and 12.1 g/cm^{-3} for tungsten dioxide to 19.3 g/cm^{-3} for tungsten. In view of this large difference between the bulk volumes of tungsten trioxide and tungsten dioxide, and between tungsten dioxide and tungsten, a better utilization of the reactor volume can be achieved if the reduction is conducted in two steps. In the first step tungsten trioxide is reduced to tungsten dioxide, while in the second step, tungsten dioxide is reduced to the metal. In both steps the same type of furnace – a stationary furnace or a rotary furnace – may be used. The first stage reduction is conducted in the temperature range of 500 to 700 °C, and the second stage in the range of 700 to 800 °C.

The stationary furnace used for reduction has three temperature zones through which the boats loaded with tungsten trioxide move before the oxide is converted to the metal. The loaded boats pass into the furnace countercurrent to the movement of hydrogen gas. Thus the gas in the highest temperature zone has the minimum moisture content, and the moisture content becomes maximum when the gas passes through the lowest temperature zone. This arrangement ensures the highest possible reduction efficiency.

4.6.2.2 **Molybdenum**

The reduction of molybdenum trioxide to the metal by hydrogen is also a three-stage process which can be represented as

$$4\,MoO_3 + H_2 = Mo_4O_{11} + H_2O$$

$$Mo_4O_{11} + 3\,H_2 = 4\,MoO_2 + 3\,H_2O$$

$$MoO_2 + 2\,H_2 = Mo + 2\,H_2O$$

In the temperature range of 400 to 700 °C the values of the equilibrium constants of the first two reactions are larger than the corresponding values for tungsten oxide reduction. Thus, for an equal moisture content in the hydrogen used, the reduction of molybdenum trioxide to molybdenum dioxide occurs at a temperature lower than that required for the reduction of tungsten trioxide to tungsten dioxide. For the conversion of molybdenum dioxide to molybdenum in the temperature range of 700 to 1100 °C, the equilibrium constant is lower than that for the reduction of tungsten dioxide to tungsten. Thus, for a given moisture content in the hydrogen used, the reduction of molybdenum dioxide to molybdenum occurs at a temperature higher than that required for the reduction of tungsten dioxide to tungsten.

The reduction of molybdenum trioxide to molybdenum has to be performed in two or three stages. The first stage reduction is carried out at 450 to 650 °C, the second stage reduction at 650 to 950 °C, and the third stage reduction at 1000 to 1100 °C. There are many reasons for proceeding in this manner. The intermediate oxide, Mo_4O_{11}, and molybdenum trioxide form an eutectic which melts at 550 to 600 °C. The conversion of molybdenum trioxide to molybdenum dioxide must, therefore, be completed before the charge attains a temperature of about 550 °C. The melting and boiling points of molybdenum trioxide, 795 °C and 1100 °C respectively, are relatively low and the molybdenum trioxide charge, when incompletely reduced and taken to these temperatures, will end up as a fused mass and also will volatilize profusely. The control of temperature during the first stage of the reduction is all the more important because the reduction of molybdenum trioxide to molybdenum dioxide is quite exothermic and the use of dry hydrogen at a relatively high temperature can cause excessive heat evolution, driving the charge temperature to values beyond the melting point of molybdenum trioxide. Somewhat moist hydrogen is acceptable (and in a way, more suitable) for the reduction of molybdenum trioxide to molybdenum dioxide. The reduction of molybdenum dioxide to molybdenum, however, requires dry hydrogen. Thus the dry hydrogen used for the reduction of molybdenum dioxide to the metal is passed on, along with the moisture produced in this step, to the stage where molybdenum trioxide is converted to molybdenum dioxide. In the conversion sequence of molybdenum trioxide to molybdenum there is a large variation in the bulk density. The bulk density values for molybdenum trioxide, molybdenum dioxide and molybdenum are respectively 0.4 to 0.5 g/cm^{-3}, 1 to 1.5 g/cm^{-3} and ~2.5 g/cm^{-3}. In other words, a boat holding 100 g of charge in the first stage can hold 200 g of charge in the second stage, and 500 g of charge in the third stage.

The production of molybdenum powder is carried out in practice in electrically heated furnaces. The charge is loaded in iron or nickel boats and reduced in a manner similar to that described for tungsten reduction. The product of the first stage reduction is molybdenum dioxide. The molybdenum powder product from the second stage reduction usually contains 0.7 to 2% oxygen. This is eliminated in the third stage reduction which is carried out at 1000 to 1100 °C. The second and the third stages are sometimes combined and the entire process becomes a two-stage operation. The conditions of reduction, such as temperature, time and hydrogen flow, influence the particle size of the molybdenum powder produced, and this is kept in the range of 0.1 to 6 μm.

In addition to tungsten and molybdenum, the other metals produced by hydrogen reduction are germanium and rhenium.

Germanium dioxide (GeO_2) is thermally reduced (at 600 to 685 °C) with hydrogen to metallic germanium

$$GeO_2 + 2\ H_2 = Ge + 2\ H_2O$$

Potassium perrhenate ($KReO_4$) is reduced by hydrogen in two stages. The first operation is carried out at 500 to 550 °C. The reduced product is washed to remove the hydroxide. The powder is then subjected to a second reduction at a higher temperature (900 to 1000 °C). The product is washed, first with dilute hydrochloric acid and then with water, and dried in vacuum or in a current of hydrogen. Solid rhenium is made by powder metallurgy techniques.

4.6.3
Silicothermy

Silicon is generally considered to be a congener of carbon and this is also reflected in the evolution of silicon as a reducing agent for metal oxides. Silicon forms a fairly stable solid oxide silica or silicon dioxide (SiO_2) and also a stable gaseous oxide silicon monoxide (SiO), both of which can be useful in oxide reduction reactions.

4.6.3.1 **Pidgeon Process**

The most important example of the use of silicon as a reducing agent in producing metals is the Pidgeon process for the production of magnesium. The process stands as one of the illustrious examples of application of physico-chemical principles of metal extraction. Since the process has been accounted for in detail in Chapter 3, it is not described here any further, except to add that the process is largely being replaced by the Magnetherm process, which has been developed in France by Societe Francaise d'Electrometallurgie, Marignac.

The magnetherm process, is essentially a modern variant of the Pidgeon process, and is carried out in a large reactor (height 5.7 m, diameter 4.3 m) shown schematically in Figure 4.14. The reactor consists of a specific feeding system for raw materials, electric energy, and a vacuum system. The furnace consists of a vacuum tight steel shell lined with refractory concrete and thermal insulation. The hearth is lined with carbon blocks and its bottom is connected to a power source. Electric power is fed through the electrode-molten slag-hearth to provide the requisite thermal energy. The charge consists of calcined dolomite, ferrosilicon and calcined bauxite. Heat is generated internally in the furnace by the passage of electric current, through the molten slag, between the carbon electrodes. Alumina lowers the melting point of the calcium silicate slag, and the slag is molten at the reaction temperature of about 1550 °C. The pressure in the reactor is kept at about 8 torr. The magnesium produced in the reaction boils out into the condenser which is maintained at 650 °C. Magnesium vapor condenses and collects as a liquid in the water-cooled steel crucible attached to the condenser, and then solidifies. Up to 7 tons of magnesium can be collected in the crucible. The process is continued after tapping the slag and the residual ferrosilicon at regular intervals from the furnace. Sufficient slag is left in the reactor so that the central electrode remains immersed in it and heating can be continued. The reaction of the Magnetherm process can be represented chemically as:

$$CaO \cdot MgO + (x\ Fe)Si + n\ Al_2O_3 \rightarrow SiO_2 \cdot CaO \cdot n\ Al_2O_3 + 2\ Mg + x\ Fe$$

Thermal magnesium, i.e., magnesium produced by the Pidgeon process earlier and by the magnetherm process at present, constitutes only 30% of the total magnesium production. The rest is produced electrolytically in which the leading examples are (i) the Dow electrolytic reduction process, and (ii) Norsk hydro process.

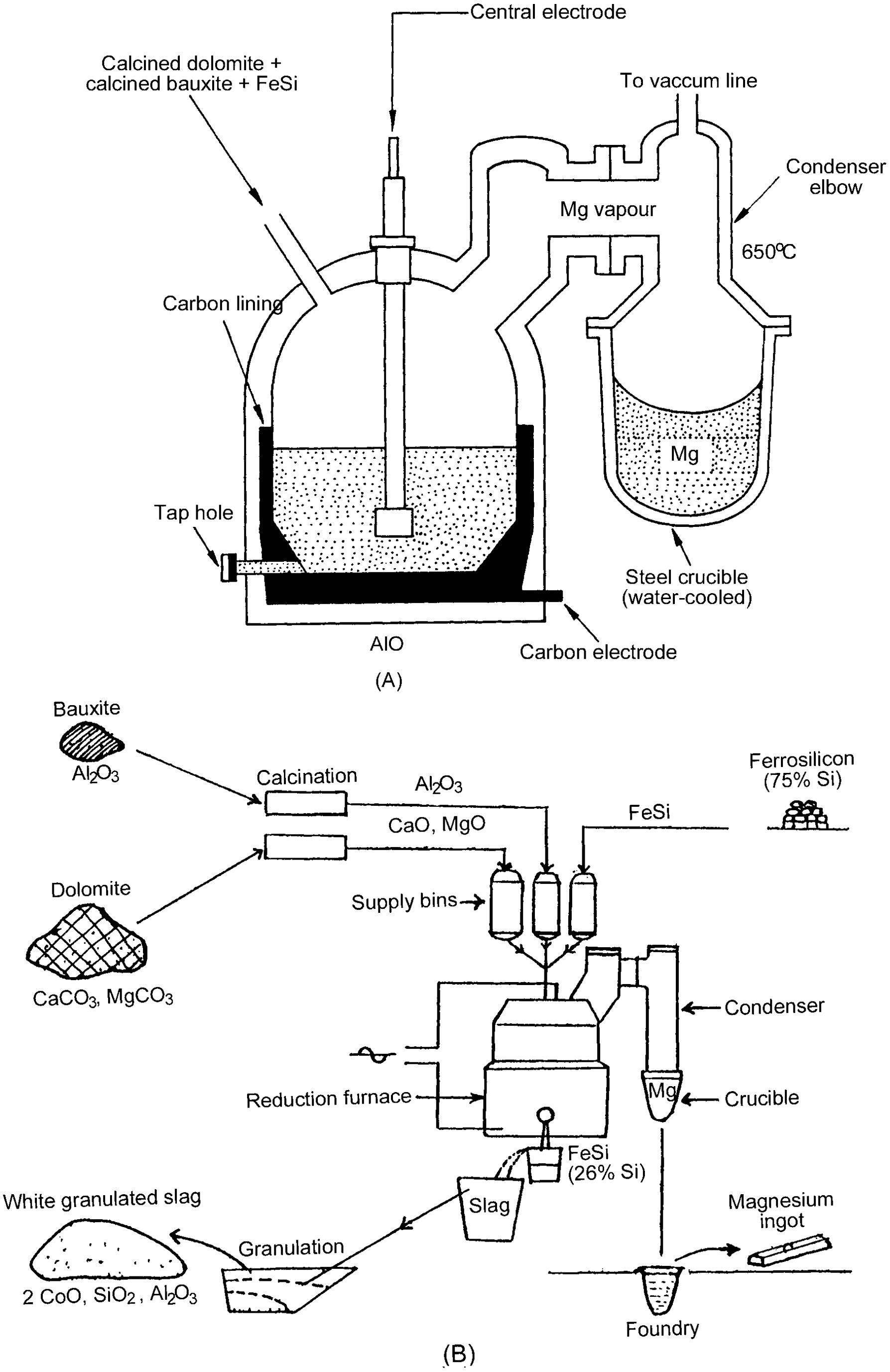


Figure 4.14 Magnetherm process for magnesium production. (A) Reactor assembly; (B) process flowsheet.

4.6.3.2 **Ferrovanadium**

Silicothermic reduction is also an important technique for the production of ferroalloys. The production of low-carbon ferrochrome and of ferrovanadium are carried out by this technique. The overall reaction for the reduction of vanadium pentoxide by ferrosilicon to yield ferrovanadium can be represented as

$$2\ V_2O_5 + 5\ (Fe_{y/5}Si)\ \text{alloy} + 10\ CaO = 4\ (Fe_{y/4}V)\ \text{alloy} + 5\ Ca_2SiO_4$$

Ferrosilicon serves as the source of silicon for the reduction and iron functions as alloying element. The above reaction is exothermic, but the exothermicity is not sufficiently high for it to be carried out in a self-sustaining manner (unlike the aluminothermic reduction processes described later). The smelting is usually performed in an electric arc furnace. During smelting, the formation of high-melting lower vanadium oxides such as vanadium sesquioxide (V_2O_3) and vanadium monoxide and their interaction with silica to form vanadium silicates complicate the reduction process. It is essential, therefore, to add lime to bind silica, making it unavailable for silicate formation. Some of the commercial silicothermic reduction processes use vanadiferrous slag instead of vanadium pentoxide as the source of vanadium in the ferroalloy.

4.6.4
Calciothermy

In addition to the nonmetals carbon and hydrogen, and the metalloid silicon, the metals calcium and aluminum form very stable oxides and can function as reducing agents for many other metal oxides. Reactions in which metals are used as reducing agents usually occur at moderate or high temperatures, and this type of reduction is known as metallothermic reduction. Prior to describing specifically the calciothermic reduction, it will be useful to have a general appreciation of the unique features of the metallothermic reductions.

The metallothermic reduction of oxides can be expressed by the general equation

$$M(I)O_n + p\ M(II) = M(I) + p\ M(II)O_{n/p}$$

where M(I) is the metal to be produced, M(II) is the metal used as the reductant, and p and n are stoichiometric coefficients. While the feasibility of the metallothermic process is determined by the condition

$$\Delta G^0\ (M(II)O_{n/p}) - \Delta G^0\ (M(I)O_n) < 0$$

its practicability is influenced by several other properties such as the melting points, the boiling points, the vapor pressures, the densities, the viscosities (for liquid components), the chemical reactivities and the alloying behaviors of the various components participating in the reaction. Computation of the standard free energy change associated with the reaction therefore covers only one aspect of the practicability of the reaction. For example, while metallothermic reduction of oxides using metals such as thorium, beryllium, magnesium, and zirconium is feasible, it is not practicable for one reason or an other. Calcium and aluminum, on the other hand, combine reducing ability with desirable physico-chemical characteristics in both free and combined forms, and have emerged as useful reducing agents.

The desirable characteristics of a metallothermic or, in general, of any reduction reaction can be summarized as: (i) the reaction should occur quickly and give a high yield of the product metal, (ii) the reaction products must be obtained in compact forms, e.g., the metal as an ingot and the slag as a well-separated layer, so that additional separation steps are not needed; (iii) the reaction should be self-sustaining and, once initiated, should proceed without the need for additional external heating; (iv) the product metal must be of high purity; (v) the reaction should proceed in an open atmosphere; (vi) the reaction should proceed safely without many risks; and (vii) the reaction should be amenable to being carried out in commercially available reactors, using readily available refractories as containers.

Generally, metallothermic reduction reactions are exothermic reactions and, by a suitable choice of process conditions, it has been possible to realize in practice many of the characteristics listed above and to obtain metals of high purity from their oxides. The use of the reductant in a powder or a particulate form usually favors a better reagent contact and once initiated, a quicker reaction. If the heat generated during the reaction is sufficient to raise the temperatures of both the slag and the metal to values beyond their melting points and if they remain molten for a sufficient length of time so that the molten metal settles down by gravity with the immiscible slag layer remaining on its top, a metal ingot, topped by a solidified slag, results on cooling. Slag and metal are then separable from each other by mechanical means. When the heat of the reaction is insufficient to result in an all-liquid reaction mixture, other forms of the metal are obtained. If the reaction occurs but the slag does not melt, the metal is formed as a powder dispersed in a slag matrix. In this case, the slag is leached away to separate the metal powder. When the reduction to the metal occurs with only the slag melting but not the metal, the metal particles usually coalesce and undergo partial consolidation into what is called a sponge. In the metallothermic reduction of oxides, metals are usually obtained in the ingot form, sometimes in the powder form but seldom in the sponge form.

Examples of metals which are prepared by the metallothermic reduction of oxides include manganese, chromium, vanadium, zirconium, and niobium. In a manner similar to the production of magnesium by the Pidgeon process, some of the rare earth metals have been produced by the metallothermic reduction–distillation process.

The metallothermic reduction of oxides is essentially a reaction involving only condensed phases. It follows therefore, that the entropy changes in these reactions are small and that the differences in the heats of formation of the pertinent compounds determine the feasibility of a given reaction. Among the metallic reductants, calcium forms the oxide whose heat of formation is the most negative. As a first approximation, calcium may be considered to be the most effective reducing agent for metal oxides.

4.6.4.1 **Vanadium**

One of the early applications of calcium as a reducing agent has been in the preparation of vanadium metal from vanadium pentoxide:

$$V_2O_5 + Ca = 2\ V + 5\ CaO$$

The form in which vanadium metal product is obtained is determined by the physicochemical conditions prevalent during reduction. This factor, elaborated below for vanadium production in ingot and powder forms, is typically illustrative of the calciothermy as applied to other metals. The standard free energy change associated with the calcium reduction of vanadium pentoxide reaction is highly negative at all temperatures, and the reaction is highly exothermic ($\Delta G^0_{287} = -1619.20$ kJ). The reaction, however, results in a slag, calcia, the melting point of which is very high (2615 °C). When the objective is to produce vanadium as an ingot, it is necessary that the calcia slag should be molten during the reaction. Even though the heat liberated by the reaction between calcium and vanadium pentoxide is large, it is generally not sufficient to raise the temperature of the reaction mixture to above the melting temperature of calcia. If the reaction is implemented under adiabatic conditions, no heat is lost to the surroundings and all the heat liberated in the reaction is used to raise the temperature of the reaction mixture. In practical reactors, however, the conditions deviate considerably from adiabatic conditions and a significant amount of the reaction heat is lost to the surroundings. Attempts have been made to offset the effects of such a heat loss by using boosters and slag fluxes. Boosters are reagents which undergo highly exothermic reactions with the reductant and thus boost the heat output due to chemical reactions in the system. Examples of booster reactions suitable for calciothermic reduction are:

$$\mathrm{Ca} + \mathrm{I_2} = \mathrm{CaI_2}; \quad \Delta H^0_{298} = -532.6\ \mathrm{kJ}$$

and

$$\mathrm{Ca} + \mathrm{S} = \mathrm{CaS}; \quad \Delta H^0_{298} = -113.8\ \mathrm{kcal}$$

Another approach is to achieve slag melting in the system with the available heat; here, slag fluxes are used. These reagents interact with calcia and result in a slag that melts at temperatures considerably lower than the melting temperature of calcia. It is instructive to recall the use of bauxite in the magnetherm process as a slag flux. The compounds calcium iodide and calcium sulfide function effectively as slag fluxes with respect to calcia. A fortuitous coincidence is that both calcium sulfide and calcium iodide can be generated in situ in the reaction mixture as products of booster reactions.

The temperature to which the components in a reaction mixture will be raised as a result of an exothermic reduction reaction is determined mainly by the heat capacities and the heats of transformations of the substances involved, and by the heat lost to the surroundings. As a first approximation, the reactor is considered to be adiabatic, i.e., no heat is lost to the surroundings, and the final temperature is calculated. According to Hess's law, the heat required to raise the reactants to a given temperature and then react them at this high temperature is the same as that required to react the system at room temperature and heat the products to the final temperature. A knowledge of the values of the heat capacities and the heats of transformation of the products is necessary, in addition to the heat of reaction, to calculate the final temperature attained in the adiabatic enclosure. As an approximation, the heats of transformation may be subtracted from the heat of reaction and the resulting value divided by 7 to obtain the final temperature. For this, the heat of reaction, after subtracting the heats of transformation, should be expressed in calories per gram atom of the product because 7 cal atom^{-1} deg K^{-1} is the average value of the heat capacity for most of the condensed substances. Another approach with regard to a better thermal management in calciothermic reduction is to use a reactor design that minimizes heat losses from the reaction mixture. This is accomplished by conducting the reaction in a closed reactor lined on the inside with a refractory such as magnesia. In the practical implementation of the calciothermic reduction process, each of the three thermal energy control measures outlined above finds a place.

In one of the reported studies, the reactor used for the calciothermic reduction of vanadium pentoxide on a laboratory scale was a steel bomb made from a cylinder provided with two flanges on to which two lids were bolted. Lead gaskets were used to ensure gas tightness which was necessary both for evacuating the bomb and for holding the high pressures which developed within the bomb during the reaction. A short length of pipe provided on one of the lids served as a port for evacuation and also for attaching an electrical ignition device for initiating the reaction. This electric ignition device consisted of insulated vanadium electrodes which terminated in a coil of vanadium wire embedded in the charge. The steel bomb was lined on the inside with magnesia. The effective capacity of the bomb was about 100 litres. The reactor was charged with a mixture of calcium chips (47 kg), vanadium pentoxide (25 kg) and sulfur. The bomb was evacuated to $8 \cdot 10^{-3}$ torr pressure and backfilled with 99.9% pure argon. The reaction was initiated by electrically heating to incandescence the vanadium filament embedded in the charge. The bomb was housed inside a concrete shelter. The reduction quickly proceeded to completion and after cooling, the vanadium regulus was separated from the slag and washed, first in water and then in 30% hydrochloric acid. About 12 kg of vanadium metal of better than 99.7% purity was obtained, and this corresponded to a metal yield of 85%.

The calciothermic reduction of an oxide is naturally designed for the obtainment of the reduced metal in the powder form because of the high melting point of the other product, namely, calcia. The formation of the metal in the form of a powder is favored by some other controllable factors also. One of these factors is that the temperature should not exceed the melting point of the metal during reduction. A second factor is that it is preferable to have the reaction temperature as low as possible, without adversely affecting the rate of the reaction.

Let the calciothermic reduction of vanadium sesquioxide (V_2O_3), according to the following overall reaction, be considered:

$$V_2O_3 + 3\,Ca = 2\,V + 3\,CaO$$

The standard free energy change associated with this reaction is negative at all temperatures, and the heat of reaction at room temperature is 681.99 kJ, which works out to –2.51 kJ per gram of the charge. The corresponding values for the calcium reduction of vanadium pentoxide are –1619.20 kJ and –4.18 kJ per gram of the charge. The sesquioxide reduction is considerably less exothermic than the pentoxide reduction. An attempt to produce consolidated vanadium metal by the sesquioxide reduction will, therefore, be a difficult task On the other hand, this reaction would be preferable to the pentoxide reduction in producing vanadium powder because the reduction conditions are not conducive to the melting of the slag or the melting of the metal. In order to inhibit melting, the exothermicity of the reaction is dampened further by using a heat sink. The role played by heat sinks is essentially the opposite of that played by heat boosters. Heat sinks are reagents which do not undergo chemical reactions but, by being present in the reaction mixture, utilize a portion of the heat released by the main reaction for raising their own temperatures. The net effect is that they bring down the heat available per gram of the charge. Calcium chloride is a useful heat sink in the calciothermic reduction of vanadium sesquioxide.

In a published study on the production of vanadium powder, a charge comprising 1 mole of vanadium sesquioxide, 6 moles of calcium and 1 mole of calcium chloride was loaded in a calcia or a magnesia-lined iron crucible and heated to 1000 °C for 1 h inside an argon-filled bell jar. A high-frequency coil was used to heat the crucible and the charge. The reduced mass was cooled, leached with 40 to 50% acetic acid, and the vanadium powder was washed thoroughly, filtered, and dried. About 80 to 85% of the vanadium in the charge was recovered. The vanadium powder thus obtained was found to be about 99.7% pure, with 0.1 to 0.25% oxygen as the major impurity.

In addition to vanadium, there are a number of other metals which yield in powder form when their oxides are straightly reduced with calcium. When calcium is used to reduce oxides which are relatively close to it in the Ellingham diagram, the exothermicity of the reduction reaction becomes small. Likewise, the exothermicity is small when calcium reduces a metal oxide with a low oxygen to metal molar (O/M) ratio. These are the two situations which generally favor metal powder preparation by calciothermic reduction. The preparation of zirconium and uranium in the powder form by the calciothermic reduction of zirconia (ZrO_2) and urania (UO_2) serve as good illustrative examples. The Ellingham lines of thoria, urania and zirconia (ThO_2, UO_2 and ZrO_2) are located close to the calcia line and the O/M ratio in these oxides is only 2. The exothermicities of the reactions

$$ZrO_2 + 2\ Ca = Zr + 2\ CaO; \qquad \Delta H^0_{298} = -169.4\ kJ$$

$$UO_2 + 2\ Ca = U + 2\ CaO; \qquad \Delta H^0_{298} = -184.7\ kJ$$

$$ThO_2 + 2\ Ca = Th + 2\ CaO; \qquad \Delta H^0_{298} = -43.9\ kJ$$

are, therefore, small and they are useful for powder preparation even without heat sinks. The Ellingham lines of niobium pentoxide and tantalum pentoxide are located considerably above that of calcium oxide and the O/M ratio of these two Group V metal oxides is also larger, viz., 2.5. The exothermicities of the reactions

$$Nb_2O_5 + 5\ Ca = 2\ Nb + 5\ CaO; \quad \Delta H^0_{298} = -1246\ kJ$$

$$Ta_2O_5 + 5\ Ca = 2\ Ta + 5\ CaO; \qquad \Delta H^0_{298} = -1129\ kJ$$

are high; when calciothermy is used to prepare niobium or tantalum metal powders, the incorporation of a heat sink in the charge is, therefore, necessary.

The reduction reactions are carried out in the following manner. The oxide and calcium are mixed, loaded in molybdenum crucibles and placed in externally heated reactors; argon gas is kept flowing continually over the reaction mixture. After completion of the reaction, the reacted mass is treated with mineral acids to leach away the slag, leaving behind the metal powder which is collected after washing, filtration and drying. Some of the metal powders so produced are pyrophoric. Zirconium powder is a well-known example. This property, i.e., pyrophoricity, is related to the characteristics of the powder obtained in the reaction. These, in turn, depend on the enthalpy of the reaction and the melting point of the metal. The calciothermic reduction reactions of zirconium dioxide and of uranium dioxide are associated with approximately the same standard free energy changes, the same heat balance, and the same slag products. However, in the case of uranium, a nonpyrophoric powder, with a particle size of approximately 75 μm is produced, whereas in the case of zirconium, a highly pyrophoric powder, with a particle size of only 3 to 4 μm, is produced. The marked difference in the size of the powders can be attributed to the higher melting point of zirconium (1825 °C) compared to that of uranium (1132 °C). Zirconium particles thus sinter and coalesce into larger particles to a much smaller extent vis-à-vis uranium particles at the temperature of the reduction reaction.

The reducing agent calcium is sometimes added as calcium hydride (CaH_2) in oxide reduction reactions. The hydride can be more easily pulverized and hence can be more intimately mixed with the oxide. During reduction, calcium hydride dissociates endothermically to calcium and hydrogen with the result that the charge temperature rarely exceeds the furnace temperature. The hydrogen produced in the dissociation reaction hydrogenates the as-reduced metal powder, making it less prone to oxidation during leaching. Calcium, in the form of its hydride, has been used for the preparation of niobium, niobium-titanium alloys and samarium–cobalt alloys.

4.6.4.2 **Alloys**

In many instances of commercial importance an alloy, rather than a metal, is obtained as the product of calciothermic reduction. The alloy may be an intermediate in metal preparation or even the end product of the process.

Calciothermic reduction of samarium oxide, in the presence of cobalt powder, yields samarium–cobalt alloys in the powder form. The process is popularly known as reduction diffusion. Samarium oxide, mixed with cobalt powder and calcium hydride powder or calcium particles, is heated at 1200 °C under 1 atm hydrogen pressure to produce the alloys. Cobalt oxide sometimes partly replaces the cobalt metal in the charge for alloy preparation. This presents no difficulty because calcium can easily reduce cobalt oxide. A pelletized mixture of oxides of samarium and cobalt, cobalt and calcium, with the components taken in stoichiometric quantities, is heated at 1100–1200 °C in vacuum for 2 to 3 h. This process is called coreduction. In reduction diffusion as well as in coreduction, the metals samarium and/or cobalt form by reduction rather quickly but they need time to form the alloy by diffusion, which warrants holding the charge at the reaction temperature for 4 to 5 h. The yield of alloy in these processes ranges from 97 to 99%. Reduction diffusion is the method by which most of the 500 to 600 t of the magnetic samarium–cobalt alloy ($SmCO_5$) are produced every year.

The reduction diffusion process has also been used for the production of powders of the magnetic neodymium–iron–boron alloy ($Nd_{15}Fe_{77}B_8$). The reaction involves use of a powder mix of neodymium oxide, iron, ferroboron and calcium. The reaction is conducted by heating the powder charge mixture at 1200 °C for 4 h under vacuum. Neodymium–iron–boron alloys are much more prone to oxidation than samarium–cobalt alloys and a proprietary leaching procedure is used for the separation of the alloy and calcium oxide.

Several other useful modifications of calciothermic reduction have been successfully developed for the preparation of this neodymium-bearing magnetic alloy. One of these is reduction–extraction which involves the reduction of neodymium sesquioxide (Nd_2O_3) with calcium in a molten calcium chloride–sodium chloride salt bath at 750 °C and the simultaneous extraction of the reduced metal into a molten neodymium–zinc or neodymium–iron alloy pool. The neodymium–zinc alloy product is treated in vacuum to remove zinc and produce neodymium metal, while the neodymium–iron alloy is itself the end product of the corresponding process. This product is useful in the production of neodymium–iron–boron magnets. While a plain calciothermic reduction of neodymium sesquioxide would have, at best, yielded neodymium powder with a relatively high oxygen content, the reduction–extraction process results in the obtainment of a relatively pure metal in a massive form.

Calcium is generated in situ for effecting reduction in another process in which elemental sodium is introduced in the charge mixture. The production of neodymium metal or of its alloys by the reduction of neodymium sesquioxide with sodium in the presence of calcium chloride is known as the "NEOCHEM" process. This process was developed at the General Motors Research Laboratories in the 1980s. The overall reaction pertinent to the process can be written as

$Nd_2O_3 + 3\ CaCl_2 + 6\ Na = 2\ Nd + 3\ CaO + 6\ NaCl$

The standard free energy change associated with this reaction is negative, as shown in Figure 4.15. This overall reaction is actually the sum of the following two reactions, and occurs in these two steps

$3\ CaCl_2 + 6\ Na = 6\ NaCl + 3\ Ca$

$Nd_2O_3 + 3\ Ca = 3\ CaO + 2\ Nd$

The standard free energies changes for these reactions also are given in Figure 4.15. While the free energy for the second step (calcium reduction) is negative at all temperatures (as

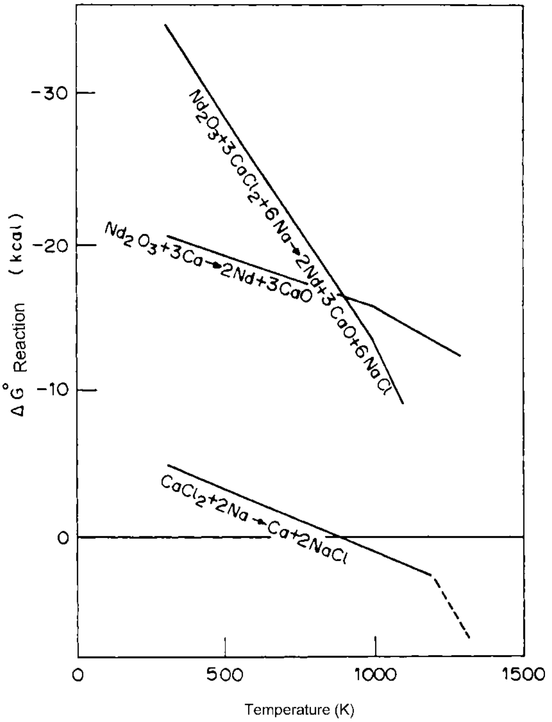


Figure 4.15 Standard free energy changes of the reduction reactions versus temperature.

shown in the figure), the free energy change for the first step (calcium generation) becomes positive above about 600 °C. If calcium is not generated by the reaction of sodium with calcium chloride, the reduction of neodymium oxide cannot take place. The temperature of the overall reaction would, therefore, be influenced by this factor.

In the reaction system, the molten phase would consist of calcium, sodium, sodium chloride, and calcium chloride. Information on the equilibria among these is provided in Figure 4.16, for temperatures between 710 and 1100 °C. A melt of 86% calcium and 14% sodium coexists with a melt of 70% calcium chloride and 30% sodium chloride at 710 °C. Thus, a melt of this composition can be produced by sodium reduction of calcium chloride under proper conditions at 710 °C. The reduction of neodymium sesquioxide to neodymium can be carried out in this melt. Melts of different compositions, yet suitable for reduction, form at higher temperatures. A metal in solution in one of its salts is more corrosive than when it is pure. Thus calcium in solution in calcium chloride or in calcium chloride–sodium chloride reacts with neodymium sesquioxide faster than does pure calcium. The solubility of calcium in calcium chloride increases with temperature, and thus higher temperatures would be preferable for reduction. An upper limit on the temperature of reduction is, however, imposed by the boiling point of sodium; above this temperature the vaporization losses of sodium become excessive, in spite of the decrease in the vapor pressure of sodium due to its dissolution in calcium. When the solubility of calcium in the calcium chloride-sodium chloride melt and the vaporization losses of sodium are considered together, 750 °C appears to be the optimum temperature at which calcium solubility is sufficient while sodium loss is not excessive. The reduction is carried out at this temperature. This temperature is 110 °C higher than the melting temperature of the neodymium-iron eutectic alloy, the form in which the reduced neodymium is extracted in this process.

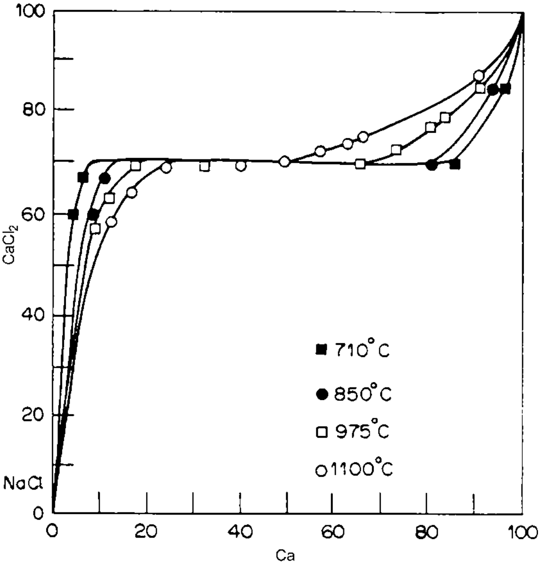


Figure 4.16 Ca–Na melts in equilibrium with $CaCl_2$-NaCl melts.

4.6.5
Aluminothermy

Aluminum forms the oxide alumina, Al_2O_3, which is among the stablest of oxides at all temperatures. Only the rare earths, uranium, magnesium, beryllium, thorium, and calcium form oxides which are stabler than alumina. On the other hand, all the Group V and Group VI refractory metals, viz., vanadium, niobium, tantalum, chromium, molybdenum, and tungsten, and metals like iron and manganese, form oxides which are considerably less stable than alumina. The oxides of Group IV refractory metals, viz., titanium, zirconium, and hafnium, are about as stable as alumina. Aluminum can, therefore, function as an useful reducing agent for many of the commercially important metals and alloys.

Even though the standard free energy change associated with an aluminothermic reduction reaction

$$3\ MO + 2\ Al = 3\ M + Al_2O_3$$

is considerably less negative than that associated with the corresponding calciothermic reduction reaction

$$MO + Ca = M + CaO$$

and even though an aluminothermic reduction reaction is considerably less exothermic than the corresponding calciothermic reduction reaction, aluminum has emerged as a more popular reducing agent than calcium due to several reasons. The product of aluminothermic reduction, alumina, melts at 2045 °C; this is a much lower temperature than the melting point of calcia (2615 °C). The melting point of aluminum (660 °C) is lower than that of calcium (842 °C), but the boiling point of aluminum (2520 °C) is much higher than that of calcium (1494 °C). Thus the relatively small exothermicity of aluminothermic reduction reactions is not a serious handicap because less heat is required to get the products molten in these reactions. Since the vapor pressure of aluminum is relatively low, the pressure in the reactor does not rise to dangerous levels in closed bomb aluminothermic reduction. Added to these points, the ready availability of relatively inexpensive pure aluminum powder and chips, and the ease of handling aluminum in the open, are the other attractive features of the aluminothermic reduction of oxides.

Aluminothermic reduction usually results in producing the metal in consolidated form and not in the powder form which is produced in some of the calciothermic reductions described above. It is, therefore, useful to assess the enthalpy of an aluminothermic reduction reaction to see if sufficient heat is indeed generated to melt the metal and the slag, and to heat them to such temperatures that the two phases might separate due to their density difference. A simple calculation is generally resorted to for a rough assessment in this regard. The ratio of the heat of reaction to the sum of the molecular weights of the reactants or the products is calculated. From this the heat of reaction per gram of the charge can be obtained. Three distinct situations can be arrived at: (i) if the value of the heat of reaction per gram of the charge is more than 950 cal, the reaction would be violent, or even explosive; (ii) if the value is less than 540 cal, the heat of reaction is insufficient to cause heating and melting of the products which is necessary for their gravity separation; and (iii) if the value is between 540 and 950 cal, the reduction reaction would proceed in a controlled manner, without the need of an external supply of heat. In order to control a violent and potentially explosive reaction, a heat sink may be incorporated. It might be an oxide that does not participate in the reduction reaction but forms a fluid slag with the oxidized product. Calcia is used as a heat sink in aluminothermic processes. A reaction which is slow and for which the enthalpy of reaction is insufficient may be accelerated by using a heat booster. The reactions that are normally used for boosting aluminothermic reduction reactions are:

$$3\ \mathrm{BaO_2} + 2\ \mathrm{Al} = 3\ \mathrm{BaO} + \mathrm{Al_2O_3}; \quad \Delta H^0_{298} = -1410\ \mathrm{kJ}$$

$$\mathrm{KClO_3} + 2\ \mathrm{Al} = \mathrm{KCl} + \mathrm{Al_2O_3}; \quad \Delta H^0_{298} = -1255\ \mathrm{kJ}$$

$$\mathrm{NaClO_3} + 2\ \mathrm{Al} = \mathrm{NaCl} + \mathrm{Al_2O_3}; \quad \Delta H^0_{298} = -1284\ \mathrm{kJ}$$

Another additive in aluminothermic reduction reactions is the slag fluidizer. Even after the reduced metal and the slag have become molten during the reaction, their gravity separation into a molten metal pool and a top slag layer may not occur quickly enough, or to a desirable extent, if the viscosity of the slag is high. Slag fluidizers such as fluorite ($\mathrm{CaF_2}$) and calcia are useful in aluminothermic reduction; these reduce the slag viscosity and aid in metal settling, thus facilitating slag metal separation.

One of the important differences between calciothermic and aluminothermic reduction of oxides concerns the interaction between the reduced metal and the reductant. Calcium does not form stable solid solutions or alloys with the reduced metals; calcium contamination in the metal is, therefore, relatively small. Aluminum, on the other hand, readily forms solid solutions with the reduced metals, and the product generally contains appreciable quantities of residual aluminum. This is not a serious problem because in many cases either a certain aluminum content is desired in the reduced metal or the residual aluminum can be effectively removed in post-reduction purification operations. The extent of the contamination of a reduced metal with the reductant can be related to factors such as the reaction temperature, the standard free energy change associated with the reaction, and the slag composition. Let the following generalized reaction be considered:

$$\mathrm{MO} + \mathrm{M'} = \mathrm{M'O} + \mathrm{M}$$

where the reactants and the products are not necessarily in their standard states. The standard free energy change associated with this reaction is related to the activities of the reaction components by the relationship

$$\Delta G^0 = -R\,T \ln \frac{a_{\mathrm{M'O}}\ a_{\mathrm{M}}}{a_{\mathrm{MO}}\ a_{\mathrm{M'}}}$$

Thus

$$\frac{a_{\mathrm{M}}}{a_{\mathrm{M}}} = \frac{\exp\left(\Delta G^0 / RT\right)}{a_{\mathrm{MO}} / a_{\mathrm{M'O}}}$$

The ratio $a'_{\mathrm{M}}/a_{\mathrm{M}}$ directly refers to the extent of contamination of the reduced metal M by the reductant M′. The conditions which minimize the value of this ratio, and hence the contamination, can be arrived at by using the above relationship. The ratio $a_{\mathrm{M'}}/a_{\mathrm{M}}$ is minimized when: (i) ΔG^0 is more negative; (ii) T, the reaction temperature, is as low as possible; and (iii) the ratio $a_{MO}/a_{M'O}$ is large. The choice of the reductant for a metal oxide fixes the value of ΔG^0. The temperature can not be brought down below a limit because of the requirement of molten metal and molten slag for their gravity separation However, the ratio $a_{MO}/a_{M'O}$ can be made large by increasing a_{MO} and decreasing $a_{M'O}$. For example, the residual aluminum content in manganese, produced by the aluminothermic reduction of manganese oxides, is brought down by letting manganese oxide pass into the slag and by slagging alumina, using calcia.

4.6.5.1 Iron

Aluminothermic reduction is one among the few pyrometallurgical processes where the actual process closely follows the route theoretically predicted from thermodynamic data. This characteristic, coupled with the simplicity associated with the whole process, makes it well suited for demonstration experiments. The reduction of magnetite by aluminum is a suitable example in this context.

A mixture of magnetite (Fe_3O_4) and aluminum is unstable even at room temperature and should result in the formation of iron and alumina. The reason why no reaction occurs at room temperature is kinetic and is related to the absence of any exchange of matter between the two solids constituting the mixture. When heated to a sufficiently high temperature, they react and separate into liquid iron and liquid alumina phases. For calculating the equilibrium between these phases, the temperature of interest is the melting point of alumina, i.e., 2045 °C, because the exchange of matter between the metal and slag phases practically stops when the slag solidifies. At 2045 °C, the standard free energy change for the reaction

$$3\ FeO + 2\ Al = 3\ Fe + Al_2O_3$$

is –562.32 kJ and the equilibrium constant K is

$$K = \frac{a_{Fe}^3\ a_{Al_2O_3}}{a_{FeO}^3\ a_{Al}^2} - 10^{13}$$

Iron and alumina are nearly pure and their activity may be assumed to be equal to unity:

$$a_{Fe} \sim 1 \quad \text{and} \quad a_{Al_2O} \sim 1$$

This implies that

$$a_{FeO}^3 \cdot a_{Al}^2 \sim 10^{-13}$$

A certain amount of iron oxide is present in the alumina slag and a certain amount of aluminum is present in the as-reduced iron. Assuming Raoult's law, an aluminum content of 1 wt-% in iron will correspond to $a_{Al} \sim 0.02$. The value of a_{FeO} is then $6 \cdot 10^{-4}$. Even a trace of aluminum dissolved in liquid iron results in a practically complete reduction of iron oxide from the slag phase. The assumption that the product phases are pure iron metal and alumina slag thus holds.

As mentioned earlier, no reaction may be expected when the components are in the solid state. Assuming that the reaction starts at low temperatures, two adjoining grains of the reactants, magnetite (Fe_3O_4) and aluminum, would soon be separated by a solid layer of alumina (Al_2O_3) and further reaction would be prevented. When the reaction occurs at above the melting point of alumina, the molten alumina would run out from between the grains and continuous reaction throughout the charge can then occur. It is, therefore, essential that the temperature of the reaction mass is raised to above 2045 °C. The situation in this regard can be described by calculating the enthalpy balance, assuming adiabatic conditions. The enthalpy of the reaction

$$3\ Fe_3O_4 + 8\ Al = 9\ Fe + 4\ Al_2O_3$$

at 25 °C ($\Delta H^0_{298} = -3347.2$ kJ) should be sufficient to raise the temperature not only to 2045 °C but to 2880 °C (boiling point of iron) with about 15% evaporation of the metal. However, adiabatic conditions are only approached and never reached, and there would be heat losses. These losses can be empirically estimated.

One form of crucible of an aluminothermic experiment is of the clay-bound graphite type, cut into two halves lengthwise and held together by tying with a wire. When this crucible is half-buried in dry sand, molten metal and slag do not run out. Before use the crucible is thoroughly dried in an oven. After loading, the charge can be ignited by using a trigger mixture consisting of about 20 g of barium oxide (BaO_2) and 2 g of aluminum dust, placed in good contact with the charge. The trigger mixture can be ignited by burning a magnesium ribbon embedded in it. Once initiated, the reaction proceeds very quickly to completion. After overnight cooling of the crucible, the products can be easily removed by separating the jointed halves of the crucible. The iron and alumina phases can be easily separated by using a hammer and chisel; the metal can be evaluated for purity and the yield and the mass balance can be calculated.

4.6.5.2 Manganese

The reduction of manganese oxides by aluminum has been used for the production of manganese metal. The process is also a classic example to illustrate thermal energy management in a typical aluminothermic reduction process.

Manganese is found in nature as pyrolusite, MnO_2. In addition to this tetravalent oxide, manganese also forms several well-defined lower oxides: Mn_2O_3, Mn_3O_4 and MnO. It is often observed in metallothermic reduction that the metal being reduced is multivalent whereas the metal used as the reducing agent is monovalent. The heat change associated with the reduction reaction is affected by this, the absolute value of the heat of reaction being larger the higher the valency of the metal in the oxide. Another relevant factor is that when the valency is higher, a larger amount of the reductant metal has to be used. A choice has, therefore, to be made: whether to start with a higher valence oxide and gain in thermal balance while sacrificing the reductant (reactive) metal, or whether to start with a lower valency oxide and save the reductant metal while compromising on thermal balance. The component with the highest melting point in the process of the aluminothermic reduction of manganese oxides is alumina. The temperature of the reacting mass must, therefore, be raised to the melting point of alumina. Let the following reactions be considered:

$$3\ \mathrm{MnO} + 2\ \mathrm{Al} = 3\ \mathrm{Mn} + \mathrm{Al_2O_3};\qquad \Delta H^0_{298} = -519\ \mathrm{kJ}$$

$$0.75\ \mathrm{Mn_3O_4} + 2\ \mathrm{Al} = 2.25\ \mathrm{Mn} + \mathrm{Al_2O_3};\qquad \Delta H^0_{298} = -634.7\ \mathrm{kJ}$$

$$1.5\ \mathrm{MnO_2} + 2\ \mathrm{Al} = 1.5\ \mathrm{Mn} + \mathrm{Al_2O};\qquad \Delta H^0_{298} = -895\ \mathrm{kJ}$$

For the products in each of the above reactions, the heat required to raise their temperature to just above the melting point of alumina can be estimated by using the pertinent heat capacity and heat of fusion values. The reaction is assumed to be conducted in an adiabatic enclosure. The heats required are 669.44 kJ for the first, 602.49 kJ for the second and 548.10 kJ for the third reaction. In terms of heat availability, using the highest oxide of manganese as the starting material appears to be the most attractive. On the other hand, if the manganese/aluminum ratio, which gives the number of gram atoms of manganese produced per gram atom of aluminum consumed, is compared, the values for the three reactions are 1.5, 1.125, and 0.75 respectively. On the basis of this ratio, the use of the first reaction, with the lowest oxide of manganese as the starting material, appears to be the most preferable option. If the lowest oxide has to be used, arrangements have to be made to provide the additional heat required by preheating the charge or by decreasing the liquidus temperature of the slag by incorporating suitable additives so that the available heat would be sufficient to effect the melting of the products and their subsequent gravity separation. As an alternative, without resorting to preheating or to the introduction of slag additives, the metals to oxygen ratio in the original charge can be adjusted to provide the required heat during the reaction, using the data given above. Using manganese dioxide gives a great excess of heat and entails the risk of the reduction reaction being explosive. Even $\mathrm{Mn_3O_4}$, when used as the starting material, gives excess heat while the heat is insufficient if manganese monoxide (MnO) is used. A mixture of MnO and $\mathrm{Mn_3O_4}$, however, can give sufficient heat for reduction; thus the process can be made self-sustaining by choosing a value of the manganese to aluminum ratio between 1.5 and 1.125. These calculations and estimations have been carried out for an adiabatic reactor. In actual reactors there would be heat losses and the appropriate value of the ratio would be closer to 1.125.

In practice, the reduction is conducted in an open magnesite crucible. The reaction is started by igniting a small amount of a mixture of manganese dioxide ($\mathrm{MnO_2}$) and granular aluminum. To this incandescent charge $\mathrm{Mn_3O_4}$, aluminum granules and powdered lime are added in calculated quantities to sustain the controlled reaction. The addition of charge is continued at regular intervals until the crucible is filled with the reacted mass consisting of a lime-alumina slag and manganese metal.

4.6.5.3 **Chromium**

The production of chromium metal by the aluminothermic reduction of chromium sesquioxide can be represented by the equation:

$$\mathrm{Cr_2O_3} + 2\ \mathrm{Al} = 2\ \mathrm{Cr\ (l)} + \mathrm{Al_2O_3\ (l)};\quad \Delta H^0_{298} = -545\ \mathrm{kJ}$$

In the absence of any additive to the oxide-aluminum charge, it is necessary to attain a temperature of about 2200 °C to render the products molten and fit for gravity separation. The heat required for this purpose can be calculated as follows:

- heat capacity of charge (1 mole of Cr_2O_3 + 2 gram atoms of aluminum) ~ 48.8 cal deg^{-1}
- heat required to raise the temperature of this mass by 2200 °C ~ 449.78 kJ
- heat of transformation and melting for 1 mole of Al_2O_3 ~ 110.03 kJ
- heat of melting of 2 gram atoms of chromium ~ 40.16 kJ

The total heat requirement is thus around 599.98 kJ, which is about 548.81 kJ more than the heat available from the reaction. This calculation, however, does not take into account the inevitable heat losses due to the nonadiabatic conditions in the reactor. An estimate of these heat losses can be made by considering the industrial practice for aluminothermic chromium metal production. The charge is preheated to about 500 °C before loading into the aluminothermic crucible. This operation adds about 96.65 kJ (i.e., 48.9 cal $deg^{-1} \cdot 475$) of heat to the system. It, therefore, appears that around 41.84 kJ (96.65 kJ – 54.81 kJ) of heat is lost due to radiation and convection for every mole of chromium sesquioxide reduced to the metal by the aluminothermic process.

The melting points of chromium (1857 °C) and of manganese (1244 °C) are considerably lower than that of alumina. The heat requirement in respect of the reactions leading to the formation of these metals was calculated by considering alumina melting as the objective. The objective changes when aluminothermy is applied to the production of the refractory metals niobium and tantalum. Niobium melts at 2468 °C and tantalum at 3020 °C. Thus, when these metals are the products, the heat requirements for reaching temperatures in excess of 2500 °C and 3050 °C have to be calculated.

4.6.5.4 **Niobium**

Niobium is a multivalent metal and forms stable oxides of compositions represented as niobium pentoxide, niobium dioxide, and niobium oxide. The heats of reaction for the reduction of each of these oxides are

$$3\ NbO + 2\ Al = 3\ Nb + Al_2O_3; \qquad \Delta H^0_{298} = -100.4 \cdot 4.184\ kJ$$

$$1.5\ NbO_2 + 2\ Al = 1.5\ Nb + Al_2O_3; \qquad \Delta H^0_{298} = -115.9 \cdot 4.184\ kJ$$

$$O \cdot 6\ Al_2O_5 + 2\ Al = 1.2\ Nb + Al_2O_3; \qquad \Delta H^0_{298} = -129.0 \cdot 4.184\ kJ$$

In the aluminothermic reduction of niobium oxides, the products must reach a temperature of at least about 2470 °C, and hence the heat required to raise niobium metal and alumina from room temperature to this temperature must be estimated. Using the values of the heat capacities and the heats of fusion for niobium and alumina, the following figures can be obtained:

$$Nb : H^0_{2740} - H^0_{298} = 25.0 \cdot 4.184\ kJ$$

$$Al_2O_3 : H^0_{2740} - H^0_{298} = 107.6 \cdot 4.184\ kJ$$

The heat required, for example, when niobium pentoxide is reduced is 554.79 kJ, whereas the heat available is only 539.73 kJ. There is no question in this case of using a lower oxide as the starting material because the corresponding reduction reaction will be highly heat starved. Even in the case of pentoxide reduction, extra heat has to be provided by one or more of the following means: preheating the charge, adding a heat booster such as potassium chlorate, and decreasing the melting points of the reaction products.

In the aluminothermic reduction of niobium pentoxide all these three methods of heat management have been used. As regards the last option, the objective here is to bring down the melting temperature of the highest melting component, which is niobium. There is no need to add an extra reagent for this purpose because aluminum itself forms a fairly extensive solid solution with niobium, with the melting temperature of the alloy decreasing with increasing aluminum content. The liquidus temperature of these alloys decreases in the following manner with increasing aluminum content: ~2400 °C for niobium – 2% aluminum; ~2300 °C for niobium – 4% aluminum; and ~2200 °C for niobium – 6% aluminum. There exists, therefore, a possibility of effecting the aluminothermic reduction of niobium pentoxide by using excess aluminum reductant, without resorting to heat booster incorporation or preheating. The product in this case would be a niobium–aluminum alloy. When the use of heat boosters or of preheating is resorted to, only the stoichiometric amount of aluminum, rather than an excess amount, may be used and the aluminum content of the niobium metal so produced would be correspondingly small.

The reactor used for the aluminothermic reduction of niobium pentoxide is shown schematically in Figure 4.17 (A). It is a steel pipe, lined on the inside with alumina and provided with a pipe cap. The charge, consisting of stoichiometric amounts of niobium pentoxide and aluminum powder, is blended and loaded in the lined pipe, and covered with alumina. The cap is closed and the reaction initiated by placing the loaded bomb in a gas-fired furnace, preheated to 800 °C, and by raising the temperature of the furnace to 1100 °C.

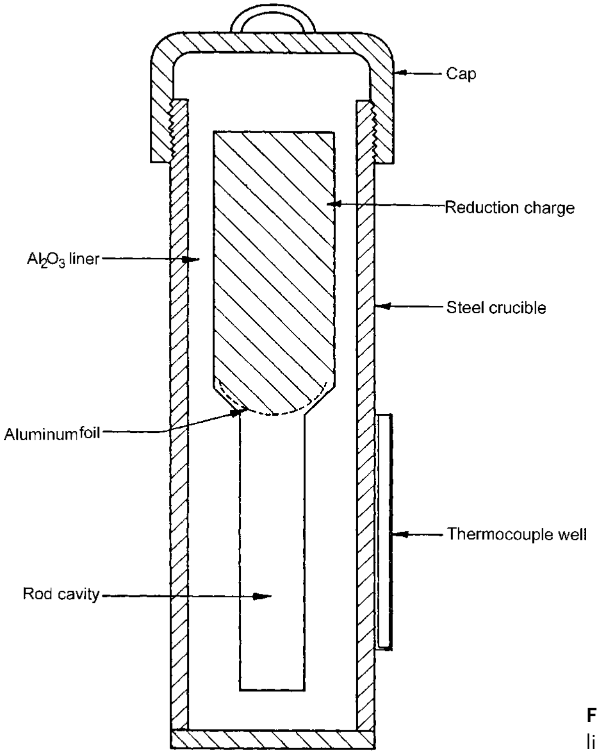


Figure 4.17 A Steel crucible with Al_2O_3 liner used for drop casting of niobium.

When the temperature of the outside of the bomb reactor is about 1000 °C, the charge ignites and the exothermic aluminothermic reduction reaction rapidly increases the temperature of the bomb wall to about 1075 °C. A thermocouple, which is used to monitor this temperature, is located in the thermocouple well shown in the figure. Under the conditions indicated, the temperature inside the bomb is high enough to result in the formation of a liquid slag and the metal phases. At the end of reduction, niobium is collected as a massive metal biscuit at the bottom of the lined pipe. In the arrangement shown in the figure, the aluminum foil supporting the charge prior to reduction gives way during the reduction reaction, thereby allowing the molten niobium metal to flow into the rod cavity, where it solidifies. The metal product in this case is obtained in the form of a rod. The rod thus obtained from a charge made up of 1596 g of niobium pentoxide and 570 g of aluminum powder (corresponding to about 5% more aluminum than that required by considerations of stoichiometry) has been found to contain approximately 2% aluminum and 0.8% oxygen. The yield of niobium in the process has been assessed to be at least 95%.

Instead of a closed-bomb reactor, an open reactor (shown in Figure 4.17 B) has also been used for this aluminothermic reduction. The mild steel reactor is lined on the inside with calcined magnesia. An arrangement is made to initiate the reaction in the center of the

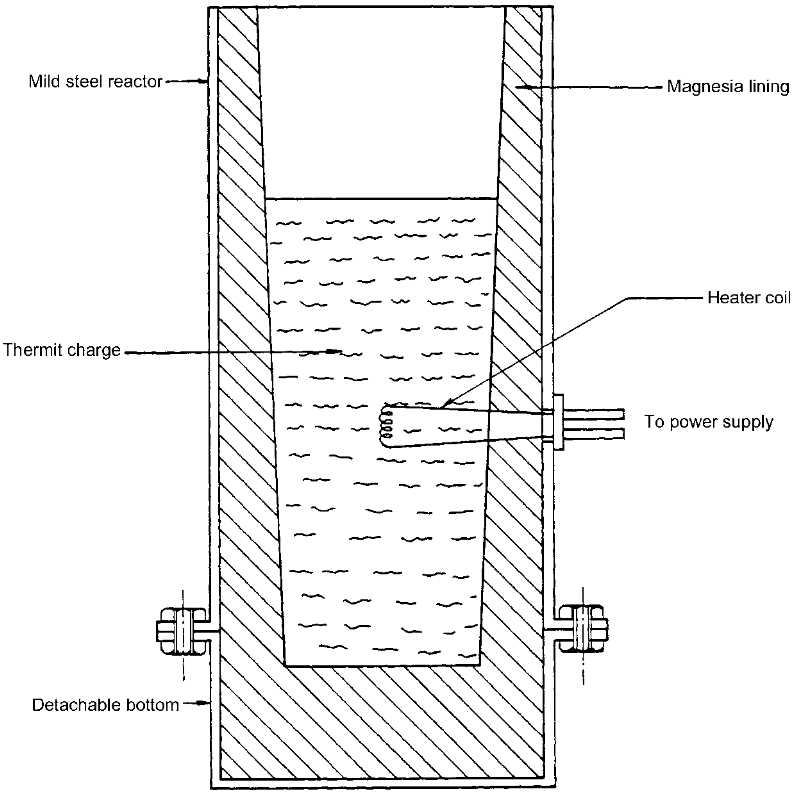


Figure 4.17 B Schematic of the reactor for open aluminothermic reduction of niobium pentoxide.

charge mass by electrical resistance heating. A detachable hearth enables discharging of the reacted mass from the bottom. The charge consists of niobium pentoxide powder, intimately mixed with aluminum powder. The quantity of aluminum used is about 15% more than the amount required by the stoichiometry of the reaction. After loading the charge, the reaction is initiated by passing an electric current through a nichrome coil embedded in the charge. Once initiated, the reduction reaction proceeds briskly to completion and yields a niobium button, well separated from the slag. The yield of niobium in this reduction procedure is more than 95%, but the metal obtained contains 4% aluminum and 0.2% oxygen.

The excess aluminum in the charge compensates for the loss of aluminum due to nonreductive air oxidation, and also provides aluminum for alloying with the niobium metal produced in the reduction. As mentioned earlier, the liquidus temperatures of niobium-aluminum alloys are lower than the melting point of niobium. The melting of this alloy and the alumina slag is achieved even with the reduced amount of heat available from the reaction implemented without preheating in the open reactor.

4.6.5.5 **Tantalum**

The only stable oxide formed by tantalum which occurs in the solid state is tantalum pentoxide. The heat of formation of tantalum pentoxide ($\Delta H^0_{298} = -2045.13$ kJ/mole) is more negative than the heat of formation of niobium pentoxide ($\Delta H^0_{298} = 1899.95$ kJ/mole). Hence, the aluminothermic reduction reaction for the former is less exothermic than that corresponding to the latter. Added to this, the heat requirement for consolidated tantalum metal preparation is much higher than that for niobium metal preparation because the melting point of tantalum is about 550 °C higher than that of niobium. All these considerations indicate that aluminothermic reduction of tantalum pentoxide can be successful only if the reduction reaction is strongly boosted by additives like potassium chlorate and if the melting temperature of the metal phase is lowered by loading tantalum with binary and ternary combinations of alloying constituents such as iron–aluminum, silicon–aluminum, manganese–aluminum, and iron–silicon–aluminum.

4.6.5.6 **Vanadium**

Vanadium forms numerous oxides, the most important of which are: vanadium monoxide, vanadium sesquioxide, vanadium dioxide and vanadium pentoxide. In the earlier examples (e.g., oxides of chromium and of niobium) the enthalpy values for the aluminothermic reduction of each of the oxides was given for the purpose of illustration. Normally, the consideration can be restricted to only those oxides which are readily obtained and which can be handled freely without any special or cumbersome precautions. In the case of vanadium for example, it is sufficient to consider the reduction of the sesquioxide (V_2O_3) and the pentoxide (V_2O_5). The pertinent reactions are:

$$V_2O_3 + 2\ Al = 2\ V + Al_2O_3; \qquad \Delta H^0_{298} = -107.5 \cdot 4.184\ kJ$$

and

$$O \cdot 6\ V_2O_5 + 2\ Al = 1.2\ V + Al_2O_3; \quad \Delta H^0_{298} = -178.0 \cdot 4.184\ kJ$$

The highest melting component in the product is alumina, and the heat requirement for the melting of the products can be obtained form the following data:

Vanadium: $H^0_{2327} - H^0_{298} = 22 \cdot 4.184$ kJ (2045 °C being the melting point of alumina)

Alumina: $H^0_{2327} - H^0_{298} = 87.9 \cdot 4.184$ kJ

The quantity of heat required for the melting of the products in the aluminothermic reduction of vanadium sesquioxide is 551.86 kJ; in the reduction of vanadium pentoxide, the corresponding value is 440.15 kJ. Therefore, when the sesquioxide is used as the starting material, the exothermicity of the reaction is not sufficient for melting the products, and extra heat has to be supplied by way of preheating and for booster additions. The reduction of vanadium pentoxide by aluminum, on the other hand, is associated with a large excess of reaction heat over and above that required for the melting of the products. The reaction can, therefore, be successfully conducted in a wide variety of reactors because even significant heat losses can be readily accommodated. An interesting possibility, a parallel of which was noted in manganese metal production, is the use of vanadium pentoxide as a booster in the aluminothermic reduction of vanadium sesquioxide. The charge in this case would be a mixture of these two oxides.

In practice, the production of vanadium by aluminothermic reduction is also governed by some other considerations. The reduction has to be carried out under an inert atmosphere (helium or argon) to avoid nitrogen pick-up from the air by vanadium metal. The composition of the oxide–aluminum charge has to be so chosen that the thermit (metal obtained by aluminothermic reduction) contains between 11 and 19% aluminum. This is necessary for the subsequent refining step in the vanadium metal production flowsheet. Pure vanadium pentoxide and pure aluminum are used as the starting materials, and the reduction is conducted in a closed steel bomb as shown in Figure 4.17 (C).

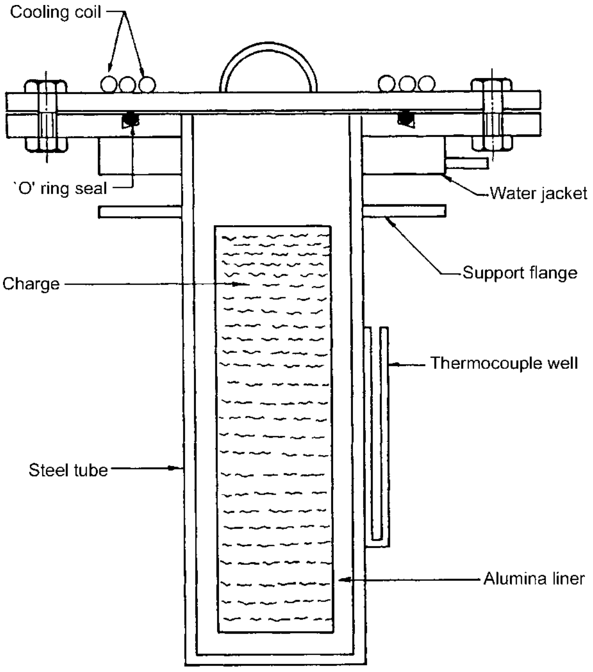


Figure 4.17 C Schematic of the closed-bomb reactor for aluminothermic reduction of vanadium pentoxide.

The charge used for reduction in a typical laboratory run consisted of an intimate mixture of vanadium pentoxide (0.9 kg) and aluminum (0.49 kg) powders. The reductant was used in the form of milled particles (0.6 × 0.3 × 0.15 mm). About 10% of the total charge was prepared by mixing vanadium pentoxide and aluminum powders, and this mixture was placed in the bottom of the reactor before adding the remainder of the charge over it. Before and during the addition of the charge, the bomb cavity was flushed with a stream of argon. After bolting the cover flange, the entire bomb was heated to 750 °C in a gas-fired furnace to start the reaction. The powder mixture at the bottom reacted first and triggered the reaction in the rest of the charge. The occurrence of the aluminothermic reduction reaction was perceived by monitoring the temperature of the bomb, as measured by a thermocouple attached to the bomb wall. The reaction rapidly proceeded to completion; when the bomb and its contents had cooled down to room temperature, the slag and the vanadium thermit were removed. The thermit was cleaned by leaching with dilute nitric acid and crushed into 6 mm pieces by an ordinary jaw crusher.

A significant development in implementing aluminothermic reduction reactions, such as the one discussed above, involves the use of a water-cooled copper crucible instead of a refractory lined steel bomb. The use of water-cooled copper crucibles for carrying out a variety of aluminothermic reduction reactions was pioneered by P. H. Perfect. An important advantage of using such crucibles is that they permit the reduction to be conducted under high purity conditions, since impurity pick-up from the refractory liner is avoided and evacuation of the crucible and its backfilling with a pure inert gas is easier. The reactor is shown schematically in Figure 4.17 (D). At first, a mixture of vanadium pentoxide and aluminum turnings is packed tightly into the crucible. A trigger mixture consisting of vanadium pentoxide, aluminum powder and iodine is placed on top of the packed charge. A coiled vanadium filament is embedded into this trigger mixture. Before starting the reduction, the crucible (loaded with this charge) is evacuated to remove nitrogen and the other gases entrapped in and adsorbed on the charge particles. The crucible is then backfilled with argon, the head assembly bolted to the flange, and the reaction triggered by passing an electric current through the vanadium wire. The exothermic reaction raises the temperature of the reaction mixture to above 2050 °C, resulting in the formation and a clean gravity separation of a molten vanadium–aluminum alloy and the slag.

The quantity of aluminum used in the charge corresponds to about 10% excess over that required by the stoichiometry of the reaction:

$$3\ V_2O_5 + 10\ Al = 6\ V + 5\ Al_2O_3$$

The quantity of aluminum in the charge determines the amounts of residual aluminum and oxygen in the product. On changing the excess aluminum content in the charge from 0 to 15%, the aluminum content in the alloy increases from 2.4 to 14.5% and the corresponding oxygen content varies inversely from 1.7 to 0.24%. An important aspect of the reduction described above was brought out in one experiment. The reactor was charged under an argon gas cover and the reduction carried out with the space above the charge in the bomb filled with argon. The nitrogen content in the thermit thus obtained was restricted to 60 ppm or less. When the reduction was carried out without the argon flushing and filling operations, a thermit containing about 700 ppm nitrogen was obtained in both types of reactors (refractory lined as well as water-cooled). Obviously, the air entrapped in the reactor supplied this nitrogen. Thermits containing more than 10% residual aluminum are obtained by design because vanadium thermits containing less than this critical quantity of aluminum cannot be effectively refined by pyrovacuum treatments to yield pure vanadium. Before the advent of aluminothermy, vanadium was regarded as a metal which was difficult to prepare. Much of the commercially produced pure vanadium metal is presently obtained by the aluminothermic reduction technique.

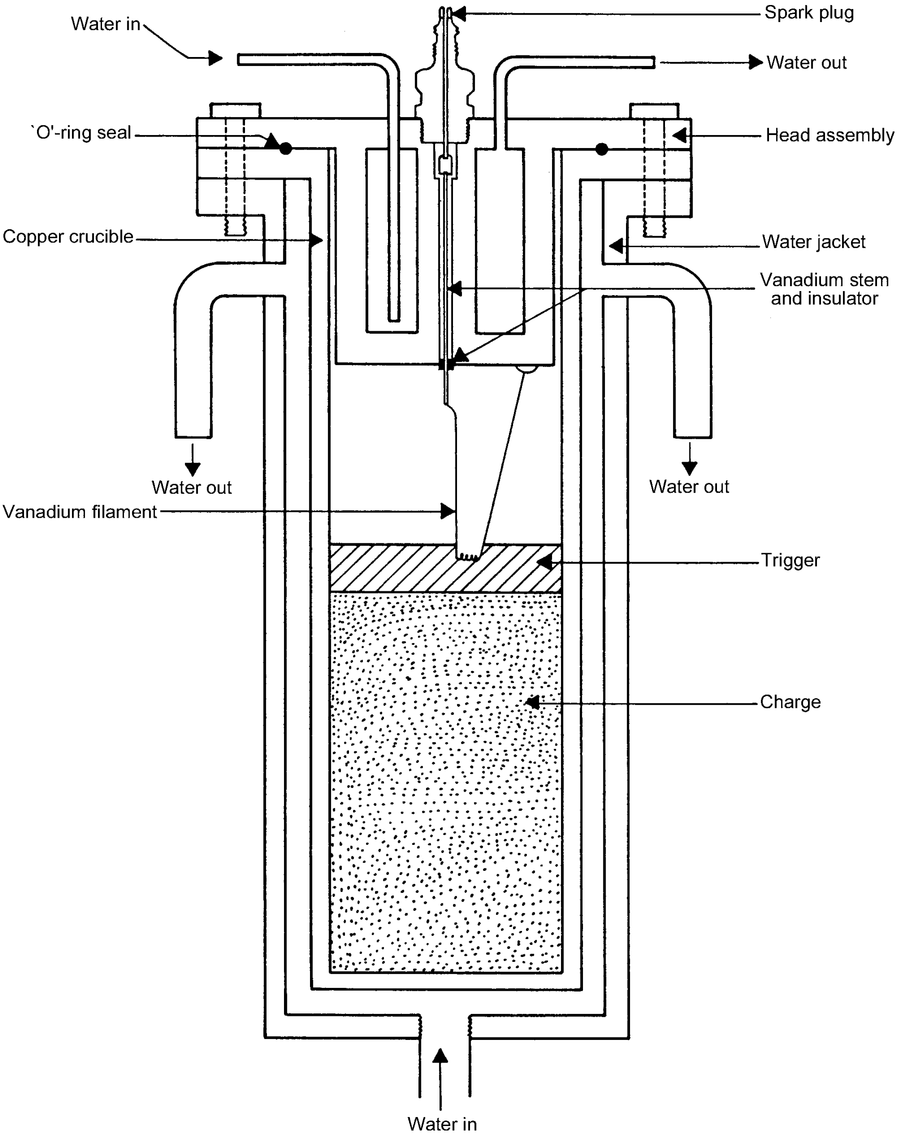


Figure 4.17 D Water-cooled copper reactor for aluminothermic reduction of vanadium pentoxide.

4.6.5.7 Ferrovanadium and Ferroniobium

Ferrovanadium stands as a major industrially used form of vanadium. Similarly, it is in the form of ferroniobium that the bulk of niobium is used industrially. Aluminothermic reduction is an elegant metallurgical process for the production of these ferroalloys in their practically carbon-free forms.

The preparation of ferrovanadium by this route is carried out batchwise in refractory-lined open reactors, with vanadium pentoxide, aluminum powder, iron scrap and lime or fluorspar constituting the charge. The reactions once initiated, proceed briskly to completion. The reaction heat is sufficient to melt the ferrovanadium and the alumina–lime/fluorspar slag, which readily separate due to density difference. The aluminothermic ferroalloy product contains practically no carbon.

Similar to ferrovanadium, aluminothermic smelting is also carried out for ferroniobium. While chemically processed, relatively pure grade niobium oxide is used for manufacturing special grade ferroniobium, standard grade ferroniobium is mostly produced from a charge in which niobium is present as a pyrochlore (ore) concentrate. The compositions of the typical reaction charge and of the ferroniobium produced and the slag generated are given in Table 4.3.

Table 4.3 Details of ferroniobium production from pyrochlore by aluminothermic reduction.

Reaction charge	***Analysis***			
	Ferroniobium		***Slag***	
Pyrochlore concentrate – 180,000 kg	Nb	66.0%	Al_2O_3	48%
(60% N_2O_5)	Fe	30.5%	CaO	25%
Iron oxide (as hematite) – 4000 kg	Si	1.5%	TiO_2	4%
(with 68% Fe)	Al	0.5%	BaO	2%
Aluminum powder – 6000 kg	Ti	0.1%	Re_2O_3	4%
	P	0.1%		(rare earth oxides)
Fluorspar – 750 kg	S	0.04%	Nb_2O_5	Traces
Lime – 500 kg	C	0.08%	ThO_2	2%
	Pb	0.02%	U_3O_8	0.05%

4.7
Halide Processes

Some metals such as titanium, zirconium, beryllium, uranium and thorium (and most of the rare earths) are known to form very stable oxides. They do not respond favorably to attempts to prepare them by oxide reduction. The behavior of zirconium and titanium is particularly instructive. It could be observed in the Ellingham diagram that when a metal forms many oxides, the standard free energies of formation (per mole of oxygen) of the lower oxides are more negative than those of the higher oxides. In other words, the oxygen potential of the metal–oxygen system decreases as the oxygen to metal (O/M) ratio de-

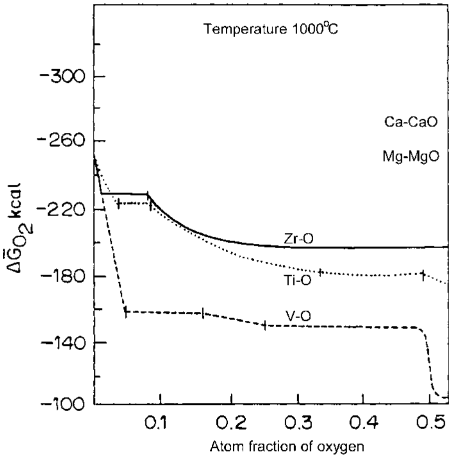


Figure 4.18 Oxygen potentials in some refractory metal-oxygen systems at 1000 °C.

creases. When the metal forms a solid solution with oxygen, the oxygen potential decreases with decreasing O/M ratio across the range of the solid solution also. The data for the zirconium–oxygen, the titanium–oxygen and the vanadium–oxygen systems are shown in Figure 4.18. In all these metal–oxygen systems, when very dilute solutions of oxygen in the metal are considered, the oxygen potential becomes very low. The lowest oxygen potential values attainable in the reduction of an oxide using aluminum, magnesium or calcium as reductants are the values of those oxygen potentials in the aluminum–alumina, the magnesium-magnesia and the calcium–calcia mixtures respectively at the pertinent reduction temperatures. These values, corresponding to a temperature of 1000 °C, are also given in the figure. It is seen that the only reducing agent which can yield a substantially oxygen-free metal product (oxygen concentration $< 0.1\%$) is calcium. There are, however, some limitations with regard to the use of calcium as a reductant, particularly because of the very high melting points of calcia and of the oxides to be reduced. An alternative to oxide reduction was needed to solve this problem.

The alternative was to use halides and to prepare the metals by the reduction of their halides. Among the metal halides, the chlorides and the fluorides have the right combination of properties in terms of the free energy of formation, the vapour pressure, and the melting and the boiling points, which makes them usable in metal-reduction processes. From readily available starting materials, these metal halides can be prepared in an essentially oxygen-free condition and can also be reduced to oxygen-free metals. The difficult problem of oxygen removal from dilute metal–oxygen solid solutions is thus circumvented.

4.7.1
Preparation of Chlorides

In chlorination, the metal values in the ore or the concentrate are recovered by converting them into chlorides. Chlorination generally refers to a process in which metal chlorides are obtained by dry methods. There are two major types of chlorination. In one type, the metal chlorides produced are nonvolatile and are recovered from the reaction mixture as molten phases or by leaching with water. In the other type, the chlorides produced are volatile and escape from the reaction mixture along with the exit gases. They are recovered from the exit gases by condensation. There is yet another type of chlorination, known as segregation. Here, the metal chlorides form during the process but they are not recovered as chlorides.

All metals, except those belonging to the platinum group, form chlorides and the free energy change for the reaction (referred to as reaction (1))

$$M + 0.5 \cdot Cl_2 = MCI_x$$

is generally negative. When alloys and intermetallics are considered, the free energy change for the reaction (referred to as reaction (2))

$$[M] + 0.5 \cdot Cl_2 = MCI_x$$

is again mostly negative; however, the free energy change for reaction (2) is less negative than that for reaction (1) by the amount $R\,T \ln a_M$:

$$\Delta G_2 = \Delta G_1 - R\,T \ln a_M$$

where a_M is the activity of the metal (to be chlorinated) in the alloy or the intermetallic. The situation is more complicated in the case of the chlorination of a metal present in a compound or a mineral. The relevant compounds are oxides, sulfides, and phosphates.

Let the chlorination of a metal oxide (MO) by chlorine be considered:

$$MO + Cl_2 = MCl_2 + 0.5\ O_2$$

The standard free energy change for this reaction is generally positive at all temperatures because oxides are invariably stabler than chlorides. An exception to this rule occurs in the case of copper because cupric chloride is more stable than cupric oxide. At 500 °C, the standard free energy change (ΔG^0) for the reaction

$$CuO + Cl_2 = CuCl_2 + 0.5\ O_2$$

is –33.47 kJ. For all other metals, the oxide can be converted to the chloride only by combining a reduction reaction with chlorination. The reducing agent used is usually carbon.

The standard free energy associated with the reduction–chlorination reaction

$$MO_2 + 2\ Cl_2 + C = MCl_4 + CO_2$$

can be expressed as

$$\Delta G^0 = \Delta G^0_{MCl_4} - \Delta G^0_{MO_2} + \Delta G^0_{CO_2}$$

In this, to the free energy change for the reaction involving the interaction of chlorine and the metal oxide, is added the large value of the free energy of formation of carbon dioxide from its constituent elements.

Another chlorination reaction involving carbon is

$$MO_2 + 2\ Cl_2 + 2\ C = MCl_4 + 2\ CO$$

The standard free energy change associated with this reaction is

$$\Delta G^0 = \Delta G^0_{MCl_4} - \Delta G^0_{MO_2} + 2\,\Delta G^0_{CO}$$

The formation of carbon monoxide aids chlorination in exactly the same way as does the formation of carbon dioxide; which of the two oxides of carbon would found in the reaction depends on the temperature at which reduction-chlorination is carried out. Below 600 °C carbon dioxide forms while above 700 °C carbon monoxide is formed. This changeover results from the variation in the free energies of formation of these two oxides with temperature. For example, at 900 °C the situation as regards the formation of titanium tetrachloride from titanium dioxide is guided by the reactions:

$$0.5\ TiO_2 + Cl_2 = 0.5\ TiCl_4 + 0.5\ \Delta G^0 = 11.2 \cdot 4.184\ kJ$$

and

$$C + 0.5\ O_2 = CO; \qquad \Delta G^0 = -52.1 \cdot 4.184\ kJ$$

Combining the two,

$$0.5\ TiO_2 + C + Cl_2 = 0.5\ TiCl_4 + CO; \quad \Delta G^0 = -40.9 \cdot 4.184\ kJ$$

The chlorination of titanium dioxide (titania) is thus entirely feasible at 900 °C. Similarly, many other metal oxides can be converted to metal chlorides by reaction with chlorine in the presence of carbon. It should be noted that carbon itself is not easily chlorinated as the standard free energy of formation of carbon tetrachloride is positive at temperatures above 500 °C.

In addition to pure oxides, oxidic minerals and ores also can be converted to metal chlorides. Examples include minerals such as zircon, bastnasite, monazite, ilmenite, etc.

Beryllia can be chlorinated using chlorine in the presence of carbon at 700 to 800 °C as per the reaction:

$$BeO + Cl_2 + 0.5\ C = BeCl_2 + 0.5\ CO_2$$

At 800 °C, the standard free energy change for the reaction is –45.60 kJ. Carbon for reduction and chlorine for chlorination are provided by certain compounds like carbon tetrachloride, and these may be used. Using carbon tetrachloride, the chlorination may be conducted at a lower temperature (650–700 °C) according to the reaction:

$$BeO + 0.5\ CCl_4 = BeCl_2 + 0.5\ CO_2$$

For this reaction the value of ΔG^0 at 800 °C is –66.94 kJ. The equilibrium constant for this reaction is $10^{3.35}$, which is considerably higher than the equilibrium constant for the previous reaction ($10^{2.1}$) in which carbon and chlorine are used.

Another example of the use of carbon tetrachloride for chlorination is the conversion of plutonium dioxide to plutonium trichloride according to the reactions

$$PuO_2 + CCl_4 = PuCl_3 + CO_2 + 0.5\ Cl_2$$

$$PuO_2 + 2\ CCl_4 = PuCl_3 + 2\ CO + 2.5\ Cl_2$$

The conversion of plutonium dioxide to plutonium trichloride has often been carried out by using phosgene ($COCl_2$) instead of carbon tetrachloride or carbon and chlorine:

$$PuO_2 + 2\ COCl_2 = PuCl_3 + 2\ CO_2 + 0.5\ Cl_2$$

The action of phosgene can be considered to be equivalent to the action of a carbon monoxide and chlorine mixture. Phosgene, a gas at room temperature (melting point: 1.04 °C; boiling point: 8.2 °C), is an unstable compound and dissociates to carbon monoxide and chlorine. The dissociation is negligible at low temperatures (< 100 °C), is about 55% at 500 °C, and 100% at 800 °C. The reaction between plutonium dioxide and phosgene is carried out at 500 to 550 °C. It is obvious that phosgene is useful for chlorination only in the temperature range where carbon dioxide is stabler than carbon monoxide.

The general advantage of using carbon tetrachloride or phosgene is that these compounds decompose at the reaction temperature to provide a uniform distribution of active carbon or carbon monoxide and chlorine at the reaction sites over the oxide surface. These reagents are, however, not as convenient to use as a carbon and chlorine mixture in large-scale operations. Besides, phosgene is *poisonous*.

The chlorination reactions described so far are some examples of the reduction chlorination process: chlorine is used in conjunction with a reducing agent (carbon or carbon monoxide). The possibility of using hydrogen as the reducing agent during chlorination can now be considered. Even though the free energy values are favorable, hydrochlorination, i.e., chlorination by chlorine in the presence of hydrogen or chlorination by hydrogen chloride, is not considered a good method for chlorination. The reason is that most of the chlorides are hygroscopic compounds and water vapor is formed as a product in hydrochlorination.

Another reducing agent relevant to chlorination reactions is sulfur dioxide. When the material to be chlorinated contains calcium oxide, it is advantageous to convert it to calcium sulfate rather than to calcium chloride. The advantages are: less chlorine consumption and easy disposal of calcium sulfate (which is water-insoluble). The chlorination of scheelite is an important example of the use of the sulfur dioxide chlorine reagent:

$$CaWO_4 + SO_2 + Cl_2 = CaSO_4 + WO_2Cl_2$$

An extension of the reduction–chlorination technique described so far, wherein reduction and chlorination occur simultaneously, is a process in which the oxide is first reduced and then chlorinated. This technique is particularly useful for chlorinating minerals which contain silica. The chlorination of silica (SiO_2) by chlorine, in the presence of carbon, occurs above about 1200 °C. However, the silica present in the silicate minerals readily undergoes chlorination at 800 °C. This reaction is undesirable because large amounts of chlorine are wasted to remove silica as silicon tetrachloride. Silica is, therefore, removed by other methods, as described below, before chlorination. Zircon, a typical silicate mineral, is heated with carbon in an electric furnace to form crude zirconium carbide or carbonitride. During this treatment, the silicon in the mineral escapes as the volatile oxide, silicon monoxide. This vapor, on contact with air, oxidizes to silica, which collects as a fine powder in the furnace off-gas handling system:

$$ZrSiO_4 + 4\ C = ZrC + SiO + 3\ CO$$

$$SiO + 0.5\ O_2 = SiO_2$$

The reduced mineral is reacted with chlorine. Both the carbide and the nitride formed during the electric furnace treatment of the mineral convert to the chloride:

$ZrN + 2\ Cl_2 = ZrCl_4 + 0.5\ N_2$

$ZrC + 2\ Cl_2 = ZrCl_4 + C$

Apart from chlorine (without or with carbon), carbon tetrachloride, phosgene, hydrogen chloride, and sulfur dioxide–chlorine mixtures, some of the metal chlorides can also function as chlorinating agents. The chlorinating action of metal chlorides is dramatically illustrated by the behavior of the silica lining in reactors used for the chlorination of titanium dioxide and beryllium dioxide.

Titanium tetrachloride is produced on an industrial scale by the chlorination of titanium dioxide–carbon mixtures in reactors lined with silica. During the reactor operation, the lining comes into contact not only with chlorine but also with titanium tetrachloride. There appears to be no attack on silica by either of these as the lining remains intact. However, the use of such a reactor for chlorinating beryllium oxide by the carbon–chlorine reduction chlorination procedure is not possible because the silica lining is attacked in this case. This corrosion of silica can be traced to the attack of beryllium chloride on silica. The interaction of beryllium chloride with silica results in the formation of silicon tetrachloride in accordance with the reaction

$SiO_2 + 2\ BeCl_2 = SiCl_4 + 2\ BeO$

The standard free energy change associated with this reaction is given by

$\Delta G^0 = (-256\ 100 + 156\ T)\ J$

which shows that the ΔG^0 value is negative and hence the reaction is feasible at all temperatures up to about 1350 °C. The absence of attack on silica by titanium tetrachloride can be similarly explained. The standard free energy change for the reaction

$SIO_2 + TiCl_4 = SiCl_4 + TiO_2$

can be expressed as

$\Delta G^0 = (98\ 300 + 12.5\ T)\ J$

by combining the values of the standard free energy change for the reactions

$TiO_2 + 2\ Cl_2 = TiCl_4 + O_2; \quad \Delta G^0 = (161\ 100 - 56.5\ T)\ J$

and

$SiO_2 + 2\ Cl_2 = SiCl_4 + O_2; \quad \Delta G^0 = (259\ 400 - 44\ T)\ J$

It follows that titanium tetrachloride can not chlorinate silica because at all temperatures the free energy change for that reaction has a large positive value. In general, in the interaction between the oxide (MO) of one metal (M) and the chloride ($M'Cl_2$) of a different metal (M′):

$MO + M'Cl_2 = MCl_2 + M'O$

the possibility of the chlorination of the metal present as the oxide is determined by the difference between the standard free energies of formation of the oxide and the chloride of each of the two metals involved. If ΔG^0 is the standard free energy change associated with the above reaction, then

$$\Delta G^0 = (\Delta G^0_{\mathrm{M'O}} - \Delta G^0_{\mathrm{M'Cl_2}}) - (\Delta G^0_{\mathrm{MO}} - \Delta G^0_{\mathrm{M'Cl_2}})$$

if the difference $(\Delta G^0_{\mathrm{MO}} - \Delta G^0_{\mathrm{M'Cl_2}})$ has a more negative value than the difference $(\Delta G^0_{\mathrm{MO}} - \Delta G^0_{\mathrm{MCl_2}})$, then the metal originally present as the oxide will be converted to its chloride. As an example, let the following reaction be considered:

$$1.5\ \mathrm{SiCl_4}\ (\mathrm{vap}) + \mathrm{Al_2O_3} = 1.5\ \mathrm{SiO_2} + 2\ \mathrm{AlCl_3}\ (\mathrm{vap})$$

The standard free energy change for this reaction is

$$\Delta G^0 = (1.5\,\Delta G^0_{\mathrm{SiO_2}} - 1.5\,\Delta G^0_{\mathrm{SiCl_4}})\ (\Delta G^0_{\mathrm{Al_2O_3}} - 2\Delta G^0_{\mathrm{AlCl_3}})$$

At 500 °C, substituting the actual values (in kJ)

$$\Delta G^0 = 1.5\ (-728 + 5\ \mathrm{O_2}) - (-1406 + 2 \cdot 577) = -339 + 252 - 20.8$$

Thus, alumina can be chlorinated by silicon tetrachloride.

The metal chlorides normally used as chlorinating agents are the low-cost reagents sodium chloride and calcium chloride. Silicates, carbonates and sulfates can be chloridized by the reactions

$$\mathrm{MSiO_3} + 2\ \mathrm{NaCl} = \mathrm{Na_2SiO_3} + \mathrm{MCl_2}$$

$$\mathrm{MCO_3} + 2\ \mathrm{NaCl} = \mathrm{Na_2CO_3} + \mathrm{MCl_2}$$

$$\mathrm{MSO_4} + 2\ \mathrm{NaCl} = \mathrm{Na_2SO_4} + \mathrm{MCl_2}$$

Let the following reactions be now considered:

$$\mathrm{MO} + 2\ \mathrm{NaCl} = \mathrm{Na_2O} + \mathrm{MCl_2};\quad \Delta G^0_1$$

$$\mathrm{Na_2O} + \mathrm{SiO_2} = \mathrm{Na_2SiO_3};\quad \Delta G^0_2$$

$$\mathrm{MO} + \mathrm{SiO_2} = \mathrm{MSiO_3};\quad \Delta G^0_3$$

If the standard free energy change associated with the metal silicate chlorination reaction is given by ΔG^0, then

$$\Delta G^0 = \Delta G^0_1 + \Delta G^0_2 - \Delta G^0_3$$

If ΔG has a value which is more negative than that of ΔG, then ΔG^0 becomes more negative than the standard free energy change for the metal oxide chlorination reaction (ΔG^0_1). An oxide which is difficult to chlorinate in the free state may, therefore, be chlorinated more easily when compounded into a silicate.

Similar considerations apply in certain reactions pertaining to the chlorination of metal oxides by metal chlorides. A typical reaction of this type is

$$\mathrm{MO} + \mathrm{CaCl_2} = \mathrm{MCl_2} + \mathrm{CaO}$$

The feasibility of this reaction can be greatly enhanced by introducing acidic oxides such as sulfur trioxide or silica because these combine strongly with calcium oxide:

$$\mathrm{MO} + \mathrm{CaCl_2} + \mathrm{SiO_2} = \mathrm{MCl_2} + \mathrm{CaSiO_3}$$

$$\mathrm{MO} + \mathrm{CaCl_2} + \mathrm{SO_3} = \mathrm{MCl_2} + \mathrm{CaSO_4}$$

Similar reactions involving sodium chloride can also be considered:

$$MO + 2\ NaCl + SO_3 = MCl_2 + Na_2SO_4$$

$$MO + 2\ NaCl + SiO_2 = MCl_2 + Na_2SiO_3$$

Reactions of the type described above could be used for the recovery of nonferrous metals from pyrite cinder. In an old commercial process (used in the Duisburgerkupferhutte plant at Duisburg in Germany), a mixture of pyrite cinder (100 parts) and sodium chloride (8–10 parts) was heated at 550–600 °C to convert the nonferrous metals present in the cinder to the corresponding metal chlorides. The chlorides were removed from the iron oxide in the product by leaching with water. Iron oxide was agglomerated and charged to the blast furnace. Sodium sulfate was removed from the leach liquor by crystallization. In another commercial process (used at the Tobata plant of Kowa Seiko Company, Japan), a pelletized mixture containing pyrite cinder, calcium chloride (4–5 wt-%) and moisture (11–12%) was fired in a rotary kiln at 1250 °C. The nonferrous metals contained in the pyrite cinder chlorinated and the chlorides volatilized to be collected in the scrubbers and in the dust collection system. For converting rare earth (RE) oxides to chlorides, reagents such as hydrogen chloride, carbon tetrachloride and thionyl chloride have been used. The best reagent is ammonium chloride, and the oxide is converted to the chloride by the relatively low-temperature reaction:

$$RE_2O_3 + 6\ NH_4Cl \xrightarrow{350\ ^\circ C} 2\ RECl_3 + 3\ H_2O + 6\ NH_3$$

Water vapor is produced in the reaction, but the hydrolysis of the rare earth chloride formed is prevented by using excess ammonium chloride. After the reaction, the remaining ammonium chloride is removed completely by heating in vacuum at 300–320 °C.

In many instances of metal processing, the sulfides need be chlorinated. Metal sulfides can be chlorinated by reactions such as

$$MS + Cl_2 = MCl_2 + S$$

$$MS + S_2Cl_2 = MCl_2 + 3\ S$$

$$MS + Cl_2 + O_2 = MCl_2 + SO_2$$

$$MS + CaCl_2 + 1.5\ O_2 = MCl_2 + CaO + SO_2$$

$$MS + 2\ NaCl + 2\ O_2 = MCl_2 + Na_2SO_4$$

Elemental chlorine can convert metal sulfides to chlorides more readily than it can convert metal oxides to chlorides. The reaction

$$MS + Cl_2 = MCl_2 + S$$

usually occurs at relatively low temperatures. At higher temperatures, and with longer contact time between chlorine and the sulfide, sulfur chlorides form:

$$2\ S + Cl_2 = S_2Cl_2$$

$$S + Cl_2 = SCl_2$$

At 300 °C, the reaction between elemental chlorine and chalcopyrite can be represented as:

$$CuFeS_2 + 3.5\ Cl_2 = CuCl_2 + FeCl_3 + S_2Cl_2$$

The sulfur chloride (S_2Cl_2) volatilizes along with the ferric chloride ($FeCl_3$) and the cupric chloride ($CuCl_2$) remains in the residue. When the reaction is conducted at 600 °C with a limited supply of chlorine, the products are different:

$$CuFeS_2 + 2\ Cl_2 = CuCl_2 + FeCl_3 + 2\ S$$

Sulfur volatilizes at 600 °C, and cupric chloride is molten at this temperature. The products are thus readily separable from one another.

Another good example of the chlorination of sulfide ores involves the following reactions. The complex sulfide ore contains pyrite, cassiterite, and zinc blende. Chlorination of the ore with elemental chlorine results in the formation of iron and zinc chlorides:

$$FeS_2 + Cl_2 = FeCl_2 + 2\ S$$

$$ZnS + Cl_2 = ZnCl_2 + S$$

Tin, which is present in the ore as stannic oxide (SnO_2), does not chlorinate under these conditions:

$$SnO_2 + Cl_2 = SnCl_2 + O_2; \quad \Delta G^0_{800} = +45 \cdot 4.184\ \text{kJ}$$

$$SnO_2 + 2\ Cl_2 = SnCl_2 + O_2; \quad \Delta G^0_{800} = +12 \cdot 4.184\ \text{kJ}$$

From the chlorination residue, iron can be removed by making use of the following reaction at 420–450 °C:

$$FeCl_2 + 0.5\ Cl_2 = FeCl_3$$

Ferric chloride is volatile and is thus separated. The chlorination of zinc blende and pyrite can also occur by the following reactions:

$$FeS_2 + 2\ FeCl_3 = 3\ FeCl_2 + 2\ S$$

$$ZnS + 2\ FeCl_3 = ZnCl_2 + 2\ FeCl_2 + S$$

Thus, for the initial chlorination of the ore, ferric chloride can very well be used instead of elemental chlorine. From ferric chloride vapor chlorine can be regenerated by the reaction

$$2\ FeCl_3 + 1.5\ O_2 = Fe_2O_3 + 3\ Cl_2$$

and recycled. Ferrous chloride also can be oxidized to yield ferric chloride and ferric oxide:

$$6\ FeCl_2 + 1.5\ O_2 = 4\ FeCl_3 + Fe_2O_3$$

Using the feasibility of chlorinating FeS_2 to $FeCl_2$ by chlorine and of regenerating chlorine for recycling from $FeCl_2$ by oxidation, a process has been developed for treating pyrite concentrates for recovering iron oxide and elemental sulfur. The feasibility of such a process relies on the standard free energy changes associated with the reactions:

$$FeS_2 + Cl_2 = FeCl_2 + 2\ S; \qquad \Delta G^0_{800} = -24 \cdot 4.184\ \text{kJ}$$

and

$$0.5\ Fe_2O_3 + Cl_2 = FeCl_2 + 0.5\ O_2; \quad \Delta G^0_{800} = 15 \cdot 4.184\ \text{kJ}$$

Molybdenite is another sulfide ore amenable to processing by chlorination. The reaction between molybdenum disulfide and chlorine, i.e.,

$$2\ MoS_2 + 7\ Cl_2 = 2\ MoCl_5 + 2\ S_2Cl_2$$

has a standard free energy change of –198.74 kJ per mole of MoS_2 at room temperature. However, a chlorination reaction, in which oxygen also participates, i.e.,

$$MoS_2 + Cl_2 + 3\ O_2 = MoO_2Cl_2 + 2\ SO_2$$

is very much more feasible because the standard free energy change at the same temperature is –1359.80 kJ per mole of MoS_2. Another attractive feature of the oxychlorination reaction is the high volatility of MoO_2Cl_2, which sublimes at 156 °C. Thus, when molybdenum disulfide is treated with a 2 : 5 mixture of chlorine and oxygen at 300 °C, a solid molybdenum oxychloride forms and readily volatilizes from the reaction mixture. This is particularly useful for processing of low-grade molybdenite ores, which contain nickel, copper and iron impurities. Because of the ease of formation and the high volatility, molybdenum values are recovered from the ore by oxychlorination as MoO_2Cl_2, leaving behind all the other metals and their chlorides in the residue.

In the sequence of presentation originally given, the last compound to be considered was phosphates. An outstanding example in this context is the chlorination of phosphate minerals of rare earths. The chlorination of monazite, for example, may be represented by the reactions:

$$REPO_4 + 4\ C + 1.5\ Cl_2 = RECl_3 + 0.25\ P_4 + 4\ CO; \quad \Delta G_{1173} = -204.3 \cdot 4.184\ \text{kJ}$$

$$REPO_4 + 4\ C + 3\ Cl_2 = RECl_3 + PCl_3 + 4\ CO; \quad \Delta G_{1173} = -260.5 \cdot 4.184\ \text{kJ}$$

$$REPO_4 + 3\ C + 3\ Cl_2 = RECl_3 + POCl_3 + 3\ CO; \quad \Delta G_{1173} = -274.8 \cdot 4.184\ \text{kJ}$$

The last reaction is the most favored of these three. The actual occurrence of the reactions with elemental phosphorus or phosphorous trichloride as products has been explained to be due to kinetic reasons. The thorium present in the ore volatilizes in the form of thorium tetrachloride ($ThCl_4$) vapor; other metallic impurities such as iron, chromium, aluminum, and titanium also form chlorides and vaporize. The product obtained after chlorination at 900 °C is virtually free from thorium chloride and phosphorous compounds, and also from the metals iron, aluminum, chromium, and titanium.

4.7.2
Properties of Chlorides

Chlorination is an important and practically useful pyrometallurgical process for a variety of reasons. It holds promise in metal extraction particularly because of the ease of formation of metal chlorides from oxides. In addition, chlorides have very desirable properties. These include low melting point, high volatility, and high aqueous solubility. The vapor pressures of some metallurgically important chlorides are given in Figure 4.19. The volatil-

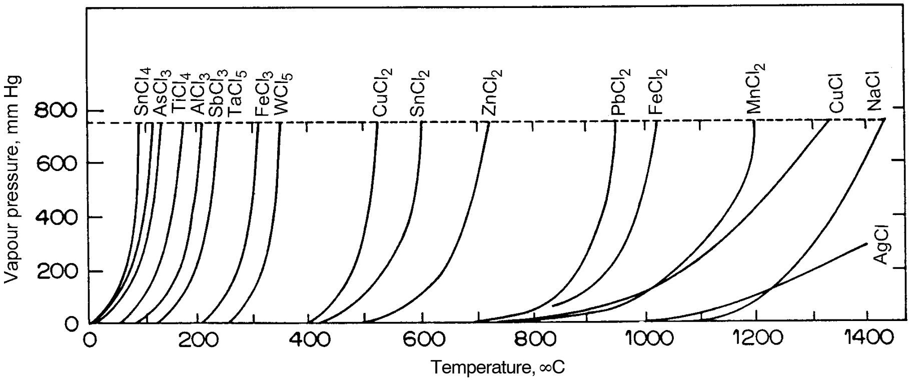


Figure 4.19 Vapour pressure of selected chlorides.

ity of the chlorides and the differences in their vapor pressure are made use of in separating one chloride from another. The preparation of pure chlorides, after chlorinating an ore, is a good example to be considered. When the vapor pressures of two chlorides are similar, they may still be separated. For example, ferric chloride and beryllium chloride have similar vapor pressures, but when a mixture of these is treated with hydrogen, ferric chloride is selectively reduced to the less volatile ferrous chloride, enabling the chlorides to be separated. A similar route is followed in separating several other pairs of chlorides.

A particularly troublesome property of chlorides is their sensitivity to moisture and their tendency to undergo hydrolysis. Titanium tetrachloride, when exposed to normal (humid) air even at room temperature, fumes-it undergoes hydrolysis:

$$TiCl_4 + H_2O = TiOCl_2 + 2\ HCl$$

$$TiCl_4 + 3\ H_3O = TiO(OH)_2 + 4\ HCl$$

Similar are the behaviors of aluminum trichloride, zirconium chloride and many other chlorides. There are, however, chlorides like sodium chloride, which do not undergo hydrolysis readily. Only at 600 to 900 °C does the reaction

$$NaCl\ (l) + H_2O\ (g) = NaOH\ (l) + HCl\ (g)$$

occur.

The tendency to readily oxidize is another characteristic of chlorides. The product is usually being the corresponding oxide. Titanium tetrachloride vapor, on reaction with oxygen, forms the titanium dioxide and chlorine. The oxide, in this case, can be obtained as a very fine powder and the titania thus produced is widely used as a white pigment. The product of the interaction of oxygen with ferric chloride is not an oxide but the oxychloride, FeOCl. As in any other chemical reaction, the relative values of the standard free energies of formation of oxides, chlorides and oxychlorides determine the reaction products. The conversion of a lower chloride to a higher chloride is also an oxidation reaction. It occurs readily with some chlorides (e.g., $FeCl_2 + 0.5\ Cl_2 = FeCl_3$), but only with great difficulty with some other chlorides (e.g., $VCl_3 + 0.5\ Cl_2 = VCl_4$).

It is clear that when the formation of a higher chloride, by the interaction between a lower chloride and chlorine is difficult, the reverse reaction, i.e., the decomposition of the higher chloride to a lower chloride and chlorine, occurs easily. For example, vanadium tetrachloride decomposes, on heating at its boiling point (148.5 °C) to the trichloride and chlorine:

$$VCl_4 = 0.5\ Cl_2 + VCl_3$$

However, heating vanadium trichloride (VCl_3) above 400 °C causes its disproportionation according to the reaction

$$2\ VCl_3 = VCl_2 + VCl_4$$

instead of a simple decomposition to the dichloride. Disproportionation, as a method for the preparation of vanadium dichloride from vanadium trichloride, requires a temperature of 750 to 900 °C.

The conversion of a higher chloride to a lower chloride by hydrogen reduction has been mentioned earlier in connection with the formation of the relatively less volatile ferrous chloride from ferric chloride. This type of reaction is more general and is widely used. Vanadium trichloride can be reduced to the dichloride by hydrogen at temperatures higher than 500 °C:

$$VCl_3 + 0.5\ H_2 = VCl_2 + HCl$$

Some other examples are:

$$NbCl_5 + H_2 = NbCl_3 + 2\ HCl$$

$$2\ NbCl_3 + 3\ H_2 = 2\ Nb + 6\ HCl$$

$$2\ TaCl_5 + 5\ H_2 = 2\ Ta + 10\ HCl$$

4.7.3
Pyrochemical Process

There are many advantages of using metal chlorides as interprocess intermediates. One of the most important advantages is that the metal chlorides could be readily purified. In other words, co-occurring metals could be more readily separated from one another as chlorides. This is particularly important when the co-occurring metals have very different technological properties and the presence of one in another in the final product is detrimental to the intended commercial application. A famous example of such co-occurrence is that of zirconium and hafnium in the mineral zircon. Not more than 100 ppm hafnium should be present in the zirconium intended for use in the nuclear reactor core. The hafnium content of zircon is about 2.5%.

The volatilities of both zirconium tetrachloride and hafnium tetrachloride are very similar to each other at normal operating temperatures, and their separation by a simple distillation or fractional distillation operation is not viable. However, when the mixed chloride vapor is contacted with an eutectic molten salt mixture of aluminum chloride and potassium chloride, zirconium chloride is preferentially absorbed. The vapor pressure difference between zirconium and hafnium tetrachlorides is greatly enhanced over the molten salt mixture as compared to the situation obtained over a mixture of the pure chlorides. Thus in a distillation column using a molten $AlCl_3$-KCl salt mixture as the carrier, hafnium tetrachloride enriches in the vapor phase and zirconium tetrachloride in the salt phase. A column having 60 stages is capable of accomplishing hafnium separation from its content of 2.5% in the feed to less than 100 ppm in the final product. The flowsheet of the whole process is shown in Figure 4.20.

The chlorination of zircon yields mixed zirconium and hafnium tetrachloride vapors along with the chlorides of many impurity elements. The impurity chlorides are removed by scrubbing the crude chloride product in a fused salt scrubber, using zirconium tetrachloride–sodium chloride and potassium chloride at 360 °C. The purified mixed chloride is then fed to the extraction distillation column in which the $AlCl_3 \cdot KCl$ eutectic extracts zirconium tetrachloride from the mixture at 300 °C. Hafnium tetrachloride, free of $ZrCl_4$, is thus collected. The zirconium tetrachloride-laden molten salt is then purged in another column with nitrogen at 450 °C to obtain hafnium free zirconium tetrachloride. The molten salt, thus stripped of its zirconium tetrachloride content, is reverted to the extraction stage.

The pyrochemical process of zirconium–hafnium separation is particularly attractive not only because it makes the entire process of nuclear-grade zirconium metal production from zircon more economical than that involving a hydrometallurgical separation stage, but also

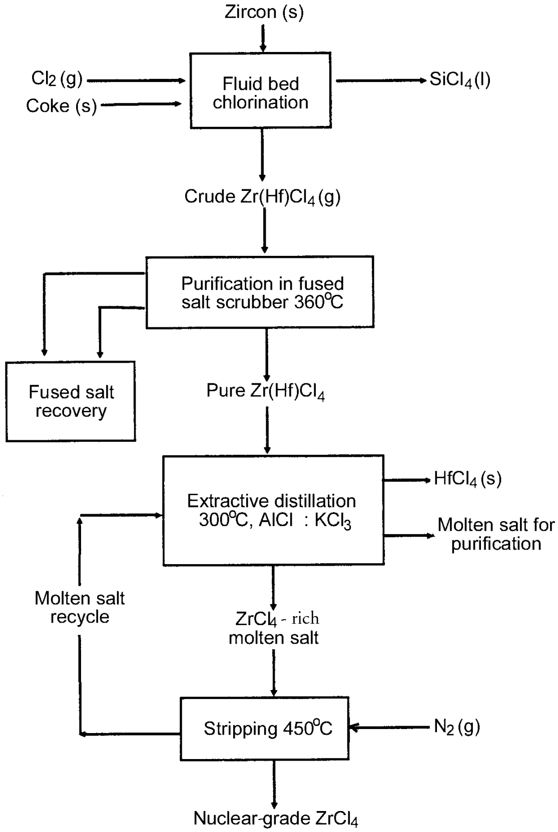


Figure 4.20 Flowsheet of the pyrochemical process for zirconium-hafnium separation.

because the process is environment friendly and has been recognized as an environmentally conscious manufacturing (ECM) technology.

4.7.4
Preparation of Fluorides

The reagents useful for the fluorination of ores and compounds include: flurosilicates, elemental fluorine, hydrogen fluoride, and alkali hydrogen fluorides. Their use is illustrated for fluorination of oxides and oxidic minerals.

The fluorination of metal oxides by fluorine, represented by the reaction

$$MO + F_2 = MF_2 + 0.5\ O_2$$

is a very useful reaction because the standard free energies of formation of fluorides and of the corresponding oxides (per gram atom of metal) are nearly equal. The greater thermodynamic stability of metal fluorides vis-à-vis the corresponding metal oxides makes reduction–fluorination a redundant operation. Hydrogen fluoride is often used as the fluorinating agent for different reasons. A typical hydrofluorination reaction,

$$MO + 2\ HF = MF_2 + H_2O$$

can be considered. Metal fluorides are less hygroscopic than metal chlorides. So, unlike in chlorination, the appearance of water as a product in fluorination does not cause any serious problem. The standard free energy change for this reaction.

$$\Delta G^0 = \Delta G^0_{MF_2} + \Delta G^0_{H_2O} - \Delta G^0_{MO} - 2\,\Delta G^0_{HF}$$

is less negative as compared to the ΔG^0 value obtained if the fluorination reaction is carried out by using elemental fluorine. The reason is that the standard free energy of formation of hydrogen fluoride (per mole of hydrogen) is more negative than the standard free energy of formation of water at all temperatures. The quantity $(\Delta G^0_{H_2O} - 2\,\Delta G^0_{HF})$ has, therefore, a large positive value, and this makes hydrofluorination thermodynamically less advantageous than fluorination. Hydrogen fluoride is, however, widely used as the fluorinating agent whenever thermodynamic feasibility can be combined with cost advantage; hydrogen fluoride is considerably cheaper than fluorine gas.

One of the most important examples of the fluorination of oxides is the fluorination of uranium dioxide. Uranium tetrafluoride (UF_4) is the intermediate compound which is reduced to uranium metal. The gaseous higher fluoride, uranium hexafluoride (UF_6) is used for the separation of uranium isotopes to obtain enriched uranium (i.e., uranium containing a higher proportion of the isotope, U^{235}, than natural uranium).

The following reactions can be considered for the preparation of uranium fluorides (UF_4 or UF_6) starting from urania (UO_2) at a temperature of 500 °C:

$$UO_2 + 2\ F_2 = UF_4 + O_2; \qquad \Delta G^0 = -700\ \text{kJ}$$

$$UO_2 + 2\ F_3 = UF_6 + O_2; \qquad \Delta G^0 = -970\ \text{kJ}$$

$$UO_2 + 4\ HF = UF_4 + 2\ H_2O; \qquad \Delta G^0 = -10\ \text{kJ}$$

$$UO_2 + 6\ HF = UF_6 + 2\ H_2O + H_2; \quad \Delta G^0 = +270\ \text{kJ}$$

Elemental fluorine, as mentioned earlier, is an effective reagent for fluorinating uranium dioxide to either uranium tetrafluoride or uranium hexafluoride. Its use is not so attractive when its high cost is taken into account, and when the intention is to produce only the tetrafluoride and not the hexafluoride. For the production of the former, hydrogen fluoride is a suitable reagent. Hydrogen fluoride can not, however, be used to fluorinate urania to yield uranium hexafluoride. The hexafluoride is best produced, therefore, by first preparing the tetrafluoride from urania by reaction with hydrogen fluoride and then converting the latter to the former, using fluorine.

Fluorination and hydrofluorination reactions are exothermic. Once the reaction is initiated by heating the reactants to the required temperature (initial preheating), the heat evolved in the reaction is sufficient to maintain the reaction temperature, and external heating can be discontinued. As mentioned earlier in this chapter, such reactions are also called autogenous reactions. When the exothermicity is large, it may sometimes become necessary to cool the reactor to keep the reaction temperature from rising to too high a value. Hydrofluorination of urania provides a good example of these features.

Hydrofluorination of urania according to the reaction

$$UO_2 + 4\ HF = UF_4 + 2\ H_2O$$

is carried out in practice at 600 °C. The enthalpy change in this reaction is large (ΔH = −53.55 kJ) but the standard free energy change is small (ΔG^0 600 °C = −30.12 kJ). The standard free energy of formation of water becomes less negative quite rapidly with rise in temperature, whereas that of hydrogen fluoride remains practically constant (becomes only slightly more negative) with rise in temperature. As a result, the standard free energy change for this reaction becomes more negative as the temperature increases. The equilibrium constant ($K = P^2_{H_2O} / P^4_{HF}$) for this reaction decreases in value with increase in temperature. This variation is shown in an explicit manner in Figure 4.21 by a change in the equilibrium composition of the gas phase in the system with changes in the temperature of the reaction. At low temperatures water vapor is the major component in the gas phase, indicating the occurrence of the desired fluorination. At higher temperatures, hydrogen fluoride becomes the major component, indicating that the equilibrium is established with only a very limited formation of the fluoride. The high exothermicity of the reaction would tend to push the reaction temperature up and hence to shift the equilibrium adversely towards the formation of uranium dioxide. This undesirable situation is avoided by controlling the reaction temperature by external cooling, if necessary. Even though it is advantageous ther-

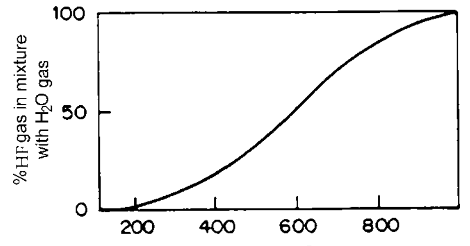


Figure 4.21 The equilibrium concentrations of HF in a mixture with H_2O for the reduction of uranium oxide by hydrogen fluoride versus temperature.

modynamically, the reaction cannot be conducted at very low temperatures (< 400 °C) because of kinetic reasons. The reaction is carried out in practice in a tubular rotary furnace, fitted with a heater and a cooler, at temperatures between 400 and 550 °C. Hydrofluoric acid is extremely corrosive, and the material of the furnace in contact with the reaction mixture is magnesium, which forms a thin impervious layer of magnesium fluoride; this layer withstands the corrosive action of hydrofluoric acid.

Plutonium tetrafluoride is prepared from plutonium dioxide by the following reaction at temperatures between 400 and 600 °C:

$$PuO_2 + 4\ HF + H_2 + 0.5\ O_2 = PuF_4 + 3\ H_2O$$

The reaction is exothermic ($\Delta H^0_{298} = -320.91$ kJ). Hydrogen is present as a contaminant in hydrogen fluoride, and this results in the formation of plutonium trifluoride (PuF_3). Oxygen is added to avoid this. Fluorination is carried out in Hastealloy-C boats lined with platinum.

Starting from rare earth oxides, rare earth fluorides can be prepared by the hydrofluorination of the oxides with anhydrous hydrogen fluoride. For example,

$$Y_2O_3 + 6\ HF = 2\ YF_3 + 3\ H_2O; \quad \Delta G^0_{1000} = -53.8 \cdot 4.184\ \text{kJ}$$

A mixture of anhydrous hydrogen fluoride and 60% argon is passed over yttrium sesquioxide (Y_2O_3) at 700 °C for 16 h. The oxide is contained in a platinum boat, and the inconel furnace tube is also lined with platinum.

The fluorination of vanadium sesquioxide (V_2O_3) to vanadium trifluoride (VF_3) can be carried out by using fluorine:

$$V_2O_3 + 3\ F_2 = 2\ VF_3 + 1.5\ O_2; \quad \Delta G^0_{800} = -1210\ \text{kJ}$$

Hydrofluorination of the oxide according to the reaction

$$V_2O_3 + 6\ HF = 2\ VF_3 + 3\ H_2O; \quad \Delta G^0_{800} = -149\ \text{kJ}$$

is also feasible. Hydrofluorination can also be carried out when the starting material is vanadium trichloride or tribromide instead of the oxide. Vanadium trifluoride is nonvolatile; so in many of the preparative methods only a surface coating of this compound forms on the substrate. This has been a major difficulty in its preparation. This difficulty is circumvented in fluoride preparations by the use of ammonium bifluoride as the fluorinating agent.

Ammonium hydrogen fluoride (NH_4HF_2) is useful for converting pure oxides or hydroxides to the corresponding fluorides. The reaction occurs through the formation of a double fluoride. For example, with vanadium sesquioxide the following reactions occur:

$$V_2O_3 + 6\ NH_4HF_2 = 2\ (NH_4)_3\ VF_6 + 3\ H_2O$$

$$S(NH_4)_3VF_6 = VF_3 + 3\ NH_4F$$

The double fluoride, ammonium hexafluorovanadate ($(NH_4)_3VF_6$), forms from the oxide at 210 to 250 °C, but decomposes at 600 to 700 °C to yield pure vanadium fluoride. Examples of metal fluorides obtainable through the double fluoride route include uranium tetrafluoride, beryllium difluoride and the rare earth fluorides:

$$2\ UO_2 + 5\ NH_4F \cdot HF \xrightarrow{150\,°C} 2\ NH4F \cdot UF_4 + 3\ NH_3 + 4\ H_2O$$

$$NH_4F \cdot UF_4\ (s) \xrightarrow{350-500\,°C} NH_4F\ (g) + UF_4\ (s)$$

$$Be(OH)_2 + 2\ NH_4F \cdot HF = 2\ NH_4F \cdot BeF_3 + 2\ H_2O$$

$$NH_4F \cdot BeF_2\ (s) = NH_4F\ (g) + BeF_2\ (s)$$

The actual fluoride-forming reaction in the ammonium bifluoride route is hydrofluorination. Hydrogen fluoride, which is present in chemical combination in the bifluoride, is readily released on heating. Bifluorides are easier to handle than hydrogen fluoride. The particular advantage of ammonium bifluoride over other alkali hydrogen fluorides is that it is volatile, and thus can be readily distilled out from the reaction mixture.

The hydrofluorination of rare earth oxides with ammonium bifluoride is carried out as a batch process by heating the rare earth oxide with 30% excess of high-purity $NH_4F \cdot HF$ in a platinum boat inside an inconel chamber at 300 °C under a stream of dry air.

Fluoridizing roasting or fluorination is similar to chlorination, and is widely used in the treatment of several rare metal ores. Beryl, the most important ore of beryllium, can be opened by fusing with sodium silicofluoride at 850 °C:

$$3\ BeO \cdot Al_2O_3 \cdot 6\ SiO_2 + 6\ Na_2SiF_6 \rightarrow 3\ Na_2BeF_4 + 2\ Na_3AlF_6 + 3\ SiF_4 + 9\ SiO_2$$

Sodium beryllium fluoride (Na_2BeF_4) is water-soluble and sodium aluminum fluoride (Na_3AlF_6) is water-insoluble. A part of the silicon volatilizes off as silicon tetrafluoride (SiF_4), while the other part remains in the residue as silicon dioxide (SiO_2). Fluorination of silicon is unnecessary and it would be economical to recover all of it as silica. This is accomplished by using soda ash, i.e., sodium carbonate (Na_2CO_3) in the reaction mixture:

$$2\ Na_2CO_3 + 3\ SiF_4 \rightarrow 2\ Na_2SiF_6 + SiO_2 + 2\ CO_2$$

The formation of sodium aluminum fluoride can also be avoided by the use of soda ash. The pertinent reaction is

$$3\ BeO \cdot Al_2O_3 \cdot 6\ SiO_2 + 2\ Na_2SiF_6 + Na_2CO_3 \rightarrow 3\ Na_2BeF_4 + Al_2O_3 + 8\ SiO_2 + CO_2$$

In place of sodium silicofluoride, sodium ferric fluoride (Na_3FeF_6) can also be used for fluorination:

$$3\ BeO \cdot Al_2O_3 \cdot 6\ SiO_2 + 2\ Na_3FeF_6 \rightarrow 3\ Na_2BeF_4 + Fe_2O_3 + Al_2O_3 + 6\ SiO_2$$

Sodium ferric fluoride is obtained as a byproduct in the solution processing of Na_2BeF_6 leach liquor. It is used for substituting for sodium silicofluoride (to an extent of up to 60%) in the ore fusion reaction.

Another silicate ore treated by fluoridizing roasting is zircon. The ore is mixed with potassium hexafluorosilicate (K_2SiF_6) and heated in a rotary kiln at 650 to 700 °C to effect the reaction:

$$ZrSiO_4 + K_2SiF_6 = K_2ZrF_6 + 2SiO_2$$

Potassium hexafluorozirconate (K_2ZrF_6) is leached with hot 1% hydrochloric acid. The hafnium present in the ore undergoes a similar reaction, forms potassium hexafluorohafnate (K_2HfF_6), and enters the solution during leaching. These two compounds, K_2ZrF_6 and

K_2HfF_6, are special in that they are useful in a process for the separation of zirconium from hafnium by fractional crystallization. It is in general very difficult to separate zirconium from hafnium as they are chemically very similar.

Chlorination and fluorination, as processes of metal extraction, are important not only because they are effective in liberating metal values from refractory ores but also because the chlorides and the fluorides are excellent interprocess intermediates for metal reduction. The chlorides have the additional advantage of being compounds which may be made very pure by certain additional processes.

4.7.5
Reduction of Chlorides

Metallothermic reduction of chlorides has been the basis of some very important processes for reactive metals production. Examples include the Kroll and Hunter processes for the preparation of zirconium and titanium, and calcium or lithium reduction processes for the rare earths.

The famous Kroll process is based on the following reaction (in the case of zirconium):

$$ZrCl_4\ (g) + 2\ Mg\ (l) = Zr\ (s) + 2\ MgCl_2\ (l)$$

Zirconium tetrachloride vapor is reacted with molten magnesium, resulting in the formation of molten magnesium chloride and solid zirconium. The temperature range for conducting this reaction is automatically fixed by the melting and the boiling points of all the components involved. The minimum temperature is the melting point of magnesium chloride (714 °C), and the maximum temperature is the boiling point of magnesium (1107 °C). This range is further narrowed to 800 to 875 °C because below 800 °C the rate of the reaction is sluggish, while above 875 °C the reaction becomes difficult to control and runaway conditions may result. The standard enthalpy and the standard free energy of the reaction are –330.53 kJ and –234.30 kJ respectively at 900 °C. The high exothermicity of the reaction points to the possibility of its occurrence as a self-sustaining process.

The product of Kroll reduction is zirconium sponge in a solidified magnesium chloride slag. The metal and the slag are not obtained in a mechanically separable form as, for example, in the aluminothermic reduction of niobium pentoxide. The method of separating magnesium chloride from zirconium sponge is based on the high volatility of the former. This chloride boils at 1418 °C, but even at 900 °C its vapor pressure is about 4 torr. Hence, by subjecting the product of Kroll reduction to a moderate vacuum all the magnesium chloride as well as any magnesium metal present (vapor pressure of liquid magnesium at 900 °C: 75 torr) could be completely removed, leaving behind pure zirconium sponge.

Though the conversion of zirconium tetrachloride to zirconium by magnesiothermic reduction appears to be a technically perfect method, the process requires careful execution on account of the high reactivity of the components involved. In the entire process sequence, moisture and gases such as oxygen and nitrogen should be totally excluded from the system because all the components, i.e., zirconium chloride, magnesium and zirconium, react readily with them; such reactions are extremely undesirable as they directly affect the product quality. Zirconium in the sponge form has a large specific surface area, and this makes it all the more reactive and prone to contamination by oxygen and nitrogen.

The Kroll reactor is, therefore, designed to keep away air and moisture from the reaction system.

A typical reactor used for the production of zirconium is shown schematically in Figure 4.22. In the hermetically sealed mild steel retort, the reactants zirconium tetrachloride and magnesium are loaded in two separate containers that can be heated and maintained at different temperatures. There is also a fully automatic pressure control system for ensuring safe operation. The system pressure is continuously monitored and is automatically maintained in the range of 1 to 3 psig by admitting air into the cooling coils, by bleeding the system in case of excessive pressure build-up, and by admitting argon in case the pressure falls below the desired level.

After loading zirconium tetrachloride powder in the upper chamber of the reactor, which contains in the lower chamber cast ingots of magnesium, the reactor is sealed, evacuated and backfilled with pure argon to a slight positive pressure. Magnesium is first melted and then the zone housing the tetrachloride is heated to sublimate the tetrachloride into molten magnesium. Any oxygen that may be present as an impurity in the zirconium tetrachloride feed is prevented from reaching the reduction zone due to the following reaction:

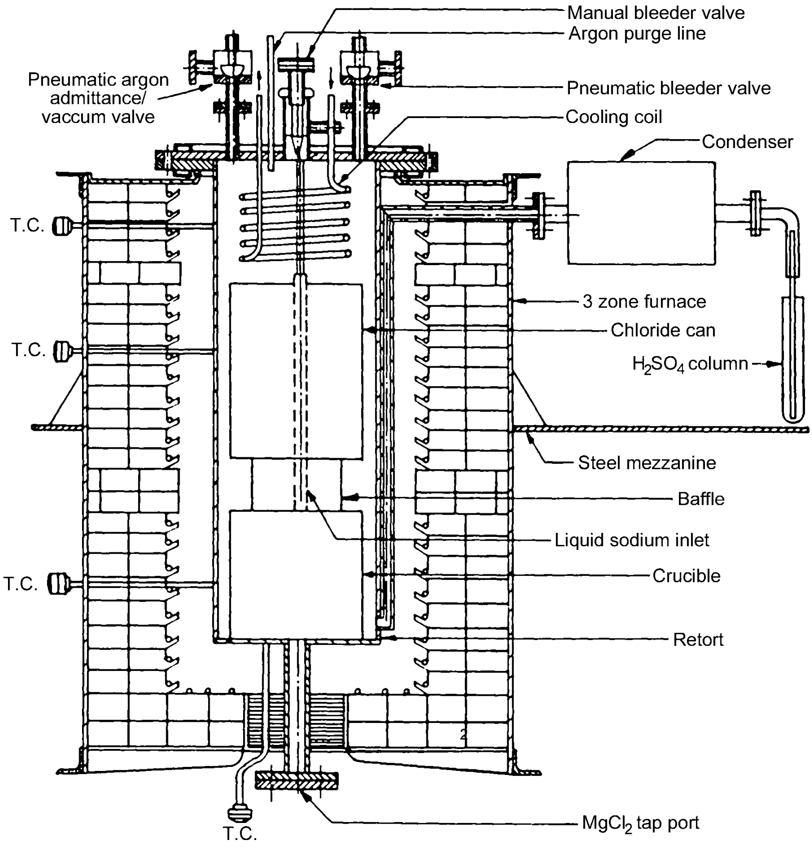


Figure 4.22 Reduction equipment.

$$2\,ZrOCl_4 \rightarrow ZrCl_4 + ZrO_2$$

The above reaction shows that the oxychloride decomposes at the sublimation temperature into the volatile tetrachloride and the nonvolatile oxide. Reduction starts as soon as the chloride vapour contacts the molten magnesium, and this exothermic reaction raises the temperature of the reaction mixture. The temperature of the reduction crucible is maintained in the range of 800 to 875 °C. The process is carefully controlled by matching the sublimation rate of zirconium tetrachloride with the reduction rate. The conclusion of the reduction is indicated by a fall in temperature and pressure.

After reduction is complete, most of the magnesium chloride is mechanically separated from the reduced mass; the remaining fraction is removed along with the excess magnesium reductant by vacuum distillation at about 900 °C under a pressure of 10^{-3} to 10^{-1} torr. A schematic diagram of the reactor used for vacuum distillation is shown in Figure 4.23.

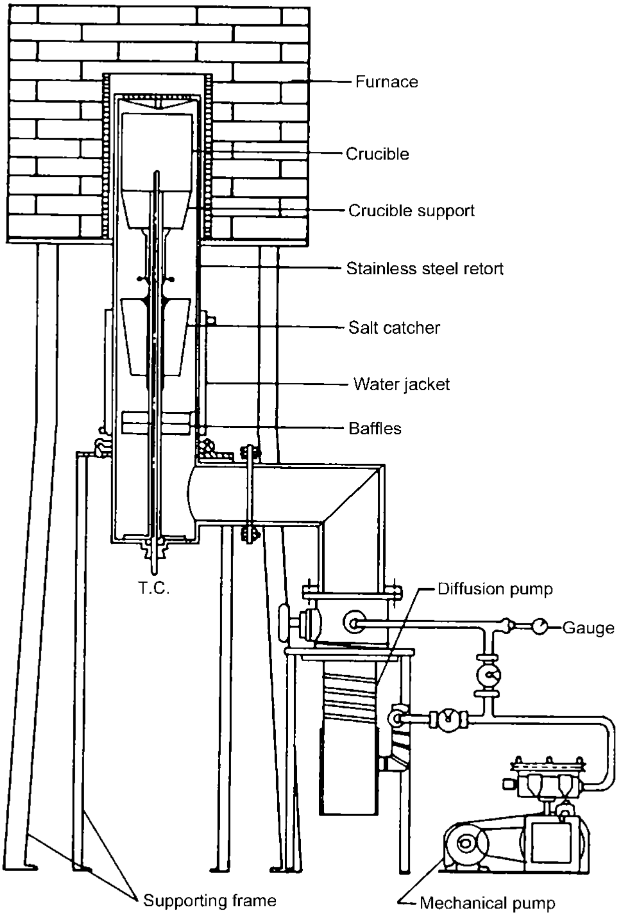


Figure 4.23 Vacuum distillation assembly for separation of zirconium/titanium metals from reduction products.

This is also a vacuum-tight vessel with arrangements for external heating and continuous evacuation. As the temperature is raised beyond the melting point of magnesium chloride (714 °C), the chloride starts draining out of the inverted reduction crucible into the salt can be kept beneath it. The magnesium chloride and the magnesium entrapped in the sponge vaporize and condense in the cooler parts of the reactor. Pure zirconium sponge, typically containing 0.09% oxygen, less than 0.01% nitrogen (and of each of the other nonmetallic impurities) and 0.03% iron, remains in the crucible.

The zirconium sponge thus obtained is highly pyrophoric. The industrial practice is to condition this sponge by the controlled admittance of air-argon mixtures at around 50 °C. Such a treatment results in the formation of a thin, protective oxide film on the sponge; this eliminates any major fire hazard in subsequent handling and crushing operations.

The process, now known as the Kroll process, was originally developed in 1940 by Wilhelm F. Kroll for the production of titanium. It is based on the reaction:

$$TiCl_4 + 2\ Mg = Ti + 2\ MgCl_2$$

The process was adopted for zirconium subsequently. The Kroll reactor for titanium is different from the one used for zirconium. Unlike zirconium tetrachloride, which is solid at room temperature (melting point: 437 °C), titanium tetrachloride (melting point: 23 °C) is a liquid and can be metered directly into molten magnesium. The reduction is conducted under an inert atmosphere in a stainless steel reactor. Magnesium, corresponding to 20% excess over that required by stoichiometry, is charged into the reactor and heated to a temperature above the melting point of magnesium chloride. External heating is then stopped and titanium tetrachloride is metered into the reactor at such a rate that the temperature is maintained between 800 and 900 °C due to the exothermic reaction. When all the chloride has been fed, the reactor is heated to 900 to 940 °C to complete the reduction of the lower chlorides of titanium that might have formed. In the course of reduction, most of the magnesium chloride product can be tapped from the reactor without interrupting the process. Magnesium, being lighter than magnesium chloride, always floats on the molten slag in the reduction crucible and thus makes itself available to the incoming liquid chloride (in titanium tetrachloride reduction) or the chloride vapour (in zirconium tetrachloride reduction). This characteristic allows magnesium chloride to be tapped without affecting the availability of magnesium for reduction. After reduction is complete, the product, consisting of titanium sponge, magnesium chloride and excess magnesium, is subjected to vacuum distillation at 900 to 1000 °C under 0.1 kPa pressure during which both magnesium and magnesium chloride are distilled away, leaving behind pure titanium sponge. A typical analysis of the sponge thus obtained is: 0.1% oxygen, less than 0.01% each of hydrogen, nitrogen and carbon, 0.05% iron and about 0.03% silicon.

Another chloride reduction process, originally developed by Hunter for titanium tetrachloride and known by his name, uses sodium as the reductant. In this process liquid sodium and titanium tetrachloride are simultaneously metered into a steel retort under an argon atmosphere. The highly exothermic reduction reaction

$$TiCl_4 + 4\ Na = Ti + 4\ NaCl$$

raises the temperature of the reactor. The temperature is maintained above the melting point of sodium chloride but below the boiling point of sodium, i.e., between 801 and

883 °C by external cooling. During this process a part of the reduction occurs between titanium tetrachloride and sodium vapor and this leads to the formation of titanium powder. To avoid this, the reduction is carried out in two steps. Initially, stoichiometric amounts of sodium and titanium tetrachloride are metered into the steel retort at 700 to 750 °C to produce titanium dichloride:

$$TiCl_4 + 2\,Na = TiCl_2 + 2\,NaCl$$

Titanium dichloride forms a low-melting eutectic with sodium chloride, and so the reaction mass is molten at this temperature. Additional sodium is then added to complete the reduction:

$$TiCl_2 + 2\,Na = Ti + 2\,NaCl$$

Titanium sponge is separated from sodium chloride and excess sodium by leaching with water.

The major limitations attendant to the use of sodium in tetrachloride reduction are the necessity to maintain the temperature of the highly exothermic reduction reaction at values between 801 and 883 °C, and the larger volume of the slag generated because of the monovalency of sodium. Another difficulty pertains to the handling of highly reactive liquid sodium.

Rare earth chlorides are more stable than magnesium chloride and thus cannot be reduced by the Kroll process. Alkali metals and calcium are the only useful reducing agents for them. Lanthanum, cerium, praseodymium, and neodymium are the rare earths with relatively low melting points. They have been prepared by heating the appropriate chloride with calcium in a tantalum crucible under vacuum or an inert gas. The crucibles used in the reduction process are inductively heated to temperatures above the melting point of the metal to be produced. Attempts to prepare gadolinium and other high-melting rare earths by calcium reduction have failed because the use of higher reaction temperatures causes frothing of the calcium chloride slag which prevents a clean slag–metal separation. The temperatures required can be brought down by producing the metal as a low-melting alloy. Thus yttrium (melting point: 1500 °C) has been produced as a yttrium–magnesium alloy (liquidus: ~950 °C) by reducing yttrium trichloride with calcium in the presence of magnesium. Another successful method of rare earth chloride reduction involves the use of lithium vapor. The rare earth chloride (e.g., yttrium trichloride), kept in a titanium or tantalum crucible, is reduced with lithium vapor and the process is implemented inside a sealed stainless steel chamber. Reduction is carried out at 1000 °C. After reduction, the lithium chloride slag is distilled away, leaving crystals of the rare earth metal behind. These crystals are consolidated in an arc furnace. In the chloride reduction process, the trichloride of the rare earths samarium, europium, and ytterbium are reduced only to the corresponding dichlorides and undergo no further reduction. These metals, therefore, must be prepared by other methods.

There are many advantages in the use of chlorides as intermediates for reduction. A persistent disadvantage is that they are hygroscopic. This, when combined with the limitations associated with the use of chlorides in reduction operations designed to produce the metal in the massive form, brings forth the fluorides as more suitable intermediates.

4.7.6
Reduction of Fluorides

Fluorides are nonhygroscopic, and their melting points are higher than those of the corresponding chlorides. Besides, the fluoride reduction reactions are considerably more exothermic. The prime examples of the use of fluorides as intermediates are: the reduction of uranium tetrafluoride by calcium or magnesium; the reduction of rare earth fluorides by calcium, reduction of beryllium fluoride by magnesium; and the reduction of potassium tantalum double fluoride by sodium.

Magnesium can be obtained in high purity at low cost. It is the preferred reducing agent whenever feasible. The reduction of uranium tetrafluoride by magnesium involves the reaction

$$UF_4 + 2\ Mg = U + 2\ MgF_2; \quad \Delta H^0_{298} = -330\ kJ$$

which is highly exothermic. However, the exothermicity is not sufficient to raise the temperature of the products to above 1263 °C, the melting point of MgF_2, even in an adiabatic reactor. The heat of fusion of MgF_2 is 57.73 kJ $mole^{-1}$ and that of uranium is 11.96 kJ $mole^{-1}$. Subtracting these values from the heat of reaction, one finds that only 202.08 kJ are available for the formation of one gram atom of uranium. The reaction involves heating 7 gram atoms for the formation of one gram atom of uranium, and if the average heat capacity is taken as 7 cal g $atom^{-1}$ deg K^{-1}, the expected temperature to which the system would rise as a result of the reaction would be only about 986 °C (~ 483,000 ÷ 49). Hence additional heat input through a booster or through preheating would be necessary. In practice preheating is used. Magnesium reduction of uranium tetrafluoride has to be conducted in a sealed bomb because of the high vapour pressure of magnesium at the temperatures attained during the reaction (~ 400 kPa at 1300 °C). As in the aluminothermic reduction of oxides, the slag and the metal are well separated after reduction.

The reduction of uranium tetrafluoride by calcium, in accordance with the reaction

$$UF_4 + 2\ Ca = U + 2\ CaF_2; \quad \Delta H^0_{298} = -540\ kJ$$

is considerably more exothermic than its reduction by magnesium. The melting point and the heat of fusion of calcium fluoride (CaF_2) are 1418 °C and 29.70 kJ $mole^{-1}$ respectively and the heat of fusion of uranium is 12.55 kJ $mole^{-1}$. Subtracting the heats of fusion, the heat available for raising the temperature of the products is 468.60 kJ, assuming an adiabatic system. Taking the average heat capacity as 7 cal g $atom^{-1}$ deg K^{-1}, this heat is very much in excess of that required for heating the products to temperatures beyond 1418 °C. Besides, the vapor pressure of calcium is not a problem because its boiling point is 1440 °C which is above the melting point of calcium fluoride. Preheating, as in the case of the magnesiothermic reduction of uranium tetrafluoride, may be used to initiate the reaction. Alternatively, the reaction can be primed internally, i.e., by locally heating a small portion of the charge to start the reaction. The main drawbacks of the use of calcium are its high cost and the difficulties in its handling.

As mentioned earlier, magnesiothermic reduction is carried out in a sealed bomb. This steel bomb (400 mm in diameter and 1000–1200 mm in height for about 100 kg of uranium) is provided with a 25 mm MgF_2 lining, which is thin enough to permit the influx of heat during the preheating period that precedes the reaction and yet is thick enough to prevent the overheating of the steel by the heat of the reaction. The bomb is evacuated, backfilled with an inert gas at a low pressure, and sealed. The reaction is initiated by heating the bomb to ~700 °C. Once initiated, the reaction proceeds quickly to completion, resulting in the formation of well-separated metal and slag products. After cooling, the solidified metal ingot and the slag layer are removed. The reduction can be carried out in larger reactors to produce large castings known as ingots (i.e., direct ingots), weighing 1 ton or more. The metal is about 99.93% pure.

In calciothermic reduction a well-blended mixture of uranium tetrafluoride and calcium metal granules is charged into a reduction bomb, lined with dry calcium fluoride powder. The bomb reactor is shown schematically in Figure 4.24. The bomb is then covered with a ball-type lid, evacuated and backfilled with argon at a low pressure. The reaction is initiated by passing a high current through a magnesium ribbon embedded in the reaction mixture. The reaction is instantaneous and its initiation and completion can be followed by observing the rise and the fall in the pressure inside the bomb by means of a pressure gauge. The

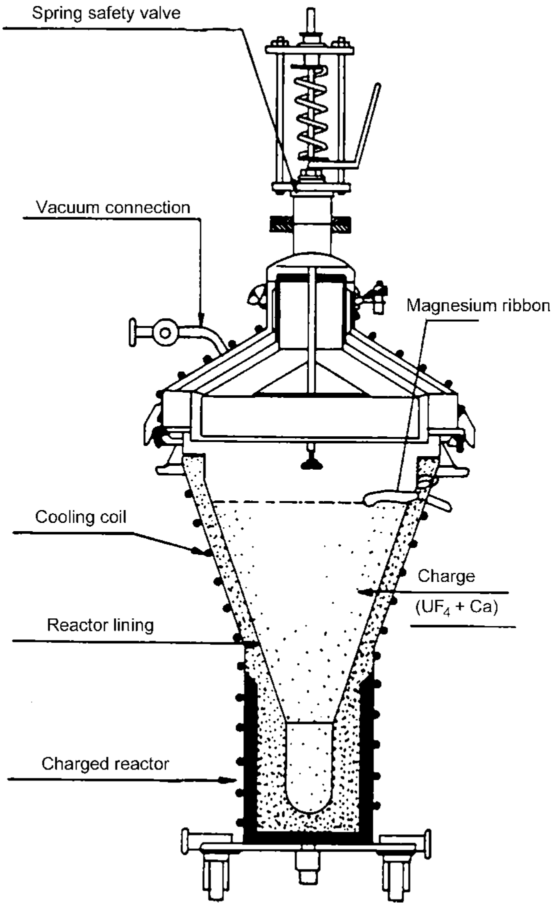


Figure 4.24 Reactor for uranium fluoride reduction with calcium.

bomb is cooled slowly by circulating water through the cooling coils provided on its outer side and also on the lid. After cooling for a day, the bomb is opened and the uranium billet and the slag are separated.

All the rare earth metals except samarium, europium, and ytterbium can be prepared in a pure form by reducing their trifluorides with calcium. Magnesium fluoride is less stable than the rare earth fluorides and so magnesium does not figure as a reductant. Lithium forms a fluoride which is stabler than some of the rare earth fluorides and thus finds some use as a reductant.

The rare earth fluoride and calcium mixture, loaded in a tantalum crucible, is externally heated in an argon atmosphere to a temperature about 50 K above the melting point of the highest melting component in the reaction mixture. It takes only a few minutes for the reaction to go to completion, resulting in a good slag–metal separation. The excess calcium and the residual slag are removed from the metal by vacuum melting and high-purity metal is obtained with 97–99% yield. Any rare earth metal, irrespective of its melting point, except samarium, europium, and ytterbium which form stable divalent halides, can be produced by this process. It is, however, very important to provide a contamination-free environment during the handling of the reactants and the products as well as during the reduction in order to obtain a pure metal.

The difference in the heats of formation of calcium fluoride and of the rare earth fluorides, on an equivalent basis, is not very large and the exothermicity of the reaction

$$REF_2 + Ca = RE + CaF_2$$

is not sufficient for a self-sustaining process. External heating is, therefore, necessary. High-temperature operation is not problematic because of the relatively low vapor pressure of calcium fluoride (3 torr, 1700 °C). As regards the use of lithium in fluoride reduction, it has mainly found application in the production of low-melting rare earth metals such as cerium, lanthanum and neodymium for which the reaction temperatures need not be very high. The process is carried out by heating the fluoride and lithium to 1200 °C in a molybdenum crucible enclosed in a steel bomb. The production of high-melting rare earths like yttrium as rare earth–magnesium alloys permits the reduction to be carried out at about 950 °C. The melting point of the calcium fluoride slag is brought down to below 950 °C by forming an eutectic with calcium chloride. Magnesium is subsequently distilled away, leaving pure yttrium behind.

The metal beryllium is prepared from its fluoride by magnesiothermic reduction. Calcium can not be used for this purpose because it would interact with beryllium to form a stable intermetallic phase ($CaBe_{13}$).

The reduction of beryllium fluoride by magnesium according to the reaction

$$BeF_2 + Mg = Be + MgF_2$$

is the commercial method for the production of beryllium metal. The reaction is exothermic, but the enthalpy change is not large enough to permit a thermit-type reduction, as in the case of uranium. In the Ellingham diagram for fluorides the beryllium fluoride and magnesium fluoride lines are located relatively close to each other and unlike uranium, which forms a tetrafluoride, beryllium forms only a difluoride. The reduction is, therefore, carried out by heating the reactants together in a graphite crucible in an induction furnace.

When stoichiometric quantities of beryllium fluoride and magnesium are used, the reduced beryllium metal does not fuse and the separation of the slag from the metal becomes very difficult. This problem has been solved by the use of excess beryllium fluoride (about 40%) in the reaction mixture. The unreacted beryllium fluoride, which forms a thin coating over the magnesium fluoride crystals, dissolves rapidly during the water leaching stage, disintegrating the slag and releasing the beryllium pebbles.

The reaction of beryllium fluoride with magnesium goes to completion at around 1000 °C. However, in practice, the temperature is raised rapidly to 1400 °C at the end of the reaction. This is well above the melting points of beryllium and magnesium fluoride. The molten slag-metal mixture is poured into a water-cooled graphite mold for solidification. Beryllium pebbles float to the surface of the slag due to the low density of beryllium. The solidified mass is then wet ball-milled to separate the beryllium pebbles from the slag.

Beryllium is a toxic element, and the reduction operation is therefore carried out in a well-ventilated special double enclosure. The furnace controls are located outside the enclosure. The ball milling of the reduced mass is carried out in walk in-type fume hoods.

The magnesium-reduced beryllium pebbles generally assay 96% beryllium and are always associated with residual magnesium and slag. These pebbles are purified to about 99.5% by vacuum induction melting in beryllia crucibles at temperatures of about 1400 °C. The ingots are machined and machined scarf is milled to produce beryllium powder. The ground metal powder is pressed and sintered under vacuum. The product is called vacuum hot-pressed beryllium, and this is machined for component manufacture.

The reduction may be performed in the presence of an alloying component such as copper or aluminum to obtain a master alloy. Such alloys may also be produced by carbothermic smelting of the oxide in the presence of the alloying constituent. The carbothermic route constitutes a cheaper mode of production, when making the alloys is the sole objective.

Neither calcium nor magnesium is used as the reducing agent in the production of tantalum by fluoride reduction. The intermediate used is potassium tantalum fluoride (K_2TaF_7), and the reducing agent is sodium. The choice of sodium is primarily guided by the need to produce tantalum in the powder form. The pertinent reaction is:

$$K_2TaF_7 + 5\ Na = 5\ NaF + 2\ KF + 2\ Ta$$

A system used for implementing the sodium reaction is shown schematically in Figure 4.25. This system is designed to enable the reduction reaction to occur in a liquid medium. The system can be considered to be in two parts; the sodium feed system, and the reduction system. The sodium feed system is repeatedly evacuated and backfilled with argon. A sufficient number of sodium bricks are placed in the dump tank under a protective blanket of argon and are melted by heating to about 200 °C. The dump tank is then subjected to argon pressurization to transfer the molten sodium through a metallic filter (this holds back sodium oxide particles which are larger than about 5 μm in size) to the storage tank. The amount of sodium fed to the tank is that necessary for a reduction batch. A level probe gauges the amount of sodium held inside the tank. The reactor is charged with potassium tantalum fluoride (K_2TaF_7) and sodium chloride, and is then assembled. The reactor is then hot evacuated at 400 °C and flushed with argon. The reactor temperature is taken to about 925 °C, maintaining a slightly positive pressure of argon. The storage tank valve is opened and molten sodium is progressively added to the molten tantalum salt inside the reactor.

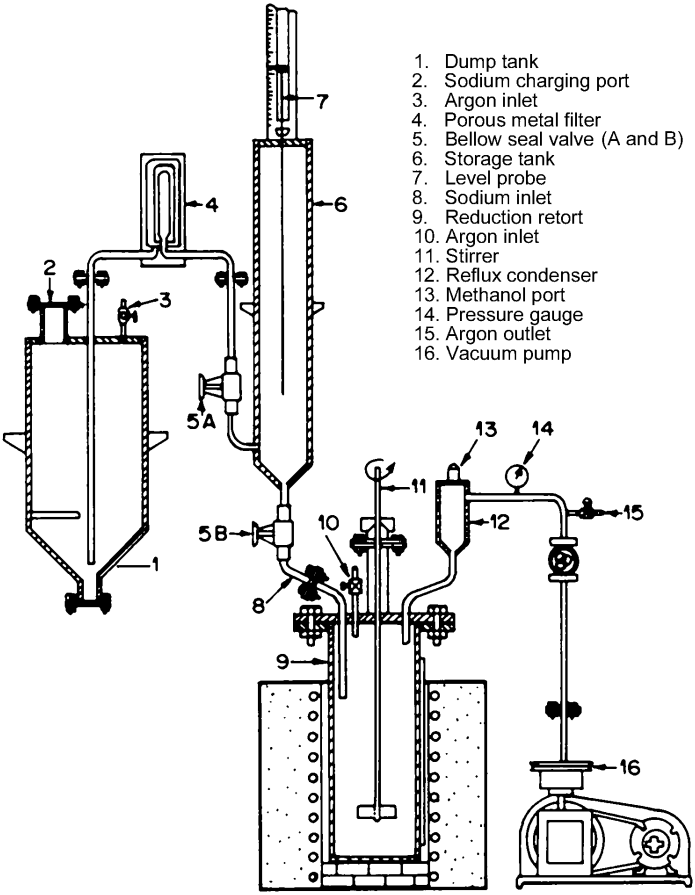


Figure 4.25 Liquid-liquid reduction assembly.

At the conclusion of reduction, the reactor is cooled and methanol is poured into it through the opening in the condenser. After taking care of any free or unreacted sodium in this way by adding methanol, the reduced product is crushed and leached with a solution containing aluminum sulfate and sulfuric acid to dissolve the sodium fluoride and the unreduced potassium tantalum fluoride. Aluminum ions, when present in the solution, enhance the dissolution of the fluorides by complexing with the fluoride ions released in the aqueous medium. This complex formation also inhibits the hydrolysis of the fluorides and the formation of hydrogen fluoride. Leaching completed, the powder is thoroughly washed, rinsed free of water and finally vacuum-dried.

Various options for the production of tantalum from pure tantalum compounds are summarized in Figure 4.26. The oxide and halide reduction reactions described above have been carried out in basically different types of reactors, using processes that are characteristically different because the forms and the physico-chemical nature of the feed materials are different. A relatively recent development with regard to process metallurgical equip-

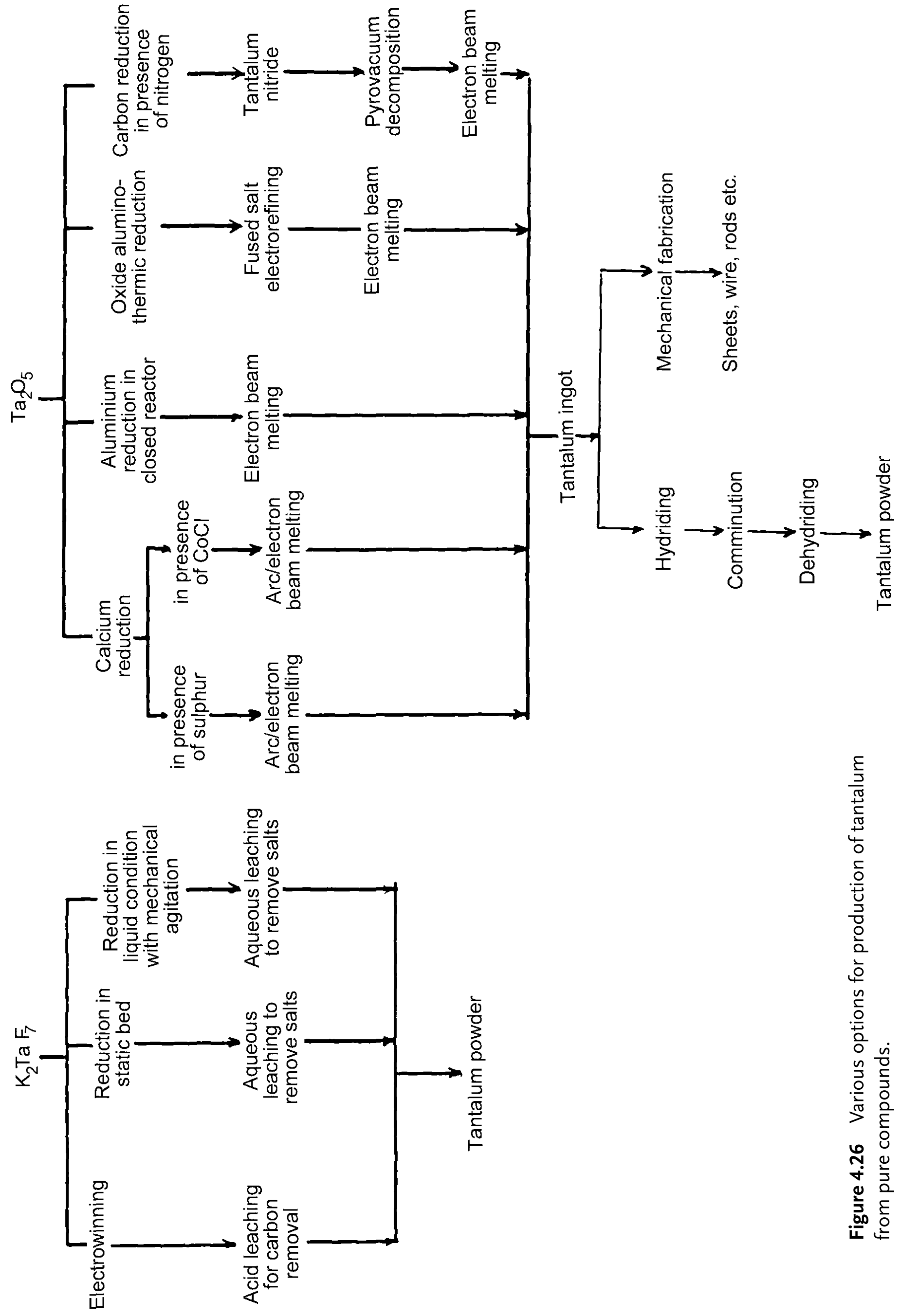


Figure 4.26 Various options for production of tantalum from pure compounds.

ment pertains to the emergence of plasma furnaces which are very versatile and can handle many functions.

4.8
Plasma Processes

A plasma is a partially ionized gas at atmospheric pressure. It is electrically conducting, and allows a stable transfer of power between two or more electrodes. A common method of generating a plasma is, therefore, to establish an arc between two electrodes in the presence of a gas. Such an assembly represents a plasma furnace or reactor. The plasma plume consists of electrons, ions, and neutral atomic species. Its temperature is very high (> 1730 °C). Depending on the chemical nature of the plasma gas, the atmosphere in the plasma reactor may be inert, oxidizing, or reducing. Thus there are now available furnaces or reactors in which materials may be subjected to very high temperatures under conditions of highly concentrated enthalpy in an environment which may be inert, oxidizing, or reducing. Such a combination of facilities indicates a wide variety of applications of plasma furnaces in chemical metallurgy. These applications range from the beneficiation of complex ores to the reduction of various compound intermediates to yield pure metals and alloys, and also to the recovery of metals from wastes.

The high temperatures attainable in a plasma furnace, with no restrictions with regard to factors such as the furnace atmosphere or the crucible material, has made processing by thermal decomposition a practicable and useful method. A good example is the thermal decomposition of low-cost zircon ($ZrSiO_4$) to produce zirconium dioxide (ZrO_2). The fur-

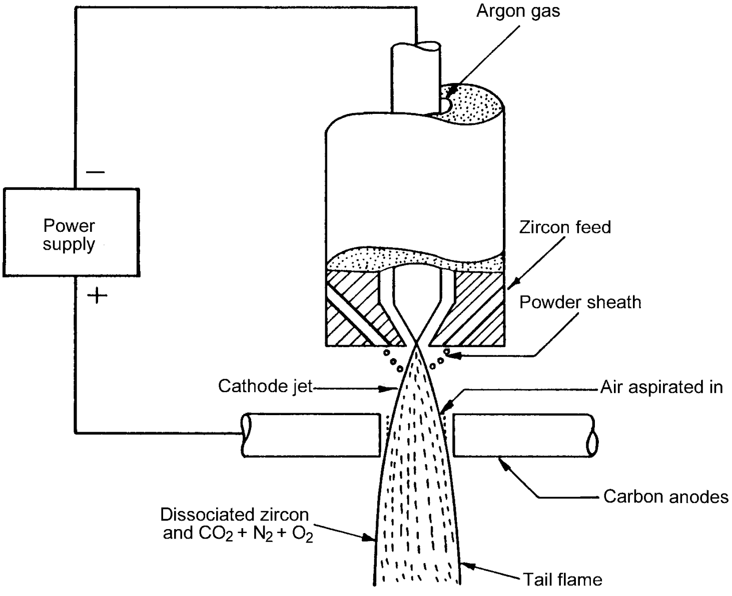


Figure 4.27 Schematic of the IONARC plasma furnace.

nace used for carrying out this decomposition is shown schematically in Figure 4.27. There are three carbon anodes radially disposed in a horizontal plane. Above them is a water-cooled, tungsten-tipped cathode. The carbon electrodes are slowly rotated to ensure even wear. The particulate feed material (zircon) is injected into the inner electrode gap. At the high temperatures prevailing in the plasma, zirconium silicate decomposes into zirconium dioxide and silica. The silica produced has a high specific surface area because of its uniform distribution in the zircon sand. This material is amenable to rapid leaching at relatively low temperatures with inexpensive lixiviants.

Plasma processes have been successfully demonstrated for production of metals from their oxides and chlorides intermediates. Reducing agents are, of course, to be used. Thus, a plasma-based process involving reduction of tantalum chloride in hydrogenous atmosphere has been claimed to yield highly pure metal powder suitable for making of porous capacitor of high capacitance.

4.9
Refining

Reduced metals often contain one or more impurities, ranging from sulfur and oxygen remaining from the original concentrate, carbon and aluminum introduced during reduction, nitrogen from the air with which the system has had contact, to other metals which also have been present as impurities in the original concentrate. These impurities have to be removed principally because of two reasons. First, their presence in the metal affects its useful properties; and secondly, the impurities themselves may be valuable in their own right. Most of the impurities mentioned are removed for the first reason, but metals such as silver, gold and the platinum group metals are examples of impurities which are removed for their worth.

The processes used for refining usually have specific objectives and refer to the specific case of a particular matrix metal and a particular impurity. Their classification can be made only in very general terms. It is useful to regard the process of refining as necessary because different elements tend to distribute differently in different phases which are afterwards physically separable one from another. Metal-refining processes may be broadly divided into the following categories: metal–slag, metal–metal, and metal–gas processes. There are, however, mixed processes which do not fit exclusively in any of these categories.

4.9.1
Metal–Slag Processes

The selective oxidation and slagging of less noble metals from a more noble matrix metal constitutes the bulk of metal-slag processes. These processes are also known by the name of fire refining. In nonferrous extraction metallurgy the most important examples of this type of processes include fire refining of copper, lead softening, and cupellation. Electroslag refining applied to nonferrous metals also enters the realm of metal–slag processes.

Blister copper, produced from sulfide ores by matte smelting and converting, is refined to the grade known as tough pitch copper by a multistage operation known as fire refining.

From blister copper, residual sulfur and impurities such as aluminum, silicon, manganese, zinc, tin, iron, nickel, arsenic, antimony and lead are first eliminated by oxidation and slagging. At the end of this stage excess oxygen remains in the partly purified copper, and this is removed by a deoxidation process.

The oxidation stage of this operation was described earlier in the section on converting. During oxidation, in addition to sulfur, some of the other impurity elements form volatile oxides and escape. Metal oxides with high melting points float on the surface. These oxides can be slagged by adding silica and then removed by skimming. When no more slag is formed, it is inferred that the copper has reached a stage of saturation with respect to oxygen: this copper contains 6 to 10% cuprous oxide (corresponding to 0.6 to 0.9% oxygen) and is known as flat set copper. Deoxidation of this flat set copper has traditionally been carried out by a method known as poling. After the last slag has been removed at the end of the preceding oxidation stage, heavy tree trunks are thrust into the molten copper bath. The wood undergoes destructive distillation due to the heat of the bath, causing the evolution of gaseous hydrocarbons, carbon monoxide, hydrogen, and water vapor. These gaseous products cause stirring in the bath. The reducing gases react with the oxygen in the flat set copper and form carbon dioxide and water vapor. In addition to being less noble than the matrix metal, if an impurity has a high activity coefficient in the metallic melt, its elimination by fire refining is more favored. The other conditions that are favorable for efficient fire refining are that the impurity oxide should have a low activity coefficient in the slag, and that the temperature should be low. The water vapor released when the poles are immersed in the bath forms bubbles which can act as nuclei for collecting the gaseous carbon oxides that are evolved in the process of reduction. In this way the oxygen content is brought down to a final value of about 0.05%. About six green tree trunk poles, each 15 to 20 cm in diameter, are needed to treat 100 tonnes of copper. The method is, however, being used increasingly less and a more efficient gaseous reduction operation in which propane gas is injected through the bath to remove oxygen is gaining wider acceptance. As mentioned earlier, the product obtained after these operations is known as tough pitch copper.

Fire refining is applied to lead to bring about the removal of tin, arsenic, and antimony. This process is also called lead softening because the refined metal is softer than the starting material, i.e., crude lead. Lead produced in the blast furnace contains deleterious impurities such as sulfur, arsenic, and bismuth as well as impurities of high value such as gold and silver. Copper, tin, and antimony are the other impurities that usually occur in lead. The refining of lead is a multistage process because of the different natures of the impurities; each stage can be designed to eliminate one or two major impurities only. Tin, arsenic, and antimony are removed from lead after copper has been removed from it. The removal of copper from lead is described in a later section.

Air is blown through the copper-free lead bullion melt, using steel lances which can be immersed in the melt to assure optimum contact between the gas and the metal. The temperatures of the bath is raised to 750 °C and tin, arsenic, and antimony are oxidized. Tin oxidizes first, forming a yellow-coloured layer of lead stannate ($PbSnO_3$). This slag is removed. Arsenic and antimony are oxidized next, forming lead arsenate and lead antimonate. Bismuth, present as an impurity in lead, is, however, not oxidized. Air blowing is continued until the antimony content drops to less than 0.01%. The slag formed is removed and the softened lead thus obtained is processed for the recovery of silver and gold.

The elimination of tin, arsenic, and antimony from lead occurs because these elements form the oxides SnO_2, Sb_2O_3 and As_2O_3 and so undergo preferential oxidation. Bismuth oxide (Bi_2O_3) is less stable than lead oxide and hence does not undergo oxidation in the presence of lead. The elements arsenic, antimony, and tin are present as impurities in the host element lead in the form of solutes in a dilute solution. In this situation, their oxides can form only at oxygen potentials much higher than those given by the pertinent Ellingham lines, and these values can be greater than the oxygen potential for lead oxide formation under standard conditions when the lead becomes almost pure. It is, therefore, clear that under fire refining conditions lead also oxidizes extensively and the slag phase consists principally of lead oxide with other oxides (SnO_2, Sb_2O_3 and As_2O_3) as minor constituents. This explains the formation of lead stannate ($PbSnO_3$) first (SnO_2 is the stablest oxide of the impurity elements) and subsequently of lead arsenate and antimonate.

The losses of lead as litharge (PbO) can be minimized if the impurity elements could be oxidized at an oxygen potential lower than that which causes the oxidation of lead. This can be achieved if the activities of the oxides of the impurity elements in the slag are decreased, for example, by the addition of an oxide which reacts very much more strongly with the oxides of the impurities than it does with lead oxide. Sodium hydroxide is a useful reagent for this purpose and sodium nitrate can be used as the source of oxygen. The reaction involved in this process, known as the Harris process, can be formally written as

$$2\,Sb + 4\,NaNO_3 + 2\,NaOH = 2\,NaSbO_3 + 4\,NaNO_2 + H_2$$

and is pertinent with regard to the removal of antimony. A similar reaction is relevant for the formation of sodium arsenate. In the Harris reactor, impure liquid lead is allowed to shower through a layer of molten sodium nitrate ($NaNO_3$), whereby the impurities are oxidized and dissolved in the molten salt layer until the layer is saturated with the impurities.

In contrast to the fire refining of copper, where the oxidation stage needs to be followed by a deoxidation step, no deoxidation step is necessary in the fire refining of lead. This is because the solubility of oxygen in liquid lead at typical refining temperatures is quite low ($2 \cdot 10^{-2}$ to 10^{-1} at-% at 600 to 700 °C).

Another classic example of fire refining is the cupellation process, which is used for freeing silver from lead. A silver-lead alloy (~2% silver + 98% lead) is obtained when lead is subjected to the desilverization step in the process flowsheet for pure lead production from lead ores. Since silver is very much nobler than lead, when molten lead containing silver is subjected to a blast of air, silver is not affected while lead oxidizes to lead oxide. The melting point of lead oxide being low (886 °C), it is readily fusible during the oxidation process. Molten lead oxide acts as a good solvent for the other base metal oxides which may be present in the raw silver. During processing, molten lead oxide is continuously run off down a sloping hearth (in a small reverberatory furnace, known as cupel) leaving behind a pool of silver which may also contain some gold. This alloy is called the Doré metal, and it can be separated into its constituents by wet methods. The hearth of the cupel is sufficiently concave to retain the pool of Doré metal. The hearth is lined with a suitable refractory which can absorb a part of the very reactive slag and leave the metal clean. Bone ash has often been used for this purpose.

4.9.1.1 Steel Making

Refining by oxidation is the basic characteristic of metal-slag processes in which many examples have been considered from nonferrous extraction metallurgy. The most well-known and also the most extensively used metal–slag process in extractive metallurgy is steel making. Even though some of the important refining reactions which are very much part of steel making do not belong to metal–slag processes, so many other reactions in steel making depend on slag–metal interaction that the topic of steel making is best considered under metal–slag processes.

Steel making, broadly speaking, is an oxidation process in which impurities such as carbon, silicon, manganese, phosphorus and sulfur present in the pig iron are removed to specified levels. It can be anticipated from the Ellingham diagram that at about 1600 °C, the elements C, Si, and Mn would oxidize preferentially before iron undergoes excessive oxidation. The oxidation reactions may be represented by

$$2\ \mathrm{P}\ (\text{in Fe}) + 5\ \mathrm{O}\ (\text{in Fe}) \rightarrow \mathrm{P_2O_5}\ (\text{in slag})$$

$$\mathrm{Si}\ (\text{in Fe}) + 2\ \mathrm{O}\ (\text{in Fe}) \rightarrow \mathrm{SiO_2}\ (\text{in slag})$$

$$\mathrm{Mn}\ (\text{in Fe}) + \mathrm{O}\ (\text{in Fe}) \rightarrow \mathrm{MnO}\ (\text{in slag})$$

$$\mathrm{C}\ (\text{in Fe}) + \mathrm{O}\ (\text{in Fe}) \rightarrow \mathrm{CO}\ (\text{gas})$$

Phosphorous pentoxide exists in the slag as a liquid under steel-making conditions. Impurity elements are shown to react with atomic oxygen dissolved in iron rather than with molecular oxygen. Oxygen dissolves in steel by dissociation of an oxide of iron at the slag–metal interface, releasing atomic oxygen to the metal.

$$\mathrm{Fe_2O_3}\ (\text{in slag}) \rightarrow 2\ \mathrm{FeO}\ (\text{in slag}) + \mathrm{O}\ (\text{in Fe})$$

In processes involving oxygen blowing, in addition to direct reaction between Si, Mn, C, P, and molecular oxygen, FeO, which is formed by iron oxidation reacts with the metalloids. Further oxidation of FeO produces $\mathrm{Fe_2O_3}$ which diffuses through the slag to release atomic oxygen to the melt by dissociating at the slag–metal interface. For the supply of oxygen to the metal, slag fluidity, turbulence, and slag–metal interfacial area therefore become important factors.

During steel making, the oxidation of Si and Mn proceed rapidly, but the oxidation of CO is delayed due to problems associated with the production of CO bubble in liquid steel. The critical radius size needed for homogenous nucleation of a CO bubble in liquid steel is very high, due to very large interfacial energy between liquid steel and CO gas. Nucleation, therefore, occurs on various materials such as refractory crevices which reduce this interfacial energy. This process is called heterogenous nucleation, and it is responsible for the oxidation of carbon after silicon and manganese. The rate at which carbon is removed by oxidation is controlled during steel making so as to tap the steel when the carbon has decreased to the desired level obviating the need for subsequent carbon content adjustment in the ladle. This practice is termed the “catch carbon” method. Oxygen transfer across the slag-metal and gas-metal interfaces is usually considered to be the rate-controlling step, and CO which forms by carbon oxidation, is insoluble in the slag and evolves into the furnace atmosphere. This evolution resembles a boiling action and is known as the “carbon boil reaction”. The boiling creates turbulence which is important for improving the reaction kinetics and in turn the production rates in the open-hearth and electric arc steel-making processes.

Phosphorus and sulfur are present in pig iron and need to be removed in steel making because these elements, if present in any significant quantities in the steel, result in deterioration of its mechanical properties. The concentration normally tolerated is 0.04% for each of these elements, though in high-quality steels much lower levels are required.

During steel making, preferential oxidation of phosphorus is possible if

$$\Delta G_{P_2O_5,1600\,^\circ C} < \Delta G_{FeO,1600\,^\circ C}$$

Considering the phosphorus oxidation reaction given earlier, and applying the Van't Hoff isotherm for nonequilibrium conditions,

$$\Delta G_{P_2O_5,1600\,^\circ C} < \Delta G_{FeO,1600\,^\circ C} + R\,T \ln \frac{a^2_{P_2O_5}\ (\text{in slag})}{a^2_P\ (\text{in Fe})\ a^5_O\ (\text{in Fe})}$$

it is indicated that ΔG P_2O_5, 1600 °C can be lowered by making the second term on the right-hand side of the above equation more negative. This is achieved, in practice, by lowering a P_2O_5 using a basic slag.

$$4\ CaO + P_2O_5 \rightarrow Ca_3PO_4 + \text{excess CaO}$$

and by increasing CaO (in Fe) through increase of oxygen supply to the metal using iron ore and mill scale additions or oxygen blowing. Another possibility of lowering ΔG P_2O_5 is by temperature control. This is indicated by the ΔG–T relationship for

$$2\ P\ (\text{in Fe}) + 5\ O\ (\text{in Fe}) \rightarrow P_2O_5\ (\text{in slag})$$

$$\Delta G^0 = -683{,}000 + 580\ T\ \text{J mol}^{-1}$$

which shows that decreasing the melt temperature, T, makes ΔG^0 more negative, encouraging forward reaction and phosphorus removal from the metal. However, decrease of melt temperature decreases slag fluidity and effects refining rates. The three conditions conducive to phosphorus removal during steel making are: formation of a basic slag; high oxygen potential in the metal; and low metal temperature.

Sulfur is removed from steel by a method similar to that used for its removal from iron. Calcium is added (in the form of CaO) to form CaS which is stabler than FeS or MnS. Greater control over sulfur elimination is possible under steel-making conditions than in the blast furnace. The conditions favorable for sulfur removal during steel making are: formation of a basic slag, low oxygen potential in the metal and high metal temperature. As regards the second condition, maximum sulfur removal is achieved using a reducing slag in which anthracite or ferrosilicon is used as the reducing agent. Using an oxidizing slag, the metalloids C, Si, Mn, and P in the iron are first oxidized, and then the reducing slag removes sulfur. This technique is most efficiently used in the electric arc steel-making process, and this process offers the highest removal of sulfur. In the oxygen-blown processes, which can achieve only limited sulfur removal, following oxidation of C, Si, Mn and P, the oxygen potential of the metal is lowered by stopping iron ore and mill scale additions or by decreasing the oxygen blowing.

The only common feature for both phosphorus and sulfur removal is a basic slag. Whereas phosphorus removal is favored by a low melt temperature and high oxygen potential, sulfur removal is favored by a high melt temperature and low oxygen potential. Conditions in the steel bath need, therefore, to be varied to ensure maximum removal of each element (normally to levels less than 0.04%). It should however be noted that, irrespective of melt temperature and oxygen potential, a highly basic slag will remove some phosphorus and sulfur. Steel making is so controlled as to ensure lowering in sulfur and phosphorus levels before the carbon has decreased to specified levels.

During steel making, at the earliest possible state, a basic slag is formed using fine powdered lime additions and a relatively high slag temperature to aid dissolution of lime in the slag. This high lime slag readily takes up phosphorus and sulfur. After removal of carbon to the required level, a deoxidant such as ferrosilicon is added to the bath to remove enough oxygen so that further decarburization does not occur. Further additions of deoxidants such as ferrosilicon, ferromanganese, and aluminum may be done after tapping the steel into a ladle, or in a vacuum degassing unit or to the mold during teaming. The amount of deoxidant is determined by the structure required in the solidified steel.

Alloying additions, up to about 4% can be added to the ladle steel without seriously giving rise to complications such as loss of compositional uniformity and undue cooling. Addition to the ladle steel prevents removal of alloying elements as slag. Greater amounts of alloying additions cannot be made to the ladle steel, but must be made to the initial charge. This however results in some loss of alloying addition because they oxidize and enter the slag. This loss can be minimized, to a certain extent, by paying attention to the thermochemical aspects of the process. Considering, for example, the production of a high-chromium alloy steel such as 18Cr-8Ni stainless steel, the key problem is to decrease by oxidation the carbon content to 0.05% without simultaneously oxidizing the expensive chromium. In practice, the required amount of chromium is melted with other charge materials in the electric arc furnace under an oxidizing slag. Chromium oxide forms and collects in the slag

$$2\ \mathrm{Cr\ (in\ Fe)} + 3\ \mathrm{O\ (in\ Fe)} \rightarrow \mathrm{Cr_2O_3\ (in\ slag)}$$

Standard free energy change of this reaction is given by

$$\Delta G^0 = -887{,}400 + 393\ T\ \mathrm{J\ mol^{-1}}$$

The second term indicates that by increasing the melt temperature, e.g., by oxygen lancing, to 1850 °C, ΔG^0 for the reaction becomes more positive and the reverse reaction leading to retention of chromium in steel becomes favorable. Addition of a deoxidant, e.g., silicon as ferrosilicon, which forms an oxide stabler than Cr_2O_3, also leads to further recovery of chromium in steel:

$$2\ \mathrm{Cr_2O_3\ (in\ slag)} + 3\ \mathrm{Si} \rightarrow 4\ \mathrm{Cr\ (in\ Fe)} + 3\ \mathrm{SiO_2\ (in\ slag)}$$

At a constant oxygen potential in the steel, the activities of carbon $a_{\mathrm{C\ (in\ Fe)}}$ and chromium $a_{\mathrm{Cr\ (in\ Fe)}}$ in the steel are related to the partial pressure of CO in the furnace atmosphere, P_{CO} by the following equation

$$a_{\mathrm{C\ (in\ Fe)}} \propto a_{\mathrm{Cr\ (in\ Fe)}}\ P_{\mathrm{CO}}$$

According to this equation, at constant P_{CO}, a decrease in $a_{C\ (in\ Fe)}$ decreased $a_{Cr\ (in\ Fe)}$. However, decreasing P_{CO} will lead to decrease in $a_{C\ (in\ Fe)}$ while $a_{Cr\ (in\ Fe)}$ is maintained, resulting in preferential oxidation of carbon. In practice, this is achieved by first melting the required alloys in the electric arc furnace, transforming the melt to an argon–oxygen decarburization (AOD) converter through the side or bottom of which oxygen and argon are blown. The flushing by the inert gas decreases the partial pressure of CO and encourages carbon to be oxidized while retaining chromium. Lowering P_{CO} at high temperatures makes ΔG_{C-CO} more negative than ΔG Cr–Cr_2O_3. As regards the other alloying elements, e.g., Ni, Co, Mo, Mn, Si, Mg, Al, Ti, Nb, and W, the first three (Ni, Co, Mo) do not present the danger of removal as slag because they form oxides that are much less stable than FeO. The contents of Mn and Si can be controlled as is done with chromium. Mg, Al, Ti, Nb, and W form stable oxides and must be added to the ladle steel after deoxidation.

4.9.1.2 **Electroslag Refining**

Secondary refining processes are those which are used for further purification of a metal after the completion of the primary extraction and refining operations. Electroslag refining (ESR) is a secondary refining process and belongs to the broad category of metal–slag processes of refining. The schematic of the process is shown in Figure 4.28. The raw material for ESR is a solid consumable electrode of the primary metal. A slag bath contained in a water-cooled mold is resistance-heated to beyond its melting temperature by an electric current which flows between the electrode and a cooled baseplate. As the temperature of the molten bath increases past the melting temperature of the primary metal, molten metal droplets fall from the tip of the electrode, through the slag, on to the baseplate where they solidify. As the process continues, the electrode is consumed as it is continuously and slowly fed into the slag bath, while the metal collecting and solidifying on the baseplate slowly builds up as an ingot. The molten slag is thus continuously displaced in the upward direction by the growing ingot. Some solidification takes place where the rising slag meets the cooled mold, and this results in the formation of a continuous shell of solidified slag between the mold and the solidifying ingot. This shell forms a smooth lining to the mold and remains intact through the whole process. When the ingot is removed from the mold, it flakes off and leaves an excellent ingot surface.

In ESR, the refining takes place because of a reaction of the metal and slag in one or more of the following three stages: as the droplet forms at the electrode tip; as the droplet detaches and falls through the slag; and after the metal droplet has collected in a pool at the top of the ingot. By suitably choosing the slag, chemical reactions such as one leading to a near-complete removal of sulfur from the metal, can be encouraged. Nonmetallic inclusions can be removed by physical flotation and by chemical extraction with the slag. Slags may also be so chosen as to ensure the retention of certain elements in the ingot.

There are a number of advantages of ESR, and they all stem from the fact that there is a very large number of degrees of freedom available in the process. This, in turn, is the result of a large number of possible combinations of slag chemistry and flexibility with regard to power requirements and choice of electrode characteristics. In ESR the key requirements of the slag are that its melting temperature should be slightly lower than that of the metal, that it should be electrically conducting, and that it should possess low volatility and appropriate thermal conductivity, thermal capacity, viscosity, and surface tension. The slag being

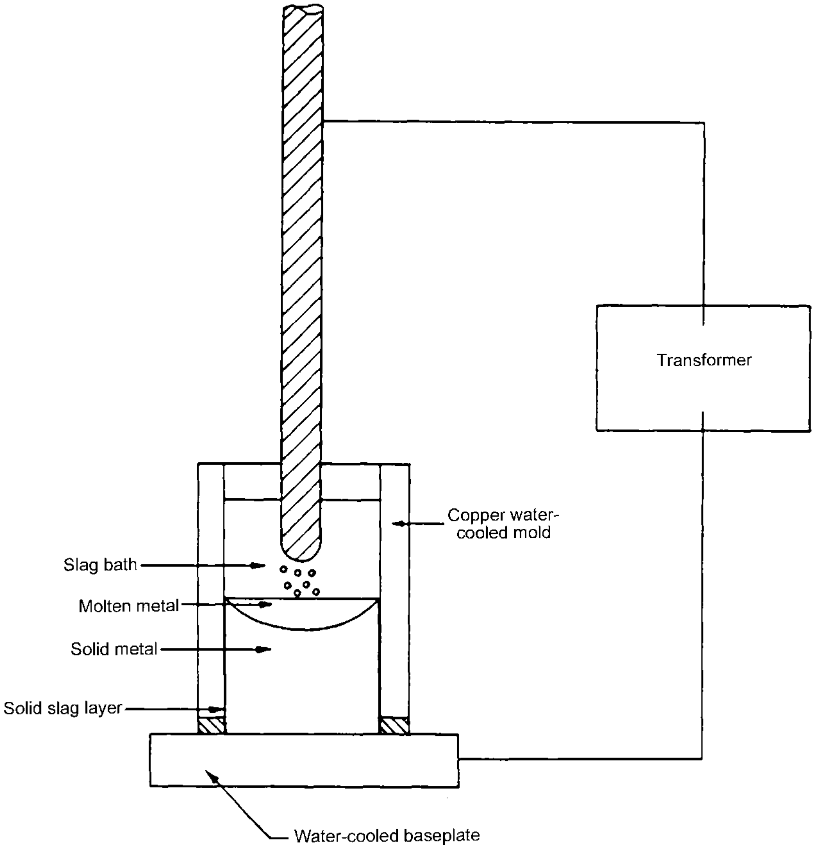


Figure 4.28 Electroslag refining schematic diagram.

the medium in which inclusions in the metal are removed by chemical reaction or dissolution and in which the necessary adjustments of oxygen, sulfur and other elements are achieved, the choice of slag reactivity must be appropriate for the control of the chemical composition of the ingot desired. The slag is usually composed of constituents such as calcium fluoride, lime, magnesia, alumina, and silica. Other useful constituents are magnesium fluoride, barium fluoride, titania, and zirconia. By suitably choosing the amounts of these constituents, many of the slag properties listed above can be suitably altered.

ESR has been applied to nickel-base superalloys, high-speed steels, high-alloy stainless and corrosion-resistant steels, low alloy and carbon steels, and nonferrous metals such as titanium, molybdenum, chromium and copper and their alloys. The purpose of applying ESR to these metals and alloys has been to impart to them one or more of several desirable characteristics which include high ingot surface quality, high yield of solid ingot free from pipes and porosity, homogeneity of composition, improved cleanliness, and good ingot structure suitable for forging and rolling. These characteristics are obtained in ESR ingots irrespective of the identity of the metal or alloy melted. In short, refining is one of the many attractive improvements that a metal or alloy undergoes when it is treated by ESR.

4.9.2
Metal–Metal Processes

A general characteristic of metal–metal processes is that the impurities from one metallic phase are collected in another co-existing metallic phase, and removed. The feasibility of refining by a metal–metal process can usually be assessed on the basis of phase diagrams in which the metal to be refined and the impurity metal are the components. A well-known example of this process is the separation of liquid zinc from lead. Crude zinc, containing iron and lead as impurities, can be refined by melting it and holding the molten bath at 420 to 450 °C in a quiescent state for up to 48 h. Three layers of molten metal separate. The bottom layer contains lead and a small amount of zinc; the middle layer comprises an iron-zinc alloy and the dross ($FeZn_7$); and the top layer contains 99.5% pure zinc, with about 0.5% lead as impurity. In the process only the top layer is drawn out of the reverberatory furnace, and crude zinc is added to make up the charge and continue the refining. Other refining operations which comes under the umbrella of metal–metal processes are described below. They include decoppering of lead, removing bismuth from lead by selective alloying, Parkes process, liquation and precipitation.

Copper is one of the several impurities present in lead produced in the blast furnace. In the multistage process adopted for refining this lead, the first stage is meant for the elimination of copper. According to the copper–lead phase diagram, the solubility of copper in liquid lead decreases drastically with a fall in temperature. On cooling the copper-bearing molten lead to a temperature which is a little above the melting point of lead (327 °C), and on holding the melt at this temperature for a few hours, a solid solution of lead in copper (lead content less than 3 wt-%) separates and floats on the surface of the melt. This material, called the dross, is skimmed off. Usually the melt is held at a somewhat higher temperature (~480 °C) so that the improved fluidity of the melt permits a faster transport of the dross from the bulk to the surface. The term “dross” is used to describe the solid phases comprising the impurity elements which, in the course of refining processes, collect and float on top of the molten metal. The dross usually entrains considerable amounts of the metal which is being refined.

The copper remaining in lead after the above operation is removed by matte formation. Finely divided sulfur is added to molten lead at temperatures slightly above its melting point, and the melt is stirred continuously. Copper sulfide forms and floats on the surface, leaving the bullion substantially free of copper (less than 0.005%). The standard free energies of formation of cuprous sulfide and lead sulfide are about the same; the observed separation must, therefore, be due to kinetic factors or to the influence of certain minor impurities that are present in the lead.

Bismuth is a common impurity in lead. It does not separate like copper by simple cooling and, being nobler than lead, cannot be eliminated by fire refining. However, it can be recovered by selective alloying. When a calcium–magnesium alloy is stirred into bismuth-bearing molten lead, calcium and magnesium form solid intermetallic compounds (Ca_3Bi_2 and Mg_3Bi_2) with bismuth; these can be skimmed off as the dross. This dross is also a major source of bismuth. Chlorination is used to remove calcium, leaving behind crude bismuth.

Among the impurities usually found in lead, silver is recovered for its intrinsic value. Desilvering of lead is carried out after it has been freed of copper, tin, arsenic, antimony, and bismuth. The process used is known as the Parkes process. It makes use of the facts that while silver forms intermetallic compounds with melting points above 600 °C with zinc, the system lead–silver shows a positive deviation from Raoult's law. A consequence of these is that when a lead-zinc-silver melt (formed by adding zinc to the impure molten lead to be refined) is slowly cooled to a temperature just above the melting point of lead, a zinc rich solid phase, containing nearly all the silver impurity and a small amount of entrained lead, separates from the liquid lead phase. This solid phase can be skimmed off. Zinc is first separated from this phase by distillation at about 1200 °C in a simple retort. The oxygen pressure in the retort is kept very low by using charcoal. Silver is recovered from the silver-rich lead phase remaining after distillation by selective oxidation of lead. The cupellation process pertinent to this operation has already been described. Some amount (~1%) of zinc remains in the desilvered lead and is removed by a vacuum treatment.

Reduced tin invariably contains iron (~1%) as an undesirable impurity; arsenic, antimony and bismuth are the other impurities usually present. A scheme for the separation of iron has been worked out on the basis of the iron–tin phase diagram. It is seen that an intermetallic phase, $FeSn_2$ (which decomposes incongruently at 496 °C), occurs in equilibrium with liquid tin, and that the solubility of iron in liquid tin at temperatures near the melting point of tin (232 °C) is very small. Thus, on cooling the impure tin melt to temperatures a little above its melting point, the intermetallic ($FeSn_2$) would separate as a solid phase, leaving behind a melt containing less than 0.0196% iron. In practice, the melt is cooled in a ladle and the solid intermetallic phase is allowed to settle. The process may also be carried out by slowly heating the impure solid tin to above its melting point in a reverberatory furnace with a sloping hearth, whereby pure liquid tin drains off. This process is known as liquation.

As in the refining of lead with respect to copper, tin can be refined with respect to the residual iron by adding sulfur and forming an iron matte. Arsenic and antimony are eliminated from tin by adding aluminum to the tin melt at about 550 °C. A dross consisting of aluminum arsenide (AlAs; melting point: 1720 °C) and aluminum antimonide (AlSb; melting point: 1070 °C) is formed and is separated. Similarly, bismuth is removed from molten tin by adding calcium and magnesium at 380 °C. This addition results in the formation of a dross comprising several compounds (Bi_2Mg_5, Bi_2Ca_3 and Bi_3Ca).

The rare earth metals are produced by the calcium reduction of rare earth fluorides in tantalum crucibles. The metals thus obtained are purified by melting in vacuum, once again in tantalum crucibles. Tantalum dissolves in the rare earth metals and the solubility increases with temperature. During vacuum melting in tantalum crucibles, a considerable amount of tantalum is, therefore, introduced into the refined metal. This contamination has to be removed. The tantalum removal technique is based on the variation of its solubility in the rare earth metals as a function of temperature. While at 1800 °C, lanthanum, cerium, praseodymium, and neodymium dissolve large amounts of tantalum, the solubility of tantalum in these metals at their melting points is low. The tantalum taken up at high temperatures can be separated, and the residual tantalum content brought down to less than 20 ppm, by holding at temperatures just above the melting points of these metals to allow tantalum to precipitate and settle at the bottom of the crucible. These tantalum dendrites are latter removed from the solidified metals by machining.

4.9.3
Metal–Gas Processes

Refining by metal–gas processes is by far the most widely used technique which has been applied extensively in the purification of the common as well as the less common, metals. The basic philosophy of these processes may be summarized as follows. If an impurity in a metal has a high vapor pressure which is significantly greater than that of the metal itself, the impurity may be distilled off, leaving behind the pure metal. The impurity, in the pure form, may be a solid or a gas at room temperature. On the other hand, if the metal itself is more volatile than the impurity, then the metal can be distilled off and collected in a pure form, leaving behind the impurity. The impurity, in this case, may be a less volatile metal or a nonmetal or a volatile element which has formed a very stable nonvolatile compound. Sometimes, a nonvolatile impurity is eliminated by the formation of a volatile compound. Refining by metal–gas processes is greatly facilitated by the use of vacuum. The use of vacuum makes it possible to carry out refining processes which could not be carried out at the atmospheric pressure. The temperature required for refining may also be brought down considerably by the use of vacuum. As the vapor pressure and vaporization behavior of metals and alloys play a decisive role in the refining of metals in many instances, these two aspects are covered first.

The variation in the vapor pressure of a pure metal with temperature is usually approximated by the relationship

$$\log P = \frac{A}{T} + B$$

where P is the equilibrium vapor pressure of the metal at the temperature T, and A and B are constants. A plot of this equation, such as the one given in Figure 4.29, is normally used for a quick comparison of the vapor pressures of different metals. The values of the con-

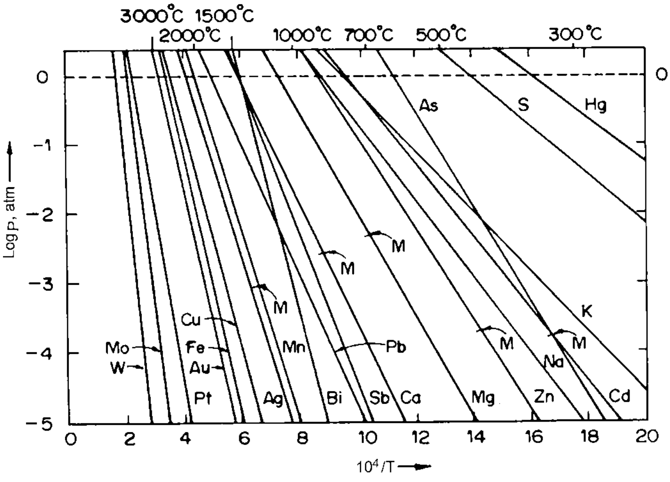


Figure 4.29 Vapour pressure of common metals, M = melting point.

stants A and B change when the condensed phase undergoes a phase transformation. For example, A and B will have one set of values in the vapor pressure equation for the solid metal, and they will have another set of values in the vapor pressure equation for the liquid metal. For an accurate calculation of the vapor pressure of a metal at any temperature, expressions of the form

$$\log P = A \cdot T^{-1} + B \log T + C\,D + D$$

are used, A, B, C and D being constants.

The vapor pressure of a metal in an alloy, P_i, is related to the vapor pressure of the pure metal, P, by the equation

$$P_i = a_i\,P_i^0 = \gamma_i\,X_i\,P_i^0$$

where a_i is the activity of the metal in the alloy, γ_i is its activity coefficient, and X_i is its mole fraction. Even though the vapor pressures of the metal and of the impurity element in their pure states may be of the same order of magnitude, in the case of a solution the vapor pressure of the impurity (over the solution) may be very much less than that of the pure metal if γ_i is very low. If the impurity forms an ideal solution, then $\gamma_i = 1$, but even than P_i will be less than P because X_i is less than unity. When the impurity shows a positive deviation from the ideal behavior, $\gamma_i > 1$ and the decrease in vapor pressure over the solution due to X_i being less than unity is partly offset. In any case, purification with respect to an impurity element by simple distillation can be feasible only if its vapor pressure in the pure state is substantially higher than that of the main metal (i.e., the metal to be purified). When this difference is small, good purification can be achieved only by fractional distillation.

4.9.3.1 **Fractional Distillation**

The most well known and also very efficient technique for separation of metals on the basis of their volatility is fractional distillation. This belongs to the class of metal–gas processes with the gas being, in effect, the metal vapor itself. Fractional distillation is conducted in a continuous, countercurrent fashion, with both distillation and condensation repeated many times. An effective mass and heat exchange occurs by the movement of the liquid (condensed vapor) stream against the rising stream of vapors. A temperature gradient is maintained in the distillation column, the top being at a lower temperature as compared with the bottom. The liquid feed is introduced at the middle of the column. As it descends, its temperature rises and evaporation occurs; the vapor rising towards the top is enriched in the more volatile component. Simultaneously, the descending liquid becomes enriched in the less-volatile component. Apart from the countercurrent flow, the positioning of a number of perforated plates or trays in the column ensures an intimate contact between the ascending vapors and the descending liquid. Ultimately, the less-volatile component is recovered as a liquid at the bottom of the column while the more-volatile component is obtained as a vapor at the top of the column. In situations where the separation is rather difficult to achieve, several columns can be connected in series. Fractional distillation is applicable to several common and less common metals. The refining of zinc, lead, calcium and the rare earths is described below.

The impurities that occur in the crude zinc produced by the carbothermic reduction of zinc oxide are 2–3% lead, 0.3–0.4% cadmium, and 0.05% iron. Zinc is more volatile than lead by several orders of magnitude whereas cadmium is an order of magnitude more volatile than zinc. Crude zinc is refined by fractional distillation and the process is implemented in two distillation columns. In the first column, which operates at a higher temperature (top: 800 °C, middle: 900 °C and bottom: 1200 °C), zinc and cadmium are volatilized together, leaving behind a liquid zinc phase which contains the impurities lead and iron. In the second column, which is operated at a lower temperature (top: 650 °C, middle: 750 °C and bottom: 900 °C), pure cadmium vapor is removed from the top and 99.99% pure zinc is collected at the bottom. This method, apart from being important with regard to the refinement of zinc, is also one of the most important methods of obtaining cadmium metal.

In relation to the separation of cadmium from zinc by volatilization, it is worth noting that the ratio P_{Cd}/P_{Zn} increases with decreasing temperature (from 5.09 at 850 °C to 7.30 at 650 °C and 12.69 at 450 °C). The liquid solution of zinc and cadmium exhibits a regular solution behavior and, therefore, the activity coefficient of cadmium dissolved in liquid zinc increases with decreasing temperature. Both these features suggest that the elimination of cadmium from zinc is more efficient at relatively lower temperatures. This is reflected in the choice of the temperatures in the second column.

The problem of the separation of zinc and lead from each other is encountered not only in the refining of zinc but also in the refining of lead. When lead is subjected to refining by the Parkes process, a certain amount of zinc, which is not insignificant, is introduced into the refined lead bullion. This zinc impurity may be removed by distillation.

In the separation of zinc from lead by distillation, the large difference in the vapor pressures of these two metals is made use of. The heats of vaporization of the pure liquid metals are 125.52 kJ (g atom^{-1}) for zinc and 192.46 kJ (g atom^{-1}) for lead. The difference between the vapor pressures is less pronounced at higher temperatures than at lower temperatures. A low-temperature operation may, therefore, lead to a better separation. However, since the absolute value of the vapor pressure of the pure metal decreases with decreasing temperature, the rate of evaporation is low at low temperatures. The choice is thus between a high-temperature operation, where the absolute values of the vapor pressures are high but the difference in the vapor pressures is low, and a low-temperature operation where the advantages of a large difference between the vapor pressures in offset by their lower absolute values. A compromise has, therefore, to be made by choosing an intermediate temperature. The boiling point of zinc is 907 °C. At this temperature the vapor pressure of zinc is 760 torr and that of lead is 0.2 torr. The separation of zinc from lead is also favored by the high activity coefficient of zinc in liquid lead. In a dilute solution of zinc in lead the value of γ_{Zn} is about 10. Using these values, the limit to which zinc can be removed from lead can be calculated in the following manner.

At the constant boiling composition, the vapor pressures of zinc and lead over the solution are equal, i.e.,

$$P_{Zn} = P_{Pb}$$

Now,

$$a_{Zn}\ P^0_{Zn} = a_{Pb}\ P^0_{Pb} \propto P_{Pb}0 \quad (\text{as } a\text{Pb} \propto 1)$$

so that,

$$X_{\mathrm{Zn}} = \frac{P^0_{\mathrm{Pb}}}{P^0_{\mathrm{Zn}}} \cdot \frac{1}{\gamma_{\mathrm{Zn}}} = 0 \cdot \frac{2}{760} \cdot \frac{1}{10} = 2.62 \cdot 10^{-5}$$

Thus the zinc content in the bullion lead can be brought down to 26 ppm (i.e., 26 parts in 106 parts) when the distillation is conducted at about 900 °C.

4.9.3.2 **Pyrovacuum Processes for Reactive and Refractory Metals**

When a metal contains impurities it is not very often that a method involving the removal of the pure metal, leaving the impurity as a residue, is chosen for its purification. Whenever possible, it is always advantageous to use a refining method where the impurity is removed, leaving the pure metal as a “residue”. The selective removal of impurities from as-reduced metals is an essential step in the flowsheet for the preparation of reactive and refractory metals because these metals, in the preceding processing steps, avidly pick up a variety of impurities. A metallic impurity is found in an as-reduced metal either because the impurity metal coexisted with the main metal in the ore, or because it was the reductant used or it occurred as an impurity in the reductant. Usually only impurities of the second category are found in as-reduced metals because ore processing and separation operations ensure that a pure compound intermediate containing very little (if any) of other metallic impurities is used for reduction. Impurities which are used as reductants and persist in the reduced metal are aluminum, calcium, and magnesium. The important nonmetallic impurities found in as-reduced reactive and refractory metals are carbon, nitrogen, oxygen and hydrogen. Carbon contamination occurs when it is used as the reductant. Nitrogen and oxygen are picked up from the gaseous atmosphere in contact with the metal during reduction. Oxygen may also be derived from the compound reduced. Hydrogen may sometimes be deliberately introduced. While the metallic impurities particularly affect the corrosion resistance and certain special properties (e.g., electronic properties) of the metal, the nonmetallic interstitial impurities (these occupy the interstices in the crystal lattice of the metal) greatly affect its mechanical properties. Purification with respect to both these types of impurities is, therefore, required. Techniques based on reactions and processes occurring at high temperatures and under high vacuum have proved to be particularly useful in refining reactive and refractory metals. Pyrovacuum treatments essentially consist of the heating of the metal at high temperatures (up to or above its melting point) under a high vacuum, resulting in refining and/or consolidation. During pyrovacuum treatments a variety of processes that contribute to the removal of the impurities from the metal occur. The principal mechanisms are simple distillation and degassing, and certain complex deoxidation reactions. The actual process or processes that come into play in the removal of a given impurity depend on its concentration in the metal, as well as on the relative concentrations of the various other impurity elements present. These aspects are covered in the survey of impurity removal mechanisms presented below.

When the boiling points of metallic impurities are much lower than the boiling point of the main metal, they can simply be distilled away in most cases. The rate and the extent of the removal by distillation of these impurity elements depend upon their partial pressures over the main metal/melt. As an example, let the feasibility of distilling magnesium and magnesium chloride from titanium and calcium from the rare earths be considered. In the first case, at 900 °C, the pertinent vapor pressure values are $P_i = 4 \cdot 10^{-11}$ torr, $P_{\mathrm{Mg}} = 105$ torr and P_{MgCl_2} = 7 torr. These values immediately suggest that it should indeed be possible to distill away magnesium and magnesium chloride from titanium. The situation is similar when zirconium is considered in the place of titanium. Rare earth metals produced by the calciothermic reduction of the corresponding fluorides have calcium as the main metallic impurity. These metals can be vacuum melted in a tantalum crucible to eliminate this calcium. Neodymium, for example, is associated with about 2% calcium as impurity. It is vacuum melted at –1100 °C to eliminate calcium. The elimination of calcium occurs because at 1100 °C, $P_{Nd} = 7 \cdot 10^{-4}$ torr and P_{Ca} = 38 torr.

Next, let the example of vanadium, which, in the as-reduced condition, may contain a variety of impurities (including aluminum, calcium, chromium, copper, iron, molybdenum, nickel, lead, titanium, and zinc) be considered. Vanadium melts at 1910 °C, and at this temperature it is considerably less volatile than many of the impurity metals present in it. The vapor pressure of pure vanadium at this temperature is 0.02 torr, whereas those of the impurity elements in their pure states are the following: aluminum: 22 torr; calcium: ~ 1 atm, chromium: 6 torr; copper: 23 torr; iron: 2 torr; molybdenum: $6 \cdot 10^{-6}$ torr; nickel: 1 torr; lead: ~ 1 torr; titanium: 0.1 torr; and zinc: ~ 1 atm. However, since most of these impurities form a dilute solution in vanadium, their actual partial pressures over vanadium are considerably lower than the values indicated. Taking this into account, the vaporization rate, m_A, of an element A (the evaporating species) can be approximated by the following free evaporation equation (Langmuir equation):

$$m_A = 44.32\, S_A\, \gamma_A\, X_A\, P_A^0 \sqrt{\frac{M_A}{T}}\ \text{g cm}^{-2}\ \text{s}^{-1}$$

where S_A is the vaporization coefficient, usually taken as equal to 1, P is the vapor pressure of the pure element A in atmospheres, M_A and T are the molecular weight of A in grams and the absolute temperature respectively, γ_A is the activity coefficient of the element A in solution and X_A is its mole fraction. Even though P is large, a low value of X_A and possibly of γ_A would seriously limit the vaporization rate. So, during the removal of these impurities by vacuum distillation from vanadium, a considerable amount of vanadium may also be lost by vaporization. The species evaporating from a melt in vacuum can be identified by mass spectrometric analysis. In the case of vanadium, the vapor has been found to contain the following metal species: aluminum, iron, titanium, manganese, vanadium, chromium, calcium, and copper.

The free evaporation equation given above refers to impurity removal from a solid or a liquid solution. When the residual impurity has not formed a solution, its activity remains unity and the Langmuir equation becomes

$$m_A = 44.32\, S_A\, P_A^0 \sqrt{\frac{M_A}{T}}\ \text{g cm}^{-2}\ \text{s}^{-1}$$

The free evaporation situation is obtained only in the case of vaporization in a high vacuum.

Among the nonmetallic impurities present in reactive and refractory metals, those of the greatest consequence are the gaseous elements – hydrogen, nitrogen, and oxygen. Their removal from the metal is termed degassing, and this is one of the most important processes occurring during pyrovacuum treatments.

A reaction of hydrogen, nitrogen, and oxygen with the metal can be represented by

$$\frac{1}{2}A_2\,(g) = [A]_M$$

where A stands for hydrogen, nitrogen or oxygen, and $[A]_M$ for the solution of the gas in the metal. If these gases have to be removed from the solid or the liquid metal at a useful rate by pyrovacuum treatments, the equilibrium pressure of the gaseous species over the solution at the degassing temperature should be high. In other words, the following conditions should be satisfied:

$$P\,(A_2) >> P_M \quad \text{and} \quad P(A_2) >> 10^{-3}\ \text{torr}$$

The first condition must be satisfied for purification to occur. The second condition ensures that degassing occurs at a reasonably fast rate. Hydrogen, nitrogen, and oxygen behave differently with respect to the above requirements in different metals.

Among the three important gaseous impurities listed earlier, hydrogen is the easiest to remove. The equilibrium pressure of hydrogen over metal–hydrogen solutions is usually quite high even at very low concentrations at moderate temperatures (< 1000 °C). As a consequence, hydrogen can usually be eliminated almost completely during pyrovacuum treatments. In fact, the feasibility of a near-complete removal has led to the development of the hydriding–comminution–dehydriding procedure for the preparation of refractory metal powders. The bulk metal is exposed to 1 atm pressure of pure hydrogen at about 500 °C, leading to the formation of the metal hydride which is brittle. The brittle hydride is ground to a fine powder. The powder is then exposed to vacuum at about 900 °C, whereby almost all the hydrogen is removed, leaving the metal in a pure powder form. This is one of the methods of converting pure tantalum ingots to capacitor-grade tantalum powder.

Many metals take up considerable amounts of nitrogen in solid solution. The engassing and degassing of nitrogen in respect of metals is represented by the equilibrium

$$\frac{1}{2}N_2 = [N]_M$$

which is governed by the Sievert's law relationship

$$[\%\,V] = K\,(P_{N_2})^{\frac{1}{2}}$$

The behavior of nitrogen in niobium is illustrated in Figure 4.30 as an example. The extent to which nitrogen can be removed from the metal at a given temperature can be readily calculated from such diagrams. Alternatively, the relationship linking the equilibrium pressure, the nitrogen content in niobium and the temperature can expressed as

$$\ln\,(\%\ \text{N}) - \frac{1}{2} \in P_{\text{N}_2} = \frac{23950}{T} - 12.0$$

and the required information can be obtained.

Unlike the case of hydrogen, the removal of nitrogen from metals can be effected only at very high temperatures and very low pressures. To achieve a residual nitrogen concentra-

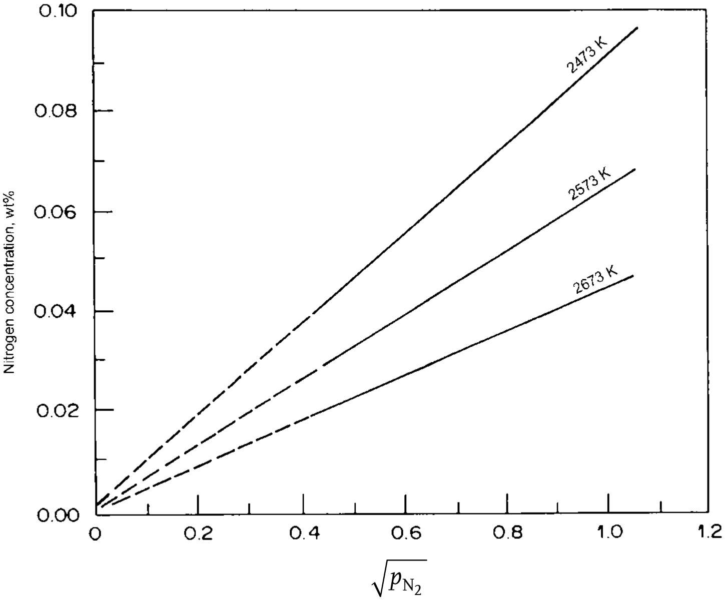


Figure 4.30 Equilibrium nitrogen pressure over niobium solid solution at high temperatures.

tion of less than 100 ppm in niobium, the pressure in the system should be less than 10^{-5} torr at 2000 °C, $5 \cdot 10^{-5}$ torr at 2200 °C, and $3 \cdot 10^{-4}$ torr at 2400 °C. These temperature and pressure levels are achievable in modern high-temperature vacuum furnaces such as the vacuum induction furnace and the electron beam melting furnace, and nitrogen elimination from metals such as niobium is possible in practice. Tantalum exhibits essentially the same behavior as niobium. The situation regarding vanadium and the Group IV metals, titanium, zirconium and hafnium, is rather discouraging. In the case of these metals, even at high concentrations of nitrogen in solid solution, the equilibrium nitrogen pressure is several orders of magnitude lower than the partial pressure of the metal itself. Pyrovacuum treatments are thus not effective for nitrogen removal from these metals. The only way to obtain them in a nitrogen-lean condition is to avoid the pick up of nitrogen by the metals at any stage of their production. For this, all the relevant processes should be carried out in a protective atmosphere (e.g., vacuum or an inert gas atmosphere).

The refractory metals, titanium, zirconium, hafnium, vanadium, niobium, and tantalum, form extensive solid solutions with oxygen. Unlike the corresponding metal–nitrogen solid solutions in which, in the cases of some of the above metals, rather high equilibrium nitrogen pressures are exhibited at high temperatures, in all the metal–oxygen solid solutions, the equilibrium oxygen pressures are very low. However, the concentration of oxygen in some of these metals decreases significantly when they are heated at high temperatures under high vacuum. This has been rationalized in terms of the formation and subsequent evaporation of certain complex oxide species. The general mechanism of oxygen removal from these metals, explains this behavior. Provided that oxygen is the only impurity in the metal, a volatile suboxide of the metal forms and evaporates, resulting thereby in oxygen removal from the metal. This reaction is expressed by the relationship

$$[O]_M + M = (MO)$$

where $[O]_M$ and (MO) represent the dissolved oxygen and the gaseous suboxide, respectively. The situation represented by this relationship is known as sacrificial deoxidation, since it involves the sacrifice of at least one atom of the metal for every atom of the oxygen removed.

All the refractory metals of Group IV and Group V form volatile suboxides at high temperatures. Just as the stability of carbon monoxide increases with an increase in temperature, these oxides also become more stable at higher temperatures. The vapor pressures of these suboxides can be calculated from the relationship:

$$p_{MO\,(g)} = a_0 \exp\left(-\Delta G^0_{MO\,(g)} / R\,T\right)$$

where a_O is the activity of oxygen in the metal and $\Delta G_{O\,(g)}$ is the standard free energy of formation of MO (g) at temperature T. Substituting these values of the activity and the free energy of formation, the following expressions can be obtained:

$$P_{TiO} = 1.6 \cdot 10^9 \exp(-63710/T)\, C_O$$

$$P_{ZrO} = 2.8 \cdot 10^8 \exp(-76890/T)\, C_O$$

$$P_{HfO} = 4.1 \cdot 10^8 \exp(-72610/T)\, C_O$$

$$P_{VO} = 1.6 \cdot 10^{12} \exp(-75090/T)\, C_O$$

$$P_{NbO} = 1.06 \cdot 10^8 \exp(-56970/T)\, C_O$$

$$P_{TaO} = 5.08 \cdot 10^8 \exp(-63050/T)\, C_O$$

where P is in torr and C_O is the oxygen concentration. These equations are valid for C_O values between O and 5 at-% oxygen: the approximate range within which Henry's law is obeyed.

The metals which form volatile suboxides would not undergo purification by sacrificial deoxidation unless they satisfy certain other criteria. The most important criterion pertains to the value of the quantity, R, which is defined as follows:

$$R = \frac{[C_O / C_M]_{vapor}}{[C_O / C_M]_{metal}}$$

where C_O and C_M are respectively the concentrations (in at-%) of oxygen and of the metal in the phases indicated by the subscripts. The R value essentially gives the relative concentration of oxygen in the vapor phase with respect to that in the condensed phase. At a given temperature, the R value changes with changes in the oxygen content. However, if the monoxide and the monoatomic metal vapor are the only important species in the vapor phase, and if oxygen is in the concentration range in which it obeys Henry's law, the factor R approaches a limiting value, independent of composition, at any temperature. The magnitude of this limiting value of R determines the feasibility of sacrificial deoxidation. If this value is greater than unity, then the metal can be purified by sacrificial deoxidation. Metal loss occurs during sacrificial deoxidation because the suboxide vapor contains the metal and there is also a simultaneous vaporization of the metal. The total metal loss that would occur during refining by sacrificial deoxidation is given, by the following expression:

$$\text{Loss of metal (\%)} = [200\ X_O\ /\ (2 - X_O)] \cdot \mathrm{M_{MO}}\ /\ \mathrm{M_M}R] + C^i_O\ X_O$$

where $X_O = (C^i_O - C_O / C_i)$; C^i_O and C_O represent the initial and the final oxygen contents (in at-%) respectively, and M is the molecular weight of the species indicated by as the subscripts: MO for the suboxide and M for the metal. This equation indicates that the loss of metal during refining by sacrificial deoxidation is inversely proportional to the *R* value. The limiting *R* values for all the Group IV and Group V refractory metals are given in Table 4.4. With reference to these values, and also taking into account the vapor pressures of the individual metal suboxides and metals, the sacrificial deoxidation tendency of each of the refractory metals is discussed below.

The vapor pressure of titanium monoxide is much higher than that of zirconium monoxide and hafnium monoxide. However, sacrificial deoxidation is not feasible for titanium because of the relatively high vapor pressure of titanium metal itself. The limiting *R* value for the titanium–oxygen system is equal to 0.1.

When zirconium is saturated with oxygen in solid solution, the vapor pressure of zirconium monoxide is 50 to 100 times higher than that of pure zirconium. The *R* value of zirconium remains at 3 to 4 up to 5 at-% oxygen, and then decreases to the limiting value of 1 at 2 at-% oxygen. This indicates that oxygen removal by sacrificial deoxidation is possible in zirconium pyrovacuum treatments only until the oxygen concentration decreases to about 2 at-%. At still lower oxygen concentrations, the *P* values are very low at the melting point of zirconium compared to the minimum pressure that can be attained in conventional vacuum furnaces.

The vapor pressure of hafnium monoxide is about 5 times higher than that of zirconium monoxide, corresponding to the same temperature and the same oxygen content in the metals. This is due to the difference in the activities of oxygen in these two metals. The limiting *R* value in the hafnium–oxygen system is 27, which indicates a good possibility of refining this metal by sacrificial deoxidation.

The feasibility of sacrificial deoxidation of vanadium is similar to that of hafnium. The vapor pressures of the metal and of the monoxide over a metal–oxygen solid solution containing upto 1 at-% oxygen are given in Figure 4.85. The *R* value of 6.3 for vanadium indicates the possibility of limited deoxidation. This aspect is discussed further after outlining the characteristics of the niobium–oxygen and tantalum–oxygen systems.

Table 4.4 *R* values for refractory metal–oxygen alloys.

Metal	*Temperature, K*	*R values at composition (in at-% O)*					*Limiting R value*
		20	*10*	*5*	*2*	*1*	
Ti	2000	0.2	0.2	0.1	0.1	0.1	0.1
Zr	2500	4.0	4.5	3.0	1.0	1.0	1.0
Hf	2500	4.0	7.0	11.0	17.0	21.0	27.0
V	2200	2.0	3.5	5.0	5.5	6.0	6.3
Nb	2800	4.0	9.0	19.0	50.0	100.0	$2.5 \cdot 10^3$
Ta	3300	4.0	9.0	29.0	50.0	100.0	$3.0 \cdot 10^3$

The vapor pressures of the monoxides in the niobium-oxygen and tantalum–oxygen systems are much higher as compared to those of the pure metals, even at oxygen concentrations as low as 0.1 at-%. The *R* values are, therefore, very large. This implies that these metals are very amenable to sacrificial deoxidation.

It is interesting to compare the effect of *R* values on the metal loss that occurs during the sacrificial deoxidation of various metals. For example, it can be seen from the expression for metal loss that for a decrease in the oxygen content from 1 at-% to 0.1 at-%, the accompanying loss of vanadium ($R = 6.3$) is about 36%, whereas only about 1% of niobium ($R = 2.5 \cdot 10^3$) would be lost under similar circumstances. Thus it appears that sacrificial deoxidation, though effective, cannot by itself be a useful method for the removal of oxygen from hafnium, vanadium or zirconium because it brings about a considerable reduction in the metal yield. In the case of niobium and tantalum, this technique is quite suitable for oxygen removal without undue metal loss. However, sacrificial deoxidation is more useful in practical processes when it operates along with carbon deoxidation.

When a metal contains both carbon and oxygen, as is invariably the case with metals prepared by carbothermic reduction under vacuum, deoxidation occurs by the following two processes at high temperatures and low pressures:

$$[\mathrm{O}]_\mathrm{M} + [\mathrm{C}]_\mathrm{M} = (\mathrm{CO})$$

$$[\mathrm{O}]_\mathrm{M} + [\mathrm{M}]_\mathrm{M} = (\mathrm{MO})$$

The process of oxygen removal from the metal-oxygen solid solution via the formation of carbon monoxide is known as carbon deoxidation. The terms $[\mathrm{O}]_\mathrm{M}$ and $[\mathrm{C}]_\mathrm{M}$ denote the oxygen and the carbon dissolved in the metal to be refined, for example, vanadium. The extent to which carbon deoxidation can occur in a metal under given conditions of temperature and pressure can be estimated by using the following relationship:

$$P_\mathrm{CO} = a_\mathrm{C}\, a_\mathrm{O} \exp(-\Delta G^0_\mathrm{CO} / R\,T)$$

where P_co is the equilibrium carbon monoxide pressure over the metal, a_C and a_O are respectively the activities of carbon and of oxygen in the metal, *T* refers to the temperature (in degrees K) to which the metal has been heated, ΔG^0_CO is the standard free energy of formation of carbon monoxide at temperature *T* and *R* is the gas constant. The relationship can be alternatively expressed as:

$$P_\mathrm{CO} = \gamma_\mathrm{C}\, \gamma_\mathrm{O}\, X_\mathrm{C}\, X_\mathrm{O} \exp(-\Delta G^0_\mathrm{CO} / R\,T)$$

where γ_C and γ_O and X_C and X_O are respectively the activity coefficients and the atom fractions of carbon and oxygen in the metal. When the carbon and the oxygen contents in the metal are very low, this relationship can be expressed as:

$$P_\mathrm{CO} = k_1 \cdot X_\mathrm{C}\, X_\mathrm{O} \exp(-\Delta G^0_\mathrm{CO} / R\,T)$$

where k_1 is a constant. The quantity $X_\mathrm{C}\, X_\mathrm{O}$ satisfies the relationship

$$X_\mathrm{C}\, X_\mathrm{O} = k_2\, W_\mathrm{C}\, W_\mathrm{O}$$

where k_2 is a constant and W_C and W_O are the concentrations of carbon and of oxygen, expressed in weight percentage. It therefore follows that at a given temperature and pres-

Table 4.5 Estimated carbon deoxidation tendencies of Group V metals at 2000 °C and 0.01 Pa.

Metal	*W_C W_O (wt-% C · wt-% O)*
V	$4.6 \cdot 10^{-3}$
Nb	$4.6 \cdot 10^{-4}$
Ta	$1.3 \cdot 10^{-3}$

sure (i.e., P_{CO}), under equilibrium conditions, the concentration product (which can be expressed as W_C W_O) assumes a constant value, irrespective of the actual concentrations of carbon and of oxygen in the metal. This constant value can be taken as a measure of the carbon deoxidation tendency of the metal. The carbon deoxidation tendencies of the Group V refractory metals are listed in Table 4.5. Carbon deoxidation is particularly relevant for the refining of the Group V refractory metals because carbothermic reduction is an important process for their preparation. The concentration product values have been obtained by using measured or estimated values of the activity coefficients of carbon and of oxygen in these metals. A low value of the product indicates a high deoxidation tendency because it corresponds to one of the three possibilities: a low carbon concentration and a high oxygen concentration; a high carbon concentration and a low oxygen concentration; or a low carbon concentration and a low oxygen concentration. As shown in the table, among the Group V metals, vanadium has the least tendency to deoxidize by carbon monoxide evolution. This means that, at a given temperature and a given value of P_{CO}, the residual carbon and/or oxygen contents in vanadium will be compared more to niobium and tantalum. In other words, the removal of carbon and/or oxygen from vanadium will occur to a much lesser extent than in the cases of niobium or tantalum. The effect of carbon deoxidation can be quite complicated if there is a significant loss of the metal by vaporization. The requirement of a low vapor pressure is also better satisfied by niobium and tantalum than by vanadium.

In the refining of the Group V metals (which are more accurately represented as metal–carbon–oxygen alloys), carbon deoxidation is not the only method by which oxygen is removed, because sacrificial deoxidation also occurs simultaneously. The relative extents to which each of these two deoxidation modes contributes to the overall removal of oxygen can be assessed by calculating the ratio of the vapor pressures of carbon monoxide and the metal monoxide over the M–C–O alloy. The value of this ratio for vanadium at 2000 K is given by the expression

$$\frac{P_{CO}}{P_{VO}} = (6 \cdot 10^{-2})\, C_C$$

where C_C stands for the carbon concentration in the metal. The values of this ratio for niobium and tantalum at 2300 K are given by

$$\frac{P_{CO}}{P_{NbO}} = (4.5 \cdot 10^{2})\, C_C$$

and

$$\frac{P_{\mathrm{CO}}}{P_{\mathrm{TaO}}} = (5 \cdot 10^2)\, C_{\mathrm{C}}$$

In the case of vanadium, the suboxide, vanadium monoxide, would be more volatile than carbon monoxide except at very high carbon concentrations in the metal. The removal of the residual oxygen from this metal by carbon deoxidation is, therefore, difficult. In the case of niobium and tantalum, the partial pressure of carbon monoxide is higher than that of niobium monoxide or tantalum monoxide, even when the residual carbon concentration in the metal is as low as 200 ppm. It may therefore be expected that practically all the oxygen would be removed by evaporation of carbon monoxide without any metal loss from niobium and tantalum metals containing both oxygen and carbon.

This expectation is consistent with the approach adopted in deoxidation practice, where the metals containing carbon and oxygen are treated at temperatures of about 2000 °C under high vacuum. It must, however, be mentioned here that the oxygen to carbon mole ratio in such metals should be more than unity in order to ensure that no residual carbon is left behind at the end of deoxidation.

The aluminum reduction of a refractory metal oxide invariably yields a metal product containing significant amounts of residual aluminum and oxygen, represented usually as a metal–aluminum–oxygen alloy. When the metal contains aluminum in addition to oxygen, a number of reactions can occur during pyrovacuum treatments. These are:

$$[\mathrm{O}]_{\mathrm{M}} + \mathrm{M} = (\mathrm{MO})$$

$$\mathrm{M} = (\mathrm{M})$$

$$[\mathrm{O}]_{\mathrm{M}} + 2\,[\mathrm{Al}]_{\mathrm{M}} = (\mathrm{Al_2O})$$

$$[\mathrm{Al}]_{\mathrm{M}} = (\mathrm{Al})$$

where $[\mathrm{O}]_{\mathrm{M}}$ and $[\mathrm{Al}]_{\mathrm{M}}$ represent solutions of oxygen and of aluminum respectively in the metal and (M), (MO), (Al_2O) and (Al) represent the vapor of the metal, of the metal monoxide, of aluminum suboxide and of aluminum metal respectively. The first two reactions represent the sacrificial deoxidation and the vaporization of the metal. The third reaction represents a deoxidation process involving the formation and the evaporation of aluminum suboxide. This process is termed aluminum deoxidation. The last reaction signifies the distillation of aluminum metal itself. Aluminum deoxidation can be considered as a technique for the removal of oxygen from a metal without incurring metal losses by vaporization. Therefore, conditions must be so chosen that most of the oxygen in the M–Al–O alloy is eliminated as (Al_2O). The feasibility of such a process can be assessed by considering the relative partial pressures of (MO) and (Al_2O) as a function of the aluminum and the oxygen contents of the alloy. The vapor pressures of (MO) and (Al_2O) are given by the relationships

$$P_{(\mathrm{MO})} = a_{\mathrm{O}}\, a_{\mathrm{M}} \exp\left(\Delta G^0_{\mathrm{MO}}\right)/R\,T)$$

and

$$P_{(\mathrm{Al_2O})} = a_{\mathrm{O}}\, a^2_{\mathrm{Al}} \exp\left(\Delta G^0_{(\mathrm{Al_2O})}\right)/R\,T)$$

Here, P represents the partial pressure, a the activity, and ΔG^0 the standard free energy of formation of the species indicated by the subscripts. The activity of oxygen in both above the relationships is the same. Hence, it follows that

$$\frac{P_{(Al_2O)}\, a_M}{P_{(MO)}\, a_{Al}^2} = \exp\,[(\Delta G_{MO}^0 - \Delta G_{Al_2O}^0/R\,T)]$$

Substituting the standard free energy values at 2200 K for vanadium and for niobium, one obtains

$$\frac{P_{(Al_2O)}\, a_V}{P_{(MO)}\, a_{Al}^2} = 9.02 \cdot 10^3$$

and

$$\frac{P_{(Al_2O)}\, a_{Nb}}{P_{(NbO)}\, a_{Al}^2} = 2.8 \cdot 10^6$$

These relationships indicate the extents to which oxygen can be removed from M–Al–O alloys by aluminum deoxidation instead of by sacrificial deoxidation. The adjustable parameter in the above equations is the activity of aluminum; a high value of the activity ensures that the partial pressure of (Al_2O) remains greater than the partial pressure of the metal monoxide (MO) irrespective of the oxygen content. However, the oxygen content influences aluminum deoxidation in a different way. The activity of aluminum in the alloy can decrease, during pyrovacuum treatments, due to the vaporization of aluminum as the metal vapor, (Al). This process is counterproductive as far as deoxidation is concerned, but its occurrence cannot be prevented completely. However, it can be ensured that more aluminum is lost during deoxidation as (Al_2O) than as (Al) by making use of the equation

$$\frac{P_{(Al_2O)}}{P_{(Al)}} = \frac{a_O\, a_{Al}}{P_{Al}^0} \exp\,[(\Delta G_{(Al_2O)}^0/R\,T)]$$

which is obtained from the relationships

$$P_{(Al_2O)} = a_O\, a_{Al}^2 \exp\,[(\Delta G_{(Al_2O)}^2/R\,T)]$$

and

$$P_{(Al)} = a_{Al}\, P_{(Al)}^0$$

where P_l is the vapor pressure of pure aluminum. Substituting the values corresponding to 2200 K, one obtains, for vanadium,

$$\frac{P_{(Al_2O)}}{P_{(Al)}} = (7.7 \cdot 10^{-1})\, C_O\, a_{Al}$$

and for niobium,

$$\frac{P_{(\mathrm{Al_2O})}}{P_{(\mathrm{Al})}} = (4.9 \cdot 10^1)\, C_{\mathrm{O}}\, a_{\mathrm{Al}}$$

where C_O represents the concentration of oxygen in the metal. According to the above relations, by providing a large excess of aluminum for a given quantity of oxygen, the partial pressure of (Al_2O) can be maintained higher than the partial pressure of (Al) during deoxidation. A decrease in the oxygen content, however, causes a decrease in the ratio of (Al_2O) to (Al) vapor pressures. It is to be noted that the situation is different for vanadium and for niobium. It is possible to refine vanadium by aluminum deoxidation, but in order to achieve this effectively, a large concentration of aluminum must be maintained in vanadium until deoxidation proceeds to completion. This is necessary to ensure that aluminum continues to be removed as (Al_2O) rather than as (Al) until the oxygen content is brought down to the desired level. The excess aluminum remaining in the metal after the completion of oxygen removal can be eliminated by distilling it off as aluminum vapor. This is one of the major attractions of aluminum deoxidation. In the case of niobium, both the ratios $P_{(\mathrm{Al_2O})}/P_{(\mathrm{MO})}$ and $P_{(\mathrm{Al_2O})}/P_{(\mathrm{AI})}$ have high values, even at very low aluminum concentrations. Thus it is not necessary to have excess residual aluminum, and purer thermits (less aluminum) can be prepared (when required) without jeopardizing the chances of adequate purification.

Carbon is much less volatile than the refractory metals. If such a metal contains only carbon as an impurity, then the carbon concentration in the metal would increase during pyrovacuum treatments because more metal than carbon would be lost by vaporization. The only method by which carbon can be removed from vanadium during a pyrovacuum treatment is carbon deoxidation. By ensuring the occurrence of a higher amount of residual oxygen in the metal, most of the carbon can be removed as carbon monoxide because at a given temperature and ambient pressure only the concentration product, $W_C\, W_O$, has a constant value and not the individual carbon or oxygen contents. When the concentration of oxygen is kept high, the concentration of carbon decreases so that their product has a constant value. The excess oxygen remaining in vanadium can be removed by sacrificial deoxidation.

The implementation of pyrovacuum processes for the refining of refractory and reactive metals is usually effected in devices that operate under high-temperature and high-vacuum conditions. In this context, electron beam melting can be taken as a good example. Its major application is in the production of ingots of reactive and refractory metals. An electron beam melting furnace can be considered to be made up of two main components: the electron gun, and the vacuum chamber. The use of vacuum inhibits the scattering of electrons by gas molecules and also provides a suitable environment for purification to take place. A water-cooled copper mold, which acts as a container for the purpose of metal melting and casting, is placed in the vacuum chamber, which is quite often called the melting chamber. The electron gun is used for the generation of the electron beam. The most common method of generating electrons is by thermionic emission, using tungsten or tantalum filaments; these metals have low work function values and high melting temperatures, which is why they are well suited for this application. The emitted electrons are accelerated by a high voltage and are focused by magnetic and/or electrostatic fields. Most of the kinetic energy of the electrons is converted into thermal energy when they hit the metal target (i.e., the metal to be melted). Only a very small fraction is used up in the generation of

X-rays. The maximum accelerating voltage used in a melting furnace is usually limited to 40 to 50 kV. At still higher voltages, although the kinetic energy of the electrons increases, the generation of characteristic X-rays also occurs, with the attendant problems pertaining to the exposure of the operating personnel. The electron guns used are made in different configurations. It may be added that for industrial use only transverse guns and circular tube guns (with arrangements for beam deflection, a separately pumped electron beam-generating chamber and an independent smelting chamber) are suitable.

4.9.3.3 **Chemical Transport Processes**

In a process described earlier on the purification of metals, it was observed that a metal can be separated from impurities by distilling it off, leaving behind an impurity-enriched residue. To accomplish this, the vapor pressure of the metal must be high; however, not many metals that need purification are that volatile. There are many reactions in which a metal in an impure state can be selectively converted to a volatile compound and can thus be separated from the impurities; however, in such situations, getting the metal back from the compound may be difficult. If this problem can be solved simply, without resorting to conventional reduction procedures, the “distillation” of metals could become more versatile. The thermodynamic properties of certain metals and compounds are such that, by a chemical reaction the metal can be converted to a volatile compound which can be transported in the gas phase to a different location in the reactor and then converted back to the metal by a simple reversal of the original chemical reaction; this can usually be brought about just by a change of temperature. These processes are known as catalytic distillation reactions or as chemical transport reactions. The most important examples of such reactions are

$$\mathrm{Ni\ (s) + 4\ CO\ (g) = NiCO_4\ (g)}$$

$$\mathrm{2\ Al\ (l) + AlCl_3\ (g) = 3\ AlCl\ (g)}$$

$$\mathrm{Ti\ (s) + 2\ I_2\ (g)\ O\ TiI_4\ (g)}$$

The operating principles in these reactions become clear when the variation in the corresponding free energies with temperature is considered. The pertinent data are given in Figure 4.31. In reactions (1) and (3) there is a decrease in the number of gas molecules during the reaction and thus the entropy of the reaction is negative. In these cases, therefore, the free energy increases with temperature. In reaction (2), there is an increase in the number of gas molecules so that the entropy of the reaction is positive; this implies that the free energy decreases with increasing temperature. The equilibrium constants of all these reactions may thus change drastically with temperature and this fact is exploited in devising processes for refining nickel, aluminum, and titanium. The Mond process for nickel, subchloride process for aluminum, and iodide refining process for titanium are described below.

According to the free energy change associated with the pertinent reaction, nickel will form nickel tetracarbonyl at low temperatures, and this carbonyl will become unstable and revert back to nickel and carbon monoxide at moderate temperatures. The Mond process for refining nickel is based on these features. In this process, impure nickel is exposed to carbon monoxide gas at 50 °C, whereby volatile nickel tetracarbonyl ($Ni(CO)_4$) forms. No impurity present in the crude nickel reacts with carbon monoxide. Since formation of the

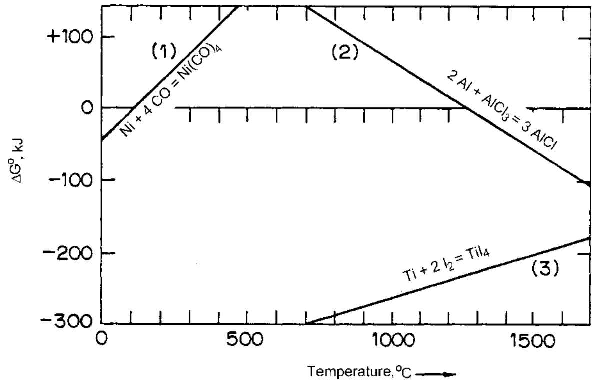


Figure 4.31 Standard free energies of some typical transport reactions.

tetracarbonyl is exothermic, it is necessary to prevent the temperature from rising by water-cooling once the reaction starts. The carbonyl is passed on to another reactor in which it comes into contact with pure metallic nickel seeds at 230 °C. The carbonyl dissociates, depositing pure nickel on the seeds. Carbon monoxide is recycled to react with crude nickel.

In this process use is made of an endothermic reaction between the aluminum (in the vapor form) in the crude feed material and gaseous aluminum trichloride

$$AlCl_3 + 2\ Al = 3\ AlCl$$

This reaction is carried out at about 1200 °C. The gaseous aluminum subchloride (AlCl) product is cooled in a separate zone to about 700 °C, to bring about decomposition of the gas into aluminum and aluminum trichloride. The aluminum is obtained in a molten, substantially pure state. The aluminum trichloride is recirculated for the production of additional amounts of the subchloride.

This process has been tried out on a pilot plant scale mainly as a means of producing pure aluminum from an impure aluminum–iron (20–45%)–silicon (2–20%) alloy, obtained by the carbothermic reduction of bauxite in an electric furnace.

Iodide refining is one of the important methods for the purification of titanium, zirconium, and hafnium. The method is also known as the Van Arkel–de Boer process, and is based on the reversibility of a reaction between a metal and iodine. Formation of the metal iodide occurs at a relatively low temperature, and decomposition of the iodide occurs at a much higher temperature. Even though the free energy change associated with the reaction remains negative in the temperature range considered, the iodide decomposes at higher temperatures because of the low pressure maintained in the reaction vessel and dissociation of the iodine molecule to monatomic iodine. The reactor used for this process is so designed that the iodine liberated during the decomposition reaction travels back and reacts with the crude metal, forming fresh tetraiodide. Iodine thus functions as a vehicle for carrying the pure metal. The process is often represented as

$$M\ (\text{crude}) + 2\ I_2 \xrightarrow{T_1} MI_4 \xrightarrow{T_2} M\ (\text{pure}) + 2\ I_2;\quad T_2 >> T_1$$

Purification occurs in this process mainly due to three reasons: (i) some of the impurities (such as oxygen, nitrogen, and carbon) present as oxide, nitride, and carbide in the feed material do not react with iodine at the temperature T_1; (ii) even if some of the impurities form their iodides at the lower temperature, they are too stable to decompose at the higher temperature, T_2; (iii) some of the impurities, which are sufficiently volatile, do not remain in the high temperature zone, even if their iodine compounds are thermally decomposed.

The process is carried out in the equipment shown schematically in Figure 4.32. This consists essentially of an evacuated vessel along the axis of which a starting metal wire or filament is aligned and electrically heated to a temperature above the temperature of decomposition of the metal iodide. This wire is made from a high-purity stock of the same metal which is being purified by iodide refining. The crude metal is stacked inside the vessel, in the annular space between the vessel wall and a concentric screen. The iodine required for driving the process is held in a separate refrigerated container and is sublimated into the evacuated vessel. When the vessel is externally heated to the desired temperature, T, pertinent to the reaction of the crude metal with iodine, and the central filament is heated to incandescence (T_2) the metal iodide vapors which form by the reaction between the iodine introduced into the vessel and the metal values in the crude feed, de-

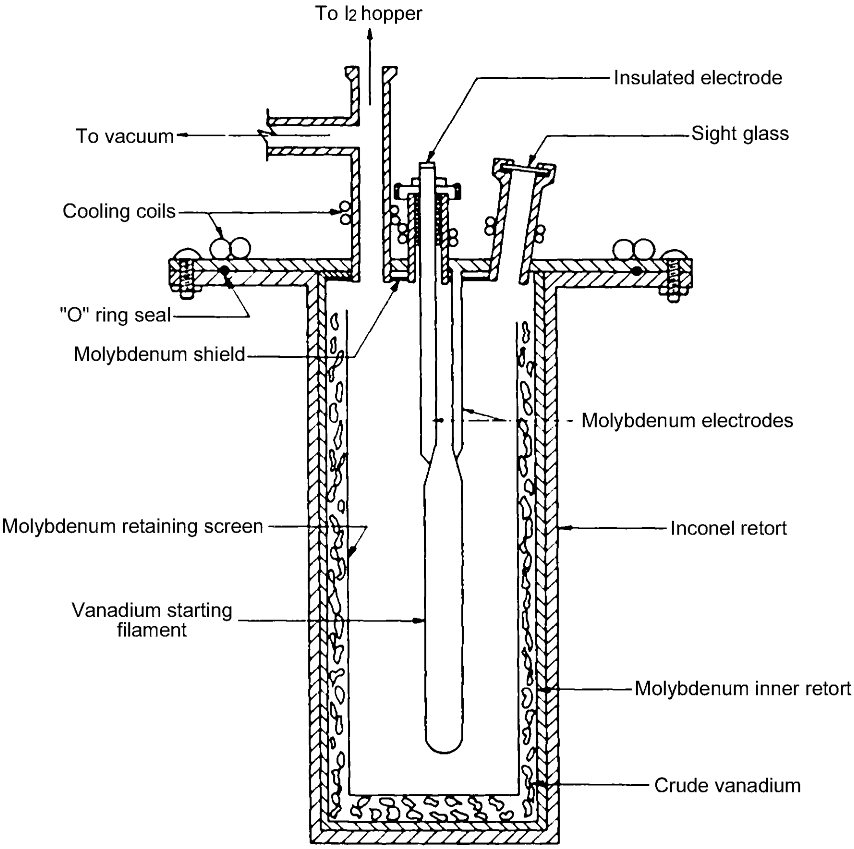


Figure 4.32 Vanadium crystal bar apparatus.

compose on the surface of the filament, resulting in the deposition of the pure metal on the filament. The liberated iodine vapors travel back for further reaction with the crude metal. The cycle continues until the required amount of metal is refined into crystal bars. In a laboratory-scale investigation, starting from crude metals of 99 to 99.5% purity, crystal bars of zirconium, titanium, and hafnium of better than 99.95% purity could be consistently prepared in kilogram quantities. In the cases of all these metals, the filament temperature was kept at about 1400 °C. The values of the lower temperature (T_1) used were: 250 °C for zirconium, 325 °C for titanium, and 750 °C for hafnium. Though very effective, iodide refining as a process is characterized by a small throughput and is suitable for meeting requirements of small quantities of high-purity metal. In addition to the Group IV metals mentioned, the method has also been used for obtaining high purity chromium and vanadium.

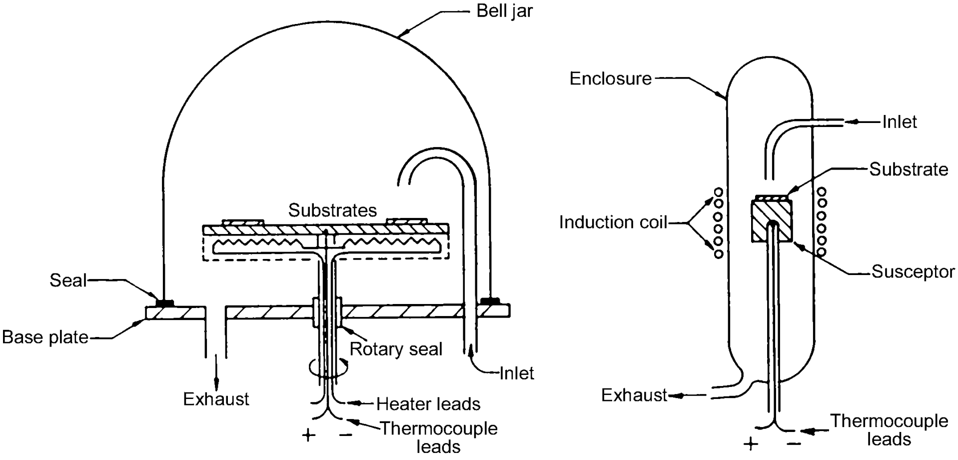
In the iodide refining process described above, several conditions are implicit. Van Arkel has listed them as: (i) the metals form volatile iodides; (ii) the melting points of the metals are higher than the dissociation temperatures of the corresponding iodides; (iii) the volatile iodides are formed at manageable temperatures; (iv) the iodides easily decompose at elevated temperatures; and (v) the vapor pressures of the metals are very low at the decomposition temperatures of the iodides.

Iodide refining, while belonging to the group of processes known as chemical transport processes, is also a good example of the class of processes known as chemical vapor deposition (CVD).

The CVD process generally involves the deposition of a solid material on to a substrate surface as a result of chemical reactions in the gas phase. A variety of gaseous or volatilized chemical compounds can react, when they contact a heated surface, to form a solid product and gaseous by-products. Among the useful CVD reactants or precursors are halides (fluorides, chlorides, bromides, and iodides), carbonyls, hydrides, hydrocarbons, and organometallic compounds. These have the characteristic of being reasonably stable in the gas phase until subjected to temperatures close to that of the substrate. The reactions they then undergo are either thermal decomposition or reduction. The products of CVD may be coatings or massive deposits and include a variety of metals, alloys, intermetallics, metalloids, carbides, oxides, nitrides, silicides, and borides. Among metals copper, beryllium, aluminum, titanium, zirconium, hafnium, thorium, germanium, tin, lead, vanadium, niobium, tantalum, arsenic, bismuth, chromium, molybdenum, rhenium, iron, cobalt, nickel, ruthenium, rhodium, osmium, iridium, and platinum have all been deposited by CVD.

The CVD precursors are generally corrosive, hygroscopic and air sensitive or toxic. Thus CVD processing is usually carried out in closed systems. However, in many cases, deposition can be accomplished at atmospheric pressure in relatively simple systems. Schematic drawings of two experimental CVD reactors are shown in Figure 4.33.

The progress of CVD reactions is governed by thermodynamics. Starting from data on the free energies of formation of the compounds of interest in CVD, which are generally available as a function of temperature, it is possible to check the feasibility of many potential CVD reactions and to estimate the preferred ranges of operating conditions. The usual procedure is to identify all the possible reaction products of a given starting mixture, relate them by stoichiometry, and minimize the total free energy of the systems The pertinent calculations are generally carried out in a computer.



(a) Resistively heated plate (b) Inductively heated pedestal

Figure 4.33 Experimental CVD reactors.

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5
Hydrometallurgy

5.1
Introduction

Hydrometallurgy is concerned with the methods of production of metals and compounds, most often from minerals but sometimes also from substances produced by another process. In order to achieve this result, at least some of the reactions occurring during the sequence of process operations are implemented in an aquatic medium. It is superfluous to record in this chapter any descriptive note to account for all the glamors and highlights of hydrometallurgy of today. The vast related literature, together with its explosive rapidity of growth over the years, many international meetings held to date, the wide and varied materials published on scientific and technical matters pertaining to hydrometallurgy (including proceedings of meetings) and the vast amount of ongoing research worldwide underline the enormity of interest in hydrometallurgy.

Hydrometallurgy is by no means a competitor to pyrometallurgy; indeed, pyrometallurgical and hydrometallurgical processes are very often combined in practice to exploit the best features of both. Examples of such combination are detailed in this chapter, the general trend of modern extractive metallurgy often being found to utilize integrated pyrometallurgical and hydrometallurgical approaches. In addition, the inclusion of electrometallurgy underlines the multidisciplinary character of hydrometallurgy.

A generalized flow diagram illustrating many of the key hydrometallurgical processes as they usually occur in sequence is shown in Figure 5.1. In almost all hydro-based process flowsheets, the starting resource invariably passes through a primary or initial preparation, which may involve crushing or grinding to desired size (or perhaps thermal treatment) before being subjected to dissolution, this constitutes the major component among the front-end operations of the flowsheet. The leach liquor is often processed directly for product recovery, and this constitutes the back-end operation. Typically, however, the leaching step is neither selective nor perfect and many undesirable constituents of the source are passed into solution along with the desirable components. Therefore, a mandatory purification process follows leaching, and this often leads to a concomitant concentration of the solution. In this way, the volume of the solution to be handled in subsequent steps is reduced. Included in the back-end operation are the different precipitation processes that lead in essence to recovery of metal values from the leached solutions. This chapter deals with the front- and back-end unit operations into which the entire subject of hydrometallurgy

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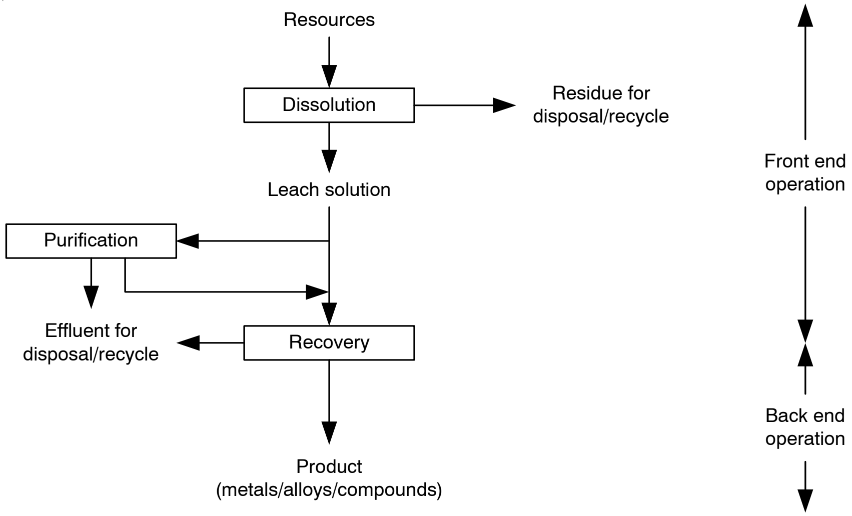


Figure 5.1 Basic unit processes in hydrometallurgy.

has essentially been woven. As an analogous example, mention may be made of the nuclear fuel cycle which is also grouped into front and back-end operations. The front-end operations incorporate uranium mining and milling, nuclear fuel fabrication, and finally loading of the fabricated fuel into the nuclear reactor, whilst the back-end operations involve the nuclear fuel as it is discharged from the reactor. Reprocessing of the spent nuclear fuel is a major back-end operation and in any country the nuclear fuel cycle represents an important scenario in that country's nuclear energy generation program. Spent nuclear fuel processing, which is a major back-end operation that permits the recovery of plutonium (another important nuclear fuel) is not used in the generation policies of some countries. However, others have opted for nuclear fuel reprocessing, and the back-end operations are very much in place. The amount of radioactive waste generated is considerably greater with reprocessing involvement than without; thus, the disposal of radioactive waste is a phenomenally large activity.

The separation of solids from liquids forms an important part of almost all front-end and back-end operations in hydrometallurgy. This is due to several reasons, including removal of the gangue or unleached fraction from the leached liquor; the need for clarified liquors for ion exchange, solvent extraction, precipitation or other appropriate processing; and the post-precipitation or post-crystallization recovery of valuable solids. Solid–liquid separation is influenced by many factors such as the concentration of the suspended solids; the particle size distribution; the composition; the strength and clarity of the leach liquor; and the methods of precipitation used. Some important points of the common methods of solid-liquid separation have been dealt with in Chapter 2.

Hydrometallurgy should not be construed as being devoid of any misgivings and so be given a clean chit, as hydrometallurgical processes have pollution problems of their own. Although problems associated with emissions of gases may appear minimal, plant effluents in both liquid and solid states may have grievous consequences unless adequately dealt with. Commonly, a number of technical solutions are available, although capital expenditure and running costs may be large and offset the gains derived from hydrometallurgy. In the ultimate analysis, the high cost factor may, list among the various deterrents of hydrometallurgy applications in any given case.

There is extensive scope for significant developments in hydrometallurgical processes. Indeed, the rising cost of energy consumption in comminution processes places the operations involving the separation of metals from the ore by leaching in a more advantageous position than ever before. The elegant technique of leaching in place has been used successfully on a number of small deposits, and is poised to attract increasing attention and applications in the near future. Although hydrometallurgical techniques such as leaching in place and dump leaching have many advantages, they also have certain limitations such as slow kinetics and low recoveries. Some types of bacteria have been established to assist leaching, and this approach has become popular in biohydrometallurgy and shows great promise for its further growth and development. If more microorganisms that act specifically on chosen minerals can be identified and grown, then the future impact of biohydrometallurgy will be profound.

At present, leaching is one of the most essential front-end operations in hydrometallurgy, but in future hydrometallurgical processes for secondary metal recovery, treatment of low grade and complex ores, and research and development into high-temperature and high-pressure processes will become increasingly important.

In order to treat complex ores that are difficult to process effectively, there will be a constant need for alternative procedures, and processing by hydrometallurgical techniques may become the common means to deal with these specific materials due to the prohibitively high energy requirements for smelting processes. There are also many choices available for further treatment of the metal salts that hydroprocesses yield. Apart from aqueous solutions of the metals, organic solutions have an extraordinary standing in hydrometallurgy, and, this brings to light the modern separation techniques of solvent extraction and ion exchange, which have unequivocally introduced a new dimension into the hydrometallurgical processing of metals. It is likely that these two efficient and powerful hydrometallurgical techniques will be used increasingly for solution concentration and purification in the future.

It would not be out of place at this point to draw a reference to solvent extraction-one of the important unit operations in hydrometallurgy. An example of this process is that of tea preparation, and this is repeated (in principle) when the nuclear industry purifies uranium and separates the components in spent nuclear fuel, when the petroleum industry removes aromatic hydrocarbons from crude oil, and when the food industry extracts edible oil from oil cake. Whilst solvent extraction is by no means a new process, the increasing sophistication and variety that is being introduced into the field represents major advances in the process. Making tea or any type of brew is the oldest and simplest example of solvent extraction. In general, solvent extraction uses a liquid solvent to separate and recover a substance from a mixture. When a tea is prepared, the hot water serves as the solvent and extracts the tannin, caffeine and other flavor substances from the tea leaves in order to produce a refreshing beverage. When the mixture containing the substances is solid (e.g., the tea leaves), the process is termed solid–liquid extraction, and treating oil cake to recover edible oil and extracting sugar from sugar-beet are some examples of this. Leaching, that is, treating minerals with water or acid solutions to dissolve metals, is also an example of solid-liquid extraction. However, solid-liquid extraction is often only the primary stage of recovering a substance, simply a way of making it dissolve. A more important process is that of liquid–liquid extraction, this being equally popularly known by the term, solvent extraction.

Other than solvent extraction and ion exchange, many more examples which have had similar impacts in hydrometallurgy may be cited, and the advent of pressure hydrometallurgy is indeed in this list. This technique has permitted the industrial realization of hydrometallurgical processes that cannot be achieved commercially by simply operating at elevated temperatures which are restricted to atmospheric boiling points and pressures of one atmosphere. It is known that several high-pressure hydrometallurgical processes are now in commercial operation, and extensive research effort has been made worldwide into the use of autoclave processes for the extraction of metals. The Bayer process, which was introduced around the turn of the 20th century to the recover alumina from bauxite, was the first pressure-hydrometallurgical extractive process to be developed on an industrial scale.

In hydrometallurgical processes, one important consideration is the possibility to recover residual reagents. The leach solutions, when turned barren, invariably contain some metal values, though if unrecovered, these are lost. The reagents used for leaching should, wherever possible, be recycled or regenerated. Raffinates generated from solvent extraction systems may contain residual extractants which, if not recovered, can add significantly to the processing costs.

5.2
Leaching

The dissolution process of the soluble ingredient(s) contained in a solid material by a solvent is the most popular and accepted definition given to leaching. In its most common form, leaching carries out the task of dissolving the value mineral(s) of an ore or concentrate, generally by an aqueous solution of the lixiviating agent. The term, leaching, may be extended to include the dissolution of secondary substances (scrap, residues and wastes). In an ideal situation, leaching gives rise to two fractions: one is the worthless material that is largely free from value minerals and is mostly destined for dumping, whilst the other is the metal-laden solution that is invariably advanced for further processing. Under some special circumstances leaching is gainfully applied to remove impurities which are otherwise not removable from a concentrate, and in these cases it becomes a means of upgrading the concentrate. The terminology that best describes this particular case is hydrometallurgical beneficiation. The general conditions likely to favor dissolution may be derived from the thermodynamic data presented in the form of Pourbaix diagrams. Developed originally for corrosion studies, these diagrams have gained widespread acceptance in various disciplines concerned with the thermodynamics of aqueous systems, including, of course geology, where its widespread use and applications abound. These diagrams are as useful to hydrometallurgists as are, for example, Ellingham diagrams to pyrometallurgists.

Thermodynamic considerations are important in leaching in that they provide basic guidance in choosing the combination of reagents and their concentrations so as to obtain favorable free energy changes associated with any proposed reaction. Kinetic considerations are of far greater importance than thermodynamics in hydrometallurgy. On account of the relatively low temperatures of operations used, hydrometallurgical processes are generally associated with low reaction rates; this is unlike pyrometallurgy, where high temperatures are used and the reactions are rapid. Thus, in hydrometallurgy larger reactor volumes are needed for a given throughput of metal and the process streams, being large in volume, are generally lean in metal concentration. A considerable amount of metal remains locked up in these process streams, and this adds to the inventory and cost of the process. The slower a process, the larger is the material hold up within the plant and the larger is the size of the plant. A hydrometallurgical plant is thus generally larger than one based on a pyrometallurgical process.

The two independent variables, the pH and the potential, are of major concern in the construction of Pourbaix diagrams. The method and details of construction of a potential-pH diagram are available in many standard texts; hence, this presentation focuses attention on the conditions and the principles behind leaching in order to determine the likely products of leaching reactions.

To sum up the entire foregoing matter, and paying particular attention to the thermodynamic aspects of leaching, it may in the first instance be recorded that the thermodynamic data be applied towards the prediction of general conditions likely to favor the dissolution of a mineral in a given aqueous medium. It has further been noted the appropriate thermodynamic are presented in the form of potential–pH diagrams, the well-known Pourbaix diagrams. The metal–water systems resulting in the simplest diagrams, and are produced from data at 25 °C.

The creation of boundaries in a potential–pH diagram results in the formation of areas, in each of which a particular species is thermodynamically stable. For example, in area X of the zinc–water systems (Figure 5.2 A), Zn^{2+} ions are thermodynamically stable species. This implies that if any other zinc species in the system is exposed to conditions of potential and pH to correspond to this area, it will tend to be converted to the Zn^{2+} ionic species. This clearly means that zinc present in the system is in either a metallic or oxide state, and so would tend to pass into solution.

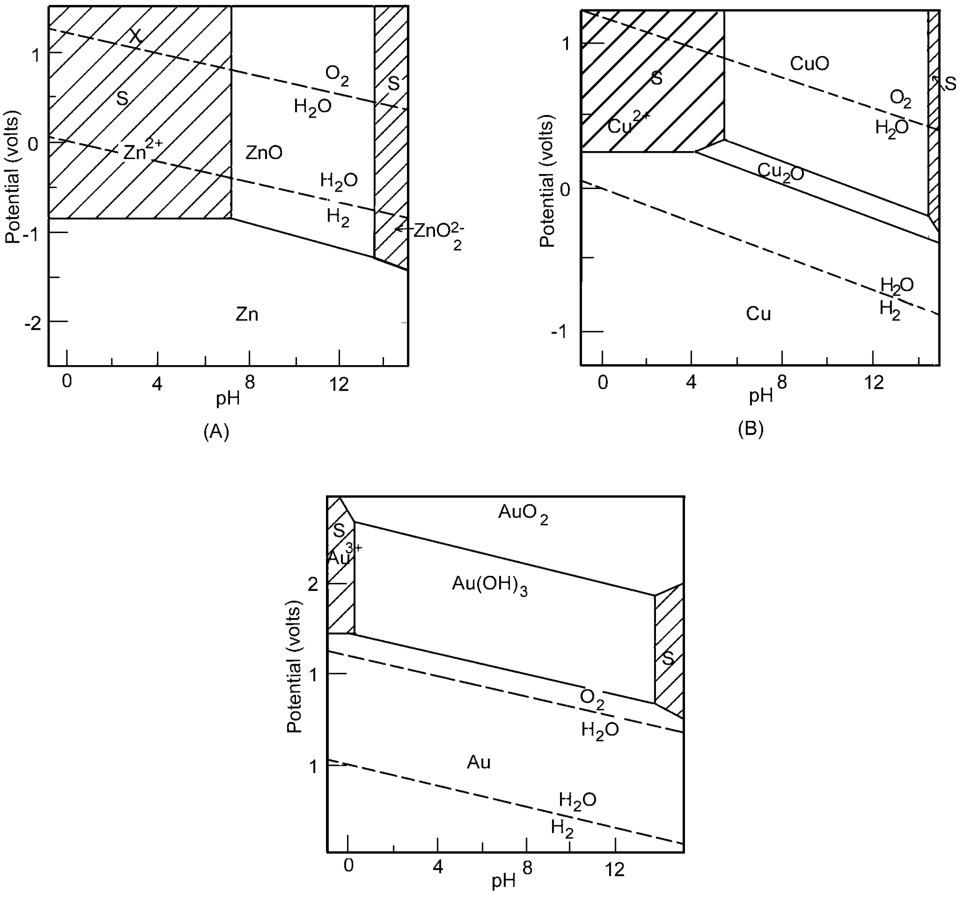
Two lines on the Pourbaix diagrams (Figure 5.2) deserve reference. These are the sloping dashed lines, and they represent the stability limits for water; they are essentially the domain of thermodynamic stability of water superimposed on potential–pH diagrams. At the upper line, oxidation of water goes according to:

$$H_2O = 2\ H^+ + 0.5\ O_2 + 2\ e^-$$

(with oxygen at 1 atm pressure), while at the lower line, reduction of water goes according to:

$$2\ H_2O + 2\ e^- = 2\ OH^- + H_2$$

(with hydrogen at 1 atm). Thermodynamically, then, the cardinal portion of the diagram lies between these lines and the potential in a solution would be: at the upper line provided it were in equilibrium with pure oxygen at one atmosphere; at the lower line provided the solution were in equilibrium with pure hydrogen at this pressure. The decomposition of water occurs with evolution of hydrogen at potentials more negative (more reducing) than the lower boundary. The decomposition of water, on the other hand, occurs with evolution



(A)

(B)

(C)

Figure 5.2 Potential (volts) – pH diagrams for metal (M)-water system (for metal (M) ion activity of 10^{-3} mol · kg^{-1} at 25 °C: (A) M = Zn, (B) M = copper, (C) M = gold. S stands for solubilization.

of oxygen at potentials more positive (more oxidizing) than the upper boundary. It will be useful now to go over to the three examples taken in Figure 5.2.

The first example relates dissolution of zinc metal. This pertains to Figure 5.2 (A) which provides the answer for conditions of dissolution. The dissolution of a metal is electrochemical in nature and, as the potential for the dissolution of zinc is more negative than both of the above reactions, each of them can serve as a cathodic process to support the anodic dissolution of zinc. It may be seen from Figure 5.2 (A) that solubilization is favorably disposed below a pH of about 6.9 with the production of Zn^{2+} ions (cations) and beyond a pH of about 13.4 with the formation ZnO_2^{2-} ions (anions).

The next two examples pertain to Figures 5.2 (B) and (C) which are respectively for copper and gold. In the case of Figure 5.2 (B) for copper, the

$$Cu^{2+} + 2\ e \leftrightarrows Cu$$

equilibrium has a more positive potential than the hydrogen evolution reaction, but it is more negative than that of the oxygen reduction reaction. It, therefore, so happens that copper is not solubilized by means of hydrogen evolution as the cathodic process. It is, for this reason, referred to as a noble metal and its solubilization is only accomplished by the reduction of oxygen or some other oxidizing agent. This will take place most favorably in acidic conditions at a pH of less than 6 or so. As regards gold, it is known to be a more noble metal than copper, and the potential of the

$$Au^{3+} + 3\ e \leftrightarrows Au$$

equilibrium is more positive even that of the oxygen reduction reaction (Figure 5.2 C). Thus, it is observed that gold is greatly stable in aqueous solution and Figure 5.2 (C) shows that it is not solubilized in noncomplexing solutions in the presence of oxygen. This is, in fact, the case and the metal does not respond to leaching by normally known strong oxidizing acids. Hence, the leaching of gold ores is not at all easy. However, this situation becomes completely modified when complexing agents are present by which potential–pH diagrams for metal–water systems alter on account of formation of complex ions of high stability. As a consequence new, modified and increased dissolution areas become established. This approach augurs very well for developing suitable and easily attainable leaching conditions for dissolution of metals which otherwise resist dissolution in normally used solutions, without complexing agent being present.

It is important to recognize some of the limitations of the Pourbaix diagrams. One factor which has an important bearing on the thermodynamics of metal ions in aqueous solutions is the presence of complex ions. For example, in ammoniacal solutions, nickel, cobalt, and copper are present as complex ions which are characterized by their different stabilities from hydrated ions. Thus, the potential–pH diagrams for simple metal–water systems are not directly applicable in these cases. The Pourbaix diagrams relate to 25 °C but, as is known, it is often necessary to implement operation at elevated temperatures to improve reaction rates, and at elevated temperatures used in practice the thermodynamic equilibria calculated at 25 °C are no longer valid.

Finally, it may be said that hydrometallurgists can, in many instances, obtain clues for leaching conditions by adjusting potential and pH so that a given leaching reaction is tailored and driven in a desired direction. Furthermore, the regions of stability of the various species in a Pourbaix diagram shift as the temperature is changed, providing a third variable that may be manipulated to achieve the desired effect. Yet another variable that can be manipulated is the concentration of the complexing agents (particularly CN^-, NH_3, and Cl^-) that can stabilize ions in solution. Pourbaix diagrams have now been constructed on the basis of experiments or theoretical calculations (or both) for a large number of mineral systems. They are very useful in examining the chemistry of potential hydrometallurgical processes, although it should be emphasized that the diagrams are based only on thermodynamic considerations and are therefore subject to certain limitations: they provide no information regarding: (i) the kinetics of leaching reactions; and (ii) the state of the system if equilibrium is either not achieved or intentionally avoided. Apart from the Pourbaix diagrams for the minerals that are to be leached, hydrometallurgists would also be interested in diagrams for gangue minerals. This can help in selecting the correct conditions to minimize the dissolution of gangue minerals, the contamination of the solution, and the wastage of reagent on the gangue.

5.2.1
Leaching Processes

The process of leaching is one of the important examples of heterogeneous reactions involving solid, liquid and, sometimes, gaseous phases. Leaching may occur through a variety of processes which may be grouped under physical, chemical, electrochemical, and electrolytic processes, each having certain well-defined characteristics.

The simplest process for dissolving a solid substance is the physical process where the aqueous phase is water and there occurs no chemical transformation. Water, while being the most common solvent, is perhaps also an ideal one as it can legitimately be considered as the cheapest and noncorrosive of all reagents commonly known and used. However, it should not be construed as being a universal solvent, as can be seen from the many substances that are insoluble in plain water. It is interesting to take note of the factors that influence aqueous solubility. The situation for water is more complex than with normal solvents because hydrogen bonding tends to keep the water molecules associated with each other.

A hydrogen ion, H^+, is a hydrogen atom which has shed its simple electron, and is therefore simply a proton. Rather than occurring by itself, it attaches itself to one or more water molecules, forming an ion such as hydronium ion, H_3O^+. In order to emphasize the fact that a proton cannot exist by itself in aqueous solution, the ionization reaction of water is written as:

$$2\ H_2O\ (l) \rightleftharpoons H_3O\ (aq) + OH^-\ (aq)$$

Like other ions in aqueous solution, both hydronium and hydroxide ions are hydrated. Moreover, hydrogen bonds are involved in attracting water molecules to hydronium and hydroxide ions. In both cases, three water molecules appear to be rather rigidly held, yielding formulas $H_3O(H_2O)_3^+$ (or $H_9O_4^+$) and $OH\ (H_2O)_3^-$ (or $H_7O_4^-$). However, for convenience, the proton is usually discussed as though it occurred in the form of H^+. Hydroxide ions, OH^-, also occur as hydrated ions, but like H^+, they are written as though they were not hydrated. The ionization of water is thus written as

$$H_2O \rightleftharpoons H^+ + OH^-$$

The equilibrium constant for the above reaction at 25 °C is

$$K = [H^+]\,[OH^-] = 10^{-14}$$

For pure water, $[H^+] = [OH^-]$ and pH = 7. Any solution with pH = 7 is by definition a neutral solution. No matter what other solutes occur in a given solution, the product of hydrogen and hydroxide ion activities will always be 10^{-14} at 25 °C. This may be noted that the value of this equilibrium constants alter with temperature, as do all equilibrium constants. For this reason at 230 °C, $K = 10^{-11.4}$ and a neutral solution would have a pH of 5.7. This brief diversion specifically focusing attention on the ionic compositional aspects of water is quite relevant with regard to its role played as a leaching agent.

In general, water is a poor solvent for nonionic solutes. Hydrocarbons in particular, such as CH_4, are practically insoluble in water. In these examples, the interaction between the molecular solute and water is so weak that not enough energy is liberated to break down the water structure. Still there are some molecular solutes which are highly soluble in water. Examples are bases like NH_3 and C_2H_5OH which dissolve in water by forming hydrogen bonds. In the case of NH_3, hydrogen bonds are established between N of NH_3 and O of H_2O, and in the case of CH_2OH, hydrogen bonds are between O of C_2H_5OH and the O of H_2O. The high solubility of sugars such as sucrose to a large extent is due to hydrogen bonding and this is on account of their having OH groups like those in C_2H_5OH.

Water is the most common solvent used to dissolve ionic compounds. Principally, the reasons for dissolution of ionic crystals in water are two. Not stated in any order of sequence of importance, the first one may be mentioned as the weakening of the electrostatic forces of attraction in an ionic crystal known, and the effect may be alternatively be expressed as the consequence of the presence of highly polar water molecules. The high dielectric constant of water implies that the attractive forces between the cations and anions in an ionic salt come down by a factor of 80 when water happens to be the leaching medium. The second responsible factor is the tendency of the ionic crystals to hydrate.

Water solubility of ionic substances is dependent on a fine balance between lattice energy, hydration energy and entropy of ions. The scheme shown hereunder as:

$$\begin{tikzcd}
 & M^+\,(g) \arrow[d, "(c)"] & + & X^-\,(g) \arrow[d, "(d)"] \\
MX\,(s) \arrow[ur, "(b)"] \arrow[r, "(a)"] & M^+\,(aq) & + & X^{d-}\,(aq)
\end{tikzcd}$$

indicates that the overall process of dissolution (a) can be resolved into a breakup stage (b), followed by hydration stages of the gaseous ions (c and d). The energy needed for the stage (b) has to be offset by hydration stages (c, d) of an ionic substance for it to be appreciably dissolved by water. The values for ΔH^0 and ΔS^0 of hydration of some common ions are known. The ΔH^0 values refer to the following process:

$$M^+\,(g) \rightarrow M^+\,(aq) \quad (c)$$

Certain facts can be observed. First of all, the values are negative which testifies exothermicity of the reaction. Secondly, ΔH^0 values are observed to be the smallest for the singly charged ions (about -400 kJ), roughly four times for doubly charged ions (about -1600 kJ), and finally turns to about ten times as large for triply charged ions (about -4000 kJ). In general, the larger the diameter of the ion or size as may be called, the smaller the ΔH^0 of hydration. The ΔS^0 of hydration also applies to the process:

$$M^+\,(g) \rightarrow M^+\,(aq) \quad (c)$$

The values are all negative. In the gaseous state, there are a large number of viable configurations, and understandably thus the entropy is very high. When the ions pass into solution, they shed much of their freedom and in the process the entropy gets considerably lowered. In the process as shown below:

M^+ (g) → M^+ (aq) (c)

as well as in the process as shown below:

X^- (g) → X^- (aq) (d)

practically all the entropy associated with a mole of gas is lost (about 50 J deg^{-1} mol^{-1}). Additionally, there is a further reduction of entropy which owes to ordering of the H_2O molecules in the solution. Once the values for ΔH^0 and ΔS^0 are known, they can be used to determine ΔG^0 for the overall reaction in question (dissolution):

MX (s) → M^+ (aq) + X^- (aq) (a)

It will be abundantly useful if the description provided above is illustrated quantifiedly through a specific example, and for this purpose, a comparison between the two halide ionic substances, AgF and AgCl, are considered. Table 5.1 presents the data. In the case of AgF, on account of enthalpy term being larger than $-T\,\Delta S^0$, ΔG^0 term ultimately turns out to be negative and the result is that AgF is found as a soluble salt. In the case of AgCl, in contrast, the enthalpy term is positive which is indicative of unfavorable disposition to dissolution. The entropy change shows favorable disposition to dissolution; however, enthalpy term is much higher and ΔG^0 term ultimately turns out to be positive and the result is that AgCl is found as not a very soluble salt. The hydration enthalpy of Cl^- is much smaller than that of F^-. The lattice of AgCl needs less energy to split, but this is not adequate. There is deficient hydration energy from Cl^- to constitute it worthwhile. The analysis carried out thus cannot be done for most solids since for most often data are not avail-

Table 5.1 Thermodynamics of dissolution processes of ionic salts in water at 25 °C.

Ionic salt	*Process breakup*	*Reactions*	*Thermodynamic data*		
			ΔH^0 kJ mol^{-1}	ΔS^0 kJ $mol^{-1}deg^{-1}$	ΔG^0 ($\Delta H^0 - T\,\Delta S^0$) kJ mol^{-1}
Silver fluoride (AgF)	Lattice splitting (b)	AgF (s) → Ag^+ (g) + F^- (g)	+959	0.200	–
	Hydration of cationic gaseous form (c)	Ag^+ (g) → Ag^+ (aq)	–69	–0.094	–
	Hydration of anionic gaseous form (d)	F^- (g) → F^- (aq)	–506	–0.155	–
	Dissolution (a)	AgF (s) → Ag^+ (aq) + F^- (ag)	–16	–0.049	–1.0
Silver fluoride (AgCl)	Lattice splitting (b)	AgCl (s) → Ag^+ (g) + Cl^- (g)	+99	0.200	
	Hydration of cationic gaseous form (c)	Ag^+ (g) → Ag^+ (aq)	–469	–0.049	
	Hydration of anionic gaseous form (d)	Cl^- (g) → Cl^- (aq)	–377	–0.097	
	Dissolution (a)	AgCl (s) → Ag^+ (aq) + Cl^- (aq)	+63	+0.009	+60

able. In such instances, tentative guidelines are appropriate. Insolubility is generally favored if charges on both anions and cations are simultaneously increased. Thus, for instance, $BaSO_4$ (both ions involved with the salt are doubly charged) is much less soluble than NaCl (both ions involved with the salt are singly charged). If a charge of only one ion is increased, the solubility is not much altered (NaCl and $BaCl_2$ are all appreciably soluble). Another common rule is that the more dissimilar in the size the anion and cation are, the more soluble a salt is susceptible to be ($MgCrO_4$ is very soluble unlike $BaCrO_4$ which is insoluble). It may ultimately be pointed out that specific interactions may support solubility. Thus, for example, BaS, has specific reaction between S^{2-} and H_2O which helps make BaS more soluble than $BaSO_4$, an insoluble salt in which specific interaction is absent.

Taking all the aspects considered thus far, the dissolution process of an ionic salt MX(s) in plain water categorized as a physical process may be represented in the manner presented below:

$$\mathrm{MX\ (s)} + (x + y)\mathrm{H_2O} \rightarrow \mathrm{M(H_2O)}_x^+\ \mathrm{(aq)} + \mathrm{N(H_2O)}_y^-\ \mathrm{(aq)}$$

where M can be Na, K and X can be say chloride. Being highly polar, the water molecules when approaching the surface of the crystal say, KCl, exert a force on the ions in the crystal lattice of KCl. The negative side of the dipole (oxygen end) attracts the positive ion or cation (K^+) and the positive side of the dipole (hydrogen end) attracts the negation ion or anion (Cl^-) to form corresponding hydrates. If the forces of hydrations of the ions exceeds the forces of holding the two ionic forms together in the KCl crystal, then the solid KCl crystal will pass into solution. This picture is portrayed by the equation presented below:

$$\mathrm{KCl(s)} + (x + y)\ \mathrm{H_2O} \rightarrow \mathrm{K(H_2O)}_x^+ + \mathrm{Cl(H_2O)}_y^-$$

A general thermodynamic treatment may be given to the dissolution process described above for the dissolution of the salt MX (s). When the salt is dissolved in water, each constituting ion will have a heat of salvation, or in other words, energies of hydration, ΔH_M^+ and ΔH_X^- for the positive and negative ions respectively. These heats of solvation or hydration essentially represent the enthalpy difference between the gaseous ion and the ion in solution. This dissolution scheme is depicted essentially an application of the first law of thermodynamics, as the heat of solution of the salt ΔH_S can be determined *b* displaying the process as occurring in two stages. The first stage is the breakup of the lattice of the solid MX (s) or in other words its sublimation to provide isolated or in other words free gaseous ions, for which ΔH is the negative of the lattice energy, E_L. The lattice energy, E_L, is defined as the energy required to bring an infinitely spaced positively charged vapor or in other words gaseous ion, M and the negatively charged vapor or in other words gaseous ion, X, together. The situation is represented as:

$$M\,X\ \mathrm{(s)} \xrightarrow{-E_L} M^+\mathrm{(G)} + X^-\mathrm{(G)}$$

The second stage is the salvation or hydration of these gaseous ions in water to provide solvated or hydrated ions in solution accompanied by the evolution of their heats of solvation or hydration as represented below:

$$M^+\mathrm{(G)} \xrightarrow{+\Delta H_{M^+}} M^+\ \mathrm{(aq)}\,; \quad X^-\ \mathrm{(G)} \xrightarrow{+\Delta H_{x^-}} X^-\ \mathrm{(aq)}$$

The sum of the two, hydration energy of the cation (ΔH_{M+}) and the hydration energy of the anion (ΔH_x^-), is called the solvation energy, ΔH_T. Thus, the following may be represented:

$$\Delta H_T = \Delta H_{M^+} + \Delta H_{x^-}$$

Then the heat of solution ΔH_S is the sum of the energy changes accompanying the first and the second stages:

$$\Delta H_S = \Delta H_T - E_L$$

ΔH_S may be either positive or negative. That principally depends on the relative magnitudes of the terms that figure on the right-hand side of the equation. In some cases heat is evolved on the dissolution of a salt in water. It is mainly due to the fact that heat evolved when the gaseous ions are hydrated (ΔH_T) is more than the heat absorbed in rupturing the crystal lattice. In the majority of cases, however, there is an absorption of heat when a salt dissolves in water.

The dissolution reaction in water is thermodynamically governed by the change in the free energy of solution, ΔF_s or simply called free energy of solution. The solubility of a salt is determined by its free energy of solution. At constant temperature and pressure, it is given by the following:

$$\Delta F_s = -R\,T \ln k_{sp}$$

where k_{sp} is the solubility product and is given by the following:

$$k_{sp} = a_{M^+} \cdot a_{X^-}$$

since the activity of the solid (MX (s)), a_{MX} is taken as unity.

It may be of interest to point out among others the effect of ionic parameters on the solubility. The free energy of solution, ΔF_s, the determining factor for solubility, is related to the heat of solution, ΔH_s, and the entropy of solution, ΔS_s, by the relation shown below:

$$\Delta F_s = \Delta H_s - T\,\Delta S_s$$

The dissolution process is associated with an increase in entropy due to the increase in disordering. This increase may be taken to be equal in a series of salts such as the alkali halides. Therefore, the solubility of a salt is approximately proportional to the heat of solution, ΔH_s, which is provided by (given earlier):

$$\Delta H_s = \Delta H_T - E_L$$

Both terms, ΔH_T and ΔH_s, figuring in the equation above, are functions of the ions making up the salt as shown below:

$$\Delta H_T \propto \frac{1}{R^+} + \frac{1}{R^-}$$

$$E_L \propto \frac{1}{R^+ + R^-}$$

Therefore, for a given set of compounds possessing the same structure R^- very much larger than R^+, the term $1/(R^+ + R^-)$ will be practically constant and nearly equals $1/R^-$. Therefore, the lattice energy, E_L will stay practically constant. The hydration energy, ΔH_T, on the other hand, will be only a function of the term $1/R^+$ which marks down with rise of R^+.

The ionic crystal solubility in water, is therefore, not only a function of the absolute dimension of the anion and the cation, but also of their ratio. As a result, when the solubility of a series of compounds of elements in the periodic table is compared, it is observed that there is either a gradual increment, a gradual decrement, or the occurrence of maxima and minima. Figuratively, it may be stated that if the ionic sizes greatly differ, the crystal stability comes down because the reduced sized ions are not sufficiently large enough to keep apart the larger-sized ions. As the large-sized ions approach one another more and more closely, mutual detestation increases and the crystal becomes more unsettled and as a result it simply becomes more soluble.

The composition and properties of the ions contained in the solution are not the same as those of ions contained in the ionic crystal lattice. It is already known that anhydrous copper sulfate ($CuSO_4$) is colorless. This implies that Cu^{2+} and SO^- ions that make up the crystal lattice of the sulfate are colorless. When the Cu^{2+} ions combine with water molecules during dissolution they turn blue (the color characteristic of copper salt). This color is therefore due to hydrated ions of copper, i.e., ions connected with the water molecules.

As examples of some water-soluble salts, mention may be made of potassium chloride, copper sulfate, and sodium vanadate. As examples of some water-insoluble salts, mention may be made of some typical ones such as lead chloride, silver chloride, lead sulfate, and calcium sulfate. The solubilities of most salts increases with increasing temperature. Some salts possess solubilities that vary very little with temperature or even decline. An interesting example is provided by ferrous sulfate, the water solubility of which increases as temperature is raised from room temperature, remains fairly constant between 57 and 67 °C, and decreases at higher temperatures to below $12\ \mathrm{g\ l^{-1}}$ at 120 °C. Table 5.2 presents the different types of dissolution reactions in aqueous solutions, and Table 5.3 in an indicative way presents the wide and varied types of raw materials that different leaching systems treat. It will be relevant to have a look at Table 5.4 which captures some of the essential and desirable features for a successful leaching system.

To provide a kinetics side of the dissolution process with water, it may be added that the rate equation for the process goes by the following equation:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{D\,A}{\delta V}\,(c_\mathrm{s} - c)$$

where c represents the solute concentration at time t, c_s the solubility of the substance in water at the experimental temperature, A the surface area, V the volume of solution, D the diffusion coefficient, and δ the thickness of the boundary layer. The equation above when integrated provides the following relationship:

$$\ln\frac{c_\mathrm{s}}{c_\mathrm{s} - c} = \frac{D\,A}{\delta A}\cdot t$$

The speed of agitation governs the rate. The boundary layer thickness decreases at high speeds. A physical process such as the dissolution of an ionic salt in plain water is associated with an activation energy of the order of less than about 5 kcal mol^{-1}. The influence of temperature on physical processes is less pronounced than that from agitation.

According to the chronological order of dissolution reactions in aqueous solutions presented in Table 5.2, the content, next to the coverage provided on physical process, enters to concentrate on chemical processes in which attention is focused on dissolution processes

Table 5.2 Types of dissolution reactions in aqueous solutions.

Type	*Solid feed*	*Characteristic*	*Examples*
Physical	Ionic solid	Dissolution is based on hydration	Sodium chloride in water $NaCl + (x + y)\ H_2O \rightarrow Na(H_2O)_x^+ + Cl(H_2O)_y^-$
Chemical	Partially-ionic-covalent-bond solids	Dissolution is based on neutralization	Aluminum hydroxide in acid or base $Al(OH)_3 + 3\ H^+ \rightarrow Al^{3+} + 3\ H_2O$ $Al(OH)_3 + OH^- \rightarrow AlO(OH)_2^-\ (aq) + H_2O$
		Dissolution is based on complex formation	Lead sulfide in saturated NaCl solution $PbSO_4\ (s) + 4\ NaCl\ (aq) \rightarrow$ $Na_2[PbCl_4]\ (aq) + Na_2SO_4\ (aq)$
		Dissolution is based on displacement	Zinc sulfide in copper sulfate solution $ZnS + Cu^{2+} \rightarrow Zn^{2+}$
		Dissolution is based on oxidation	Sulfides in oxygenated water $FeS\ (s) + 2\ O_2\ (aq) \rightarrow Fe^{2+} + SO_4^{2-}$
		Dissolution is based on protonation	Compounds of weak acids in strong acids, or formation of volatile acids
Electro-chemical	Conducting solids	Dissolution is based on redox process	Iron in acid $Fe + 2\ H^+ \rightarrow Fe^{2+} + H_2$
	Semiconducting solid sulfide	-do-	Zinc sulfide in oxygenated water $ZnS\ (s) + 2\ O_2\ (aq) \rightarrow ZnSO_4\ (aq)$
	Semiconducting solid oxide	-do-	Uranium oxide in sodium carbonate solution $UO_2 + 3\ CO_3^{2-} + \frac{1}{2}\ O_2 + H_2O \rightarrow$ $[UO_2(CO_3)_3]^{4-} + 2\ OH^-$
Electrolytic	Conducting or semiconducting solids	Dissolution is implemented by imposed emf	Metals $Ni \rightarrow Ni^{2+} + 2\ e^-$ Sulfides $Ni_3S_2 \rightarrow Ni^{2+} + 2\ NiS + 2\ e^-$ $NiS \rightarrow Ni^{2+} + S + 2\ e^-$

Table 5.3 Various raw materials that can be treated by leaching.

Raw materials	***Representative examples***
Metals	Precious metals; copper; nickel; cobalt
Oxides and hydroxides	Bauxite; laterites; copper oxide ores; uranium ores; zinc ores and calcines; manganese ores and nodules
Complex oxides	Chromite; niobite–tantalite; pyrochlore; ilmenite; wolframite; scheelite
Sulfides	Sulfides of primary metals such as copper, nickel, lead, or zinc; molybdenite
Selenides and tellurides	Anodic slimes from copper electrolysis
Arsenides	Cobalt and nickel arsenide ores
Phosphates	Phosphate rock; monazite sand
Silicates	Clays, napheline–syenite; beryllium ores; serpentine
Chlorides and sulfates	Pyrite cinder from chloride and sulfate processes
Slags and sludges	Copper converter slag; vanadium sludge (from aluminum industry); ferroalloys slag
Spent catalysts	Nickel/molybdenum/vanadium – bearing spent catalyst
Speisses	These are alloys of heavy metals like iron, cobalt and nickel with arsenic and antimony, occasionally also with tin. Lead smelting typically yields this complex source

Table 5.4 Essential and desirable features for a successful leaching system.

Essential feature	***Desirable features***
1. The valuable metal must be soluble in an economically usable solvent.	1. The gangue minerals should not consume excessive amounts of solvents.
2. The metal must be economically recoverable from solution.	2. The solvent should be recoverable (or capable of regeneration) for recycle.
3. The impurities that are co-extracted during leaching must be capable of further separation from the solution.	3. The feed should be free of clay materials, as they make separation of leach liquor from the treated solids difficult.
	4. The feed material should be porous to the solution allowing direct contact between the solvent and the phase to be dissolved, and providing a high liquid/solid area for reaction for a given mass of material.
	5 The solvent should preferably be noncorrosive to materials used in plant equipment to minimize capital and maintenance costs, and should be non-toxic.

based on (i) neutralization, (ii) complex formation, (iii) displacement, (iv) oxidation, and (v) protonation. In general, in chemical processes, the solid in question may be partially ionic and partially covalent or principally covalent. The first type encompasses oxide, hydroxide, sulfide, sulfate, some halide, and carbonate compounds. In contrast, the second type encompasses only a limited number; principally silica and silicates. All these substances are characterized by insolubility in water. They, however, dissolve as a consequence of presence of certain specific reagent in the aqueous medium which brings about an alteration of the dissociation towards right. The reaction towards left is kept almost on a hold.

The enhanced aqueous solubility of aluminum hydroxide in the presence of an acid or alkali is an example where neutralization reaction plays a part. In pure water, the solubility of aluminum hydroxide is low which is very well reflected in the following equation:

$$Al(OH)_3\ (s) \rightleftharpoons Al^{3+}\ (aq) + 3\ (OH)^-\ (aq) \qquad K = 1.9 \cdot 10^{-33}$$

when an acid is added, the OH^- ions are neutralized and their concentration decreases. This disturbs the equilibrium and more aluminum hydroxide dissolves. The overall process is then represented as:

$$Al(OH)_3 + 3\ H^+ \rightarrow Al^{3+} + 3\ H_2O \qquad K = 1.9 \cdot 10^9$$

The dissolution process in presence of an alkali, on the other hand, occurs because aluminum hydroxide can behave like an acid and the overall process in that case may be represented as:

$$Al(OH)_3\ (s) \rightleftharpoons AlO(OH)_2^-\ (aq) + H^+\ (aq) \qquad K = 4 \cdot 10^{-13}$$

When an alkali is added, the H^+ ions are neutralized and the equilibrium is shifted to the right. This results in enhancing the dissolution of hydroxide.

$$Al(OH)_3 + OH^- \rightarrow AlO(OH)_2^- + H_2O \qquad K = 40$$

This way a neutralization reaction can lead to an enhancement of the solubility of an otherwise insoluble or sparingly soluble material. Because of its ability to dissolve both in acid and alkali, aluminum hydroxide is known as an amphoteric hydroxide.

Many salts and minerals display an enhanced tendency to decompose and dissolve by processes involving complex ion formation and chloride acts as a ligand in these complexes. Lead sulfate has a poor solubility in water. However, in the presence of chloride ions, a complex chloroplumbate ion is formed and thereby solubility is enhanced. The relevant reactions are:

$$PbSO_4\ (s) \rightleftharpoons Pb^{2+}\ (aq) + SO_4^{2-}\ (aq) \qquad \text{(represents poor solubility)}$$

and

$$Pb^{2+} + 4\ Cl^- \rightarrow PbCl_4^{2-} \qquad \text{(represents chlorplumbate formation)}$$

and the overall process becomes

$$PbSO_4 + 4\ NaCl \rightarrow Na_2[PbCl_4] + Na_2SO_4$$

The reaction presented above is utilized to leach lead sulfate obtained by thermal oxidation of a mixture of sulfide minerals. The rate of dissolution chemically with a reagent in an aqueous medium increases with increased concentration of the reagent, and the case of dissolution of aluminum hydroxide in an acid is a good example in this respect.

Chemical process having the characteristic basing on displacement involves, for example, dissolution of a sulfidic substance in a solution holding a metal ion that yields a less-soluble sulfidic substance. The dissolution of zinc sulfide in copper sulfate solution is a worthwhile example that can be taken in the present context. In analyzing the reaction, reference first is drawn to the final reaction as shown below:

$$\mathrm{ZnS} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu} \qquad K_0 = \frac{(\mathrm{Zn}^{2+})}{(\mathrm{Cu}^{2+})}$$

The reaction shown above may be treated to occur in the following steps:

$$\mathrm{ZnS\ (s)} \rightarrow \mathrm{Zn}^{2+} + \mathrm{S}^{2-}\ \mathrm{(aq)} \qquad K1 = (\mathrm{Zn}^{2+}) \cdot (\mathrm{S}^{2-})$$

$$\mathrm{S}^{2-}\ \mathrm{(aq)} + \mathrm{Cu}^{2+}\ \mathrm{(aq)} \rightarrow \mathrm{CuS\ (s)} \qquad K_2 = \frac{1}{(\mathrm{S}^{2-}) \cdot (\mathrm{Cu}^{2+})}$$

where K_1 is the solubility product of ZnS and that K_2 is the inverse of the solubility product of CuS. It is evident that $K_0 = K_1\ K_2$ and substituting in it the value of K_1 of $1 \cdot 10^{-20}$ and K_2 of $0.125 \cdot 10^{45}$ the value of K_0 turns out to be a large number which reflects the reaction to progress.

Dissolution based on oxidation, the last but one of the chemical processes as the listing goes in Table 5.2, may best be described in a brief manner by taking a typical example of ferrous sulfide, the dissolution of which occurs as a consequence of oxidation of sulfide ion to sulfate:

$$\mathrm{FeS\ (s)} \rightarrow \mathrm{Fe}^{2+}\ \mathrm{(aq)} + \mathrm{S}^{2-}\ \mathrm{(aq)}$$

$$\mathrm{S}^{2-} + 2\ \mathrm{O}_2 \rightarrow \mathrm{SO}_4^{2-}$$

The all-inclusive reaction is shown below:

$$\mathrm{FeS\ (s)} + 2\ \mathrm{O}_2\ \mathrm{(aq)} \rightarrow \mathrm{Fe}^{2+} + \mathrm{SO}_4^{2-}$$

In the reaction presented above, oxygen shares electrons with sulfide ion which is unlike that from oxidation–reduction processes described later where transfer of electrons occurs.

Dissolution occurring to belong to protonation involves the processes highlighted out in Table 5.2. The dissolution of calcium carbonate in acids, the decomposition of calcium fluoride by concentrated sulfuric acid, the dissolution of ferrous sulfide in hydrochloric acid are some of the examples that can be pointed out as protonation-based dissolution.

The covalently bonded solids such as silica cannot be easily broken by aqueous solutions. For example, the strong Si–O bonds silica is not dissolvable by boiling with concentrated acids except hydrofluoric acid because of the formation of silicon fluoride which is a gas and expels; otherwise else it may form fluosilicic acid by reaction with water.

The electrochemical process differs from the chemical process by the fact the solid to be dissolved has to be electrically conducting (as for example, a metal), or a semiconductor (as for example, certain oxides and metal sulfides). As some specific examples of dissolution occurring electrochemically, mention may be made of (i) metals in oxygenated water,

(ii) metals in dilute acids, (iii) metals by displacement, (iv) metals with complex formation, (v) dissolution of oxides in presence of oxidizing or reducing agents, and (vi) dissolution of sulfides. The electrochemical dissolution of sulfides is considered for outlining the principles involved.

It is found that the dissolution of zinc sulfides occurs more rapidly when they are in contact with copper sulfide or iron sulfide than when the sulfides of these types are absent. This enhancement is brought about by the formation of a galvanic cell. When two sulfide minerals are in contact, the condition for dissolution in acidic medium of one of the sulfides is that it should be anodic to the other sulfide in contact. This is illustrated schematically in Figure 5.3 (A). Thus, pyrite behaves cathodically towards several other sulfide minerals such as zinc sulfide, lead sulfide and copper sulfide. Consequently, pyrite enhances the dissolution of the other sulfide minerals while these minerals themselves understandably retard the dissolution of pyrite. This explains generally the different leaching behavior of an ore from different locations. The ore may have different mineralogical composition. A particle of sphalerite (ZnS) in contact with a pyrite particle in an aerated acid solution is the right system combination for the sphalerite to dissolve anodically. The situation is presented below:

Anodic reaction: $ZnS = Zn^{2+} + S + 2\,e^-$

Cathodic reaction (on pyrite): $0.5\,O_2 + 2\,H^+ + 2\,e^- = H_2O$

Overall reaction: $ZnS + 0.5\,O_2 + 2\,H^+ = Zn^{2+} + S + H_2O$

It is known that chalcopyrite is quite inert in dilute acid at room temperature; however, on addition of iron powder, the situation dramatically changes. There is an immediate gen-

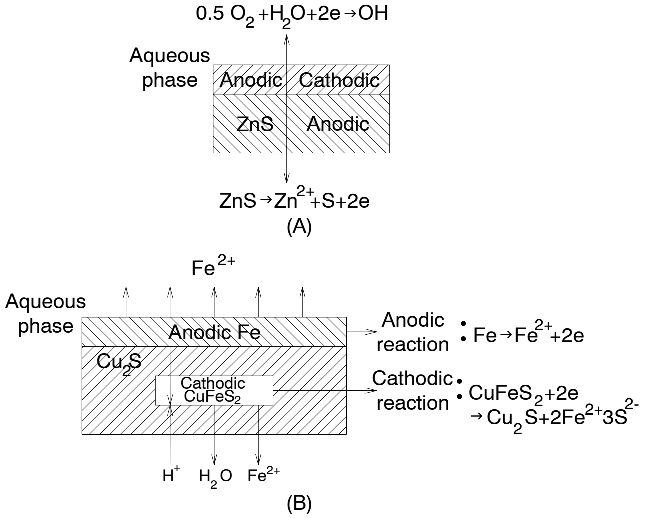


Figure 5.3 Galvanic action facilitating the dissolution process:
(A) two sulfides in contact exhibiting galvanic disposition;
(B) chalcopyrite in contact with iron exhibiting galvanic disposition.

eration of H_2S and the chalcopyrite is attacked leaving behind a copper sulfide rich phase with iron passing into solution. The galvanic effect comes into play which is shown in Figure 5.3 (B), and this also conveys the reactions at the anodic iron and at the cathodic chalcopyrite.

In the electrolytic process of dissolution, an electric current is imposed on a solid, and this technique can bring about its dissolution in the liquid with which it is in contact. For example, if nickel sulfide is connected to a direct current source such that it becomes the anode and the cathode is any conducting material, dissolution will occur according to the following overall anodic reaction:

$$Ni_3S_2 \rightarrow 3\ Ni^{2+} + 2\ S + 6\ e^-$$

The cathodic reaction is:

$$Ni^{2+} + 2\ e^- \rightarrow Ni$$

In the case of metal as anode instead of its sulfide the reaction is:

$$M \rightarrow M^{n+} + n\ e^-$$

The two electrolytic processes, one with the metallic sulfide and the other with the metal itself, are industrial processes. The first one allows simultaneous recovery of metal and sulfur, and second one allows purification of impure metal.

5.2.2
Pretreatments

It has often been found that for deriving the optimum results in leaching, it becomes necessary to have the starting feed material pretreated. These pretreatments generally fall in to the following categories: comminution, concentration, and pyrotreatments.

Comminution leads to an increase in surface area and exposes the mineral grains to attack by the solvent. The mineral grains may not, however, be liberated completely from the associated gangue material by this process. As long as a direct contact between some portions of the mineral grain and the leachant is not inhibited or lost, the mineral leaching process proceeds in an uninterrupted manner.

Mineral concentration carried out by using any one or combinations of such physical beneficiation processes as magnetic separation, electrostatic separation, heavy media separation, flotation, etc. is advantageous in so far as mineral leaching is concerned. The major advantages are that the volume of the reagent required and the consumption of the solvent by the gangue minerals are reduced. A higher metal concentration in the leach liquors also follows.

The changes that occur in minerals as a result of *thermal pretreatments* are wide and varied. Some examples are given in Table 5.5. The resources listed, in their untreated conditions, are not amenable to dissolution by common reagents. The treatments mentioned have converted them to altered forms, which dissolve more readily. In these examples only the valuable components of the different resources have been altered. There are however, examples where the gangue is converted into its insoluble or less-soluble forms. In such situations the leaching reagent loss is cut down. As an example, reference may be drawn to

Table 5.5 Typical pyrometallurgical treatments prior to aqueous leaching.

Resource	*Pyrometallurgical pretreatment*	*Description of chemical and other changes*	*Nature of hydroprocessing*
Sphalerite	Dead roasting at 900 °C in air	$ZnS + 1.5\ O_2 \rightarrow ZnO + SO_2$	Sulfuric leaching
Chalcopyrite	Sulfatizing roasting at 680 °C in air	$2\ CuFeS_2 + 7.5\ O_2 \rightarrow 2\ CuSO_4 + Fe_2O_3 + 2\ SO_2$	Water leaching
Pentlandite	Chloridization roasting at 400 °C in air	$2\ NiFeS + 4\ NaCl + 5.5\ O_2 \rightarrow 2\ NiCl_2 + Fe_2O_3 + 2\ Na_2SO_4$	Water leaching
Laterite	Reduction roasting	$2\ NiO + C \rightarrow 2\ Ni + CO_2$	Ammonia–ammonium carbonate leaching in the presence of oxygen
Zircon	Alkali fusion at 600 °C	$ZrSiO_4 + 4\ NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2\ H_2O$	Water leaching
Vanadium pentoxide	Salt roasting	$V_2O_5 + 2\ NaCl + H_2O \rightarrow Na_2V_2O_6 + 2\ HCl$	Water leaching
Gold telluride	Thermal treatment	$AuTe_2 \rightarrow Au + 2\ Te$	Cyanide leaching
Spodumene	Heated to about 1100 °C and rapidly cooled	The mineral, $Li_2O \cdot Al_2O_3 \cdot 4\ SiO_2$, occurring naturally in α form upon heat treatment converts to the β form. The volume change accompanying the phase transformations makes the material easily crushable.	Hot concentrated sulfuric acid leaching
Beryl	Melted and quenched	An amorphous glassy product is produced.	Dilute sulfuric acid leaching

the presence of pyrrhotite, FeS, in gold-bearing ores, which leads to a high consumption of the cyanide in accordance with the reaction:

$$FeS\ (s) + 2\ H^+\ (aq) + 6\ CN^-\ (aq) \rightarrow Fe(CN)_6^{4-}\ (aq) + H_2S\ (g)$$

However, by heating the ore in an atmosphere of oxygen, pyrrhotite is converted to hematite:

$$2\ FeS\ (s) + 3.5\ O_2\ (g) \rightarrow Fe_2O_3\ (s) + SO_2\ (g)$$

This hematite is not soluble in the cyanide solution. The oxidative pretreatment of gold ores thus reduces the cyanide consumption. Some impurity elements inhibit leaching reactions, examples include elements, carbon, sulfur and arsenic in gold ores are such impurities, but these can be removed by heating in air.

5.2.3
Leaching Techniques

The leaching process is often implemented in industry countercurrently and comprises a series of units, in each of which the solid from the previous unit is mixed with the liquid from the successive unit, and the mixture is permitted to settle. The solid then traverses to the next successive unit, and the liquid to the previous unit. As the liquid runs down from unit to unit, it becomes progressively enriched in solute, whilst as the solid traverses from unit to unit in the reverse direction, it becomes progressively depleted of solute. The solid emerging from one end of the set-up is well extracted, and the solution passing from the other end is strongly loaded in solute. The extent of extraction depends on the quantity of solvent and the number of units used in any given leaching operation. In principle, the unextracted solute can be brought down to any desired level, provided that enough solvent and enough number of units are deployed. Any suitable mixer and settler can be selected for the individual units in a countercurrent leaching set-up.

Various techniques are available for the dissolution of metal values from ores and concentrates. These can be divided into two broad classes: percolation leaching, and agitation leaching. In percolation leaching, the ore body remains static and the leaching reagent is allowed to percolate up or down the body to effect dissolution. In-situ leaching (both true and modified), heap leaching, dump leaching and vat leaching are all based on the process of percolation through a stationary ore body. The techniques which belong to the category of agitation leaching, on the other hand, keep the finely ground ore body in suspension by agitating the slurry mechanically or pneumatically. Agitation leaching results in higher metal recoveries in a short time, but requires higher capital investment as compared with percolation leaching. The leaching operation may be performed in batch, concurrent, or countercurrent modes at slightly below atmospheric, atmospheric, or above atmospheric pressures, and at ambient or somewhat higher temperatures. A classification of the various leaching techniques is presented in Figure 5.4.

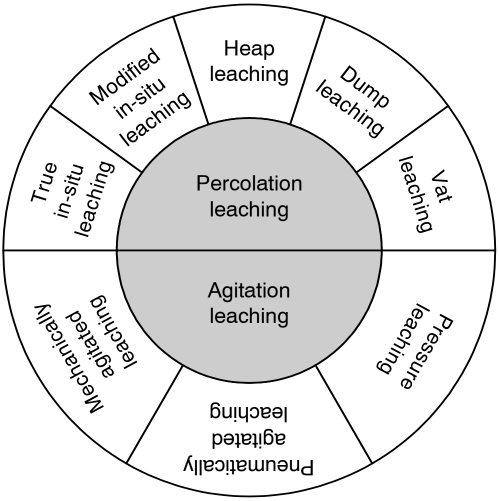


Figure 5.4 Various techniques of leaching.

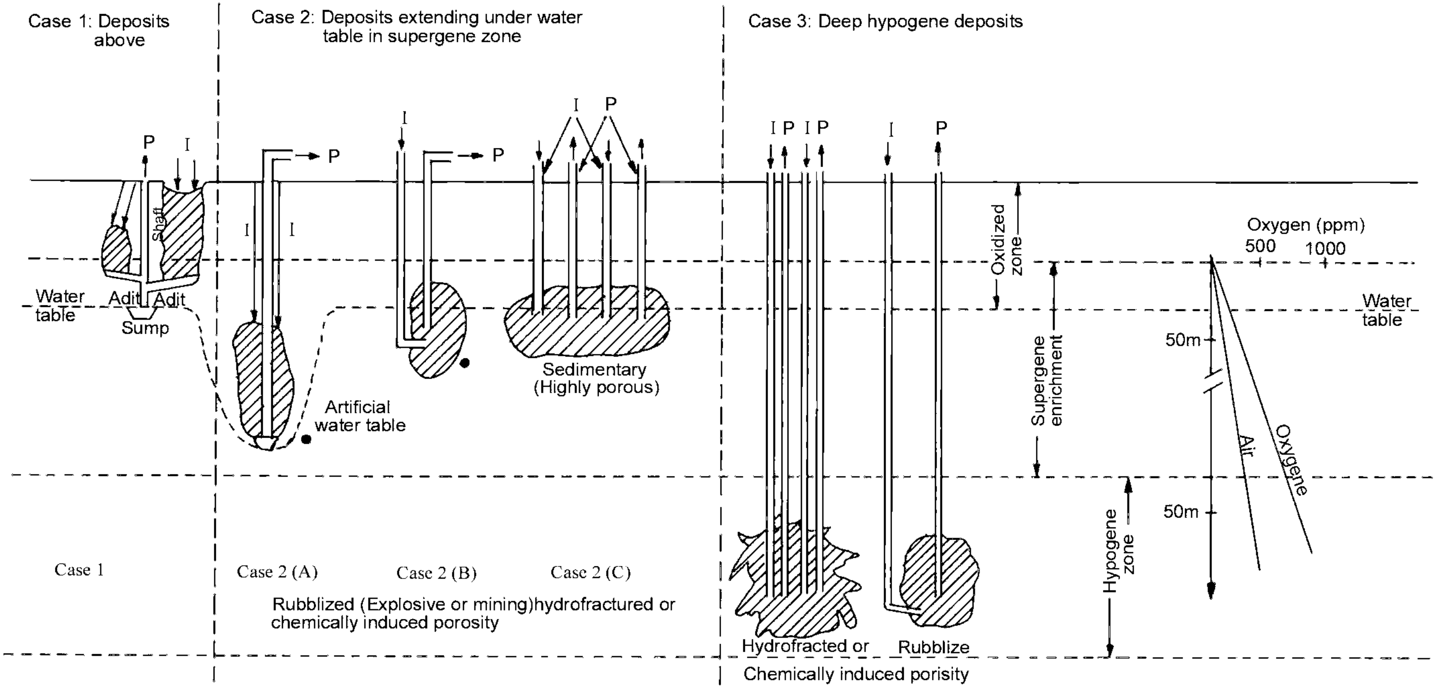


Figure 5.5 Various cases of in-situ leaching of ore deposits below the water table (I = injection of leach solutions; P = recovery of pregnant solutions).

5.2.3.1 In-situ/Modified In-situ Leaching

In-situ leaching, or solution mining as it is sometimes called, is concerned with the dissolution of metal values from minerals present in the undisturbed ore body in place. The process essentially involves injection of leaching solutions into the ore body, dissolution of metal values by the leachant, and final recovery of pregnant solutions for processing above ground. This technique is particularly suitable for treating low-grade ores, and its specific treatment cost is significantly lower than those of the other leaching schemes. It finds application in the extraction of metals such as gold, silver, copper and uranium.

Successful application of in-situ leaching demands certain prerequisites. It is important that the ore body should be permeable to the solution and should preferably be bounded by relatively impermeable strata so as to avoid loss of the solution. The deposit must be below the water table so that the leach liquor does not mix with natural ground water, leading to metal loss and contamination of ground water. In case the ore body is not permeable enough it has to be fractured by explosives. Such an approach is termed modified in-situ leaching. The various cases of in-situ leaching of ores are presented in Figure 5.5. The first case represents deposits above the water table; the second case illustrates three general conditions encountered in shallow deposits below the water table in supergene zone. Three situations of the second case have been identified. The first two, case 2 (A) and case 2 (B), have been starred to represent rubblized (explosive or mining), hydrofractured, or chemical induced porosity to distinguish from case 2 (C) which is a highly porous deposit with high natural porosity. The case 2 (A) is an artificially depressed water table produced by pumping, with or without using grouting to deter water inflow. This deposit, if sufficiently rubblized, may be percolation leached. The case 2 (B) has been rubblized by partial mining or fracturing by using either explosives, hydraulic pressure (hydrofracturing), or chemicals. Leaching solutions are being injected through a well into the bottom of the deposit and rise upward. The presence of natural porosity permits flow of leach solution horizontally in the case 2 (C). This type of in-situ leaching may require many years to complete the leaching of an ore body, during which time numerous bore holes would be drilled, operated, and finally closed. The third case represents deep hypogene deposits and it, in essence, is a variation of case 2 (B). The deposit is well below the water table and may not be accessible by mining. Apart from well-proven methods, a good potentiality exist for use of nuclear devices for fracturing such deep-seated deposits. In this particular case of deep hypogene deposits advantage can be taken of higher solubility of oxygen caused by the large hydrostatic pressure (the figure depicts this situation). Sulfide deposits can also be thus leached efficiently.

In-situ leaching requires the drilling of a monitor well around the ore body periphery. The wells are used during and after mining to check on possible ground water contamination by the mining solutions. Some of the major problems of in-situ leaching are the blockage of the well and the loss of permeability of the ore body due to the precipitation of insoluble compounds. For example, during in-situ leaching of uranium ore with sulfuric acid the precipitation of calcium sulfate can result in a significant drop in the permeability of the ore. In such a case, ammonium carbonate is preferred to sulfuric acid as it is highly selective towards uranium minerals and does not generate impermeable deposits.

5.2.3.2 **Dump and Heap Leaching**

Mining and milling operations, in general, leave behind numerous waste rock dumps, and these may bear significant amounts of metal value. One method of recovering such values is by dump leaching, and this concept has been very useful in the recovery of copper from the huge dumps made of mined waste (overburden). In leaching dumps of copper sulfide operations according to the reaction,

$$\mathrm{CuS} + 2\ \mathrm{O_2} = \mathrm{CuSO_4}$$

the use of water and air are sufficient; as the solvent trickles down through the dump, copper passes into solution as copper sulfate. The oxygen required for the reaction passes into the dump from the outside through the interstices between the particles. In reality, the solution sprayed over the dump is acidic, the acid usually being self-generated within the dump by the oxidation of other sulfide minerals (such as pyrite). Bacteria play an important role in the leaching reactions. (More about this particular aspect is presented in a later section dealing with bacterial leaching.) Ideally, the dump sits on a surface that is impervious to the solution and is slightly sloped so that the solution flows from one side. In some instances, the dump might have to be moved to such a surface.

In some cases dump leaching is used to leach low-grade ores directly (rather than the waste rock); in such a situation this is called heap leaching. In the process, mined low-grade ores are broken and piled into relatively small heaps on impervious ground or on a concrete or asphalted surface with drainage channels and pipes to carry away the pregnant solution to a collection pond. It may thus be described that the heap leaching operation sequentially involves the construction of leaching pads, the formation of the heaps, the distribution of the lixiviant, the collection of the leach liquor in the solution pond and the recirculation of the barren solution to the heaps after the recovery of metal values. A major advantage of heap leaching is the elimination of expensive milling operations since the ore body need not be crushed to sizes much smaller than 20 to 25 mm. Some expenses are, however, incurred in ore comminution in heap leaching. In case the crushed ore body is associated with too much of fines, its agglomeration is recommended to ensure good permeability. Some of the drawbacks of such ore treatment schemes are longer leaching periods and smaller recoveries. Heap leaching has found good applications in the processing of gold, silver, uranium, and copper ores. In comparison to heaps, dumps are much bigger in size. The overburden does not undergo any further size reduction before dumping. There is, therefore, no cost involved on this account in leaching a dump. It is clear from the description that dump leaching and heap leaching are similar to each other but differ in the type and amount of material being leached. Dump and heap leaching have been applied extensively to mine wastes and low-grade copper ores. Historically, applications of the two date back at least to the eighteenth century at Rio Tinto mines in Spain.

5.2.3.3 **Vat Leaching**

Vat leaching is a more complex technique as compared with the techniques described earlier. Here, the ore meant to be leached is loaded into vats that are typically made of concrete and are a few meters deep and several meters in horizontal dimensions. The vats are often fitted with filter-type bottom to facilitate solution flow through the ore bed. Usually, several vats are employed and leaching solution is pumped continuously from one tank to the top of the next. When leaching has been completed, the residual solids are dug out of the vat and replaced by a fresh batch of ore. It is the usual practice to so arrange the tanks that a countercurrent scheme is implemented. The vat leaching process is well suited to porous and sandy materials, but not to materials which have a tendency to pack into impervious masses. A good percolation results from regularly sized particles. With unequal-sized particles, the smaller particles pack in the openings between the larger ones, thereby clogging the channels; this causes the extraction to slow down and channelling of solutions through the bed occurs. The process is, therefore, unsatisfactory if much slime is present. The advantages of the process are: low solvent consumption, the production of a good grade leach solution, and the elimination of the use of expensive thickeners or filters. Leaching of copper oxide ores by dilute sulfuric acid to produce aqueous copper sulfate solution is one example of the application of vat leaching.

5.2.3.4 **Agitation Leaching**

Agitation of the mixture of the particles and the solution (in contrast with the leisurely flow of the solution which is typical of the leaching methods described so far) brings about an enhancement of the leaching process. Agitation leaching is generally conducted by charging the slurry of the milled ore and the lixiviant in steel cylinder lined with rubber/FRP/glass/titanium or unlined stainless steel vessels and keeping it agitated either pneumatically or mechanically. The slurry is brought to the desired temperature by steam heating. In comparison to percolation leaching, agitation leaching provides more aggressive leaching conditions, leading to higher recoveries and shorter duration of leaching brought about by finer size of the ore, turbulent flow conditions, higher lixiviant concentration, higher leaching temperature and sometimes elevated pressure.

Pneumatic agitation of the slurry is carried out in a pachuca, which is a tall cylindrical vessel with a conical bottom and a draft tube, open at both ends, positioned coaxially. Compressed air is introduced at the lower end of the tube. The density of the slurry surrounding the tube is much higher than that of the slurry located inside the tube, due to the presence of air bubbles; the latter, therefore, rises and overflows, leading to a continuous circulation of the charge. Such leaching is carried out in a continuous fashion in large-scale operations by placing a number of pachucas in series and allowing the slurry to move successively from one to the next. The slurry can be readily heated in pachucas by introducing live steam, and temperatures up to 60–70 °C are readily achieved.

Mechanical agitation for an intimate mixing of the ore and the lixiviant can be achieved by using a rotating paddle or a propeller or a turbine mixer. Among all the variations the turbine mixer provides the highest speed and the most intimate mixing and is found to be very suitable for carrying out diffusion controlled leaching reactions.

5.2.3.5 **Pressure Leaching**

Pressure leaching has gained a good deal of acceptance as a means of accelerating the dissolution of ores or of concentrates, despite the added cost of working in autoclaves. There are two types of pressure leaching that need to be distinguished. In the first type, leaching is carried out in the absence of oxygen; the ore is heated with the leaching agent at a temperature above the boiling point of the solution to achieve a high reaction rate. An example is the leaching of bauxite with caustic soda solution. The other type of pressure leaching is carried out in the presence of oxygen; the pressure in the autoclave is the resultant of the solution pressure and the oxygen pressure (or air pressure if air is used instead of oxygen). In this case the rate of leaching depends on the oxygen partial pressure and not on the total pressure. This approach is adopted mainly for leaching sulfide ores or uranium oxide ores. High-temperature pressure leaching is carried out in autoclaves and is the most of expensive of the leaching methods because of both high capital costs and high operating costs. The autoclaves may be horizontal, spherical, vertical, or in the form of long horizontal tubes. Horizontal autoclaves are agitated mechanically either by impellers or, as in spherical autoclaves, by rotating the entire autoclave around its horizontal axis. Besides avoidance of the settling out of solids rotation reduces maintenance problems because the rotating mechanism is not in contact with the slurry. Among the several forms of autoclaves the horizontal types are mainly employed. This type is generally divided into three or four compartments each containing an impeller for agitation. Pulp is pumped under pressure into one end of the autoclave and flows through the vessel from compartment to compartment. Heating is usually carried out by the injection of live steam and, once the required temperature has been attained, it can usually be discontinued in the case of exothermic reactions. It may so happen that it may be necessary to control the temperature by cooling, and this is generally achieved by internal circulating water-cooling coils. Vertical autoclaves are usually steam-agitated and are easy to maintain because they have no moving parts; but steam agitation is generally less efficient than mechanical agitation. In tube autoclaves, the slurry is pumped into one end and discharged a short while (2 to 5 minutes) later from the other end. These too are relatively maintenance free and also have a high thermal efficiency. Autoclaves are usually made of mild steel (in which case they may be rubber or brick-lined), stainless steel, or occasionally titanium. More recently, however, glass fiber-reinforced plastic autoclaves have been put into use.

5.2.4
Examples of Leaching Practices

5.2.4.1 Aluminum Ores

It will be seen from the various types of leaching reactions given in Table 5.2, that the dissolution of aluminum hydroxide essentially belongs to the chemical process category. The dissolution of the hydroxide in acid or alkali occurs by a mechanism involving neutralization.

The major raw materials used at present for the production of alumina are bauxites, which are found in the following mineral forms gibbsite ($Al(OH)_3$), boehmite ($AlO \cdot OH$), and diaspore ($AlO \cdot OH$). The major impurities are the oxides of iron, silicon, and titanium, and organic compounds, all of which must be removed before alumina is suitable for aluminum production. The process objectives are, therefore, separation of impurities and compound production in the present case. Bauxite is first dried to facilitate grinding, destroy organic matter, and oxidize the associated ferrous minerals to the ferric state. The temperature of drying is not allowed to exceed 150 °C, because at higher temperature a part of the combined water is expelled and the solubility is affected adversely.

The acid process uses sulfuric acid, but this process is restricted to the manufacture of aluminum sulfate used in water treatment and in the paper industry. The chief advantage of this method lies in adaptability to low-grade ores which are high in silica and are not suitable for leaching by the alkali process. However, the dissolution of ferric oxide is a disadvantage.

The alkali process uses sodium hydroxide and is well known as Bayer's process. It involves relatively simple inorganic and physical chemistry and the entire flowsheet can be divided into caustic digestion, clarification, precipitation and calcination. Although mineral assemblage in bauxites is extensive, processing conditions are primarily influenced by the relative proportions of alumina minerals (gibbsite and boehmite), the iron minerals (goethite and hematite), and the silica minerals (quartz and clays-usually as kaolinite).

The bauxite first undergoes a size reduction prior to dissolution by caustic. In the case of gibbsite, for example, the dissolution is described by the following equation:

$$\mathrm{Al(OH)_3\ (s) + 2\ NaOH\ (aq) \xrightarrow{150\ ^\circ C} NaAl\ (OH)_2\ (aq)}$$

The concentrations of alumina which is obtained in solution are determined by the chemical equilibria between the solutions and the mineral phases. There are considerable differences in the caustic concentrations needed to obtain a given concentration with the three different bauxite minerals. Besides this fact, the kinetics of dissolution reactions have been found to depend on the mineral phase present. The combination of these equilibrium and kinetic considerations has led to the adoption of three distinct treatment conditions. Unlike essentially gibbistic bauxites and bauxites containing significant amounts of boehmite, diasporic bauxites are virtually insoluble under normal Bayer process digest conditions. However, it is not an important mineral in bauxites processed in all countries. It is found in east European bauxites and is known to be rendered soluble in caustic by giving a preliminary calcination treatment to bauxite. As the digestion reactions show the silica dissolution reaction is of equal importance to that of the hydrated alumina minerals, because for every ton of silica solubilized in digestion, one ton of alumina is lost and 1.2 tons of caustic soda are consumed. The clarification accomplishing separation of sodium aluminate liquor from the mud residue is a critical processing step. The system essentially comprises a liquor phase, which is highly caustic, near the boiling point, and a solid phase of diverse mineralogy from bauxite residues and compounds resulted from digestion, often in finely divided state. Although the digested mud slurry is naturally slightly flocculated, a flocculant is added to achieve practical settling rate and compaction. In precipitation, the alumina dissolved from the bauxite is recovered from the liquor by the reaction,

$$\mathrm{NaAl(OH)_4\ (aq) \rightarrow NaOH\ (aq) + Al(OH)_3\ (s)}$$

using seeded crystallization. Despite high supersaturation and heavy seeding, the reaction is slow with a large fraction of soluble alumina remaining in the spent liquor. The precipitation product which is essentially gibbsite is thermally decomposed to metal-grade alumina by high temperature calcination. In the industry two distinct types of alumina are produced – sandy type and floury type. The former type is relatively coarse and free-flowing, whereas the latter types resembles flour in being fine, clumpy, and relatively nonflowing. Apart from these physical differences, chemically floury alumina has a much higher alpha-alumina content than the sandy alumina. This difference arises due to difference in calcination used for the two types.

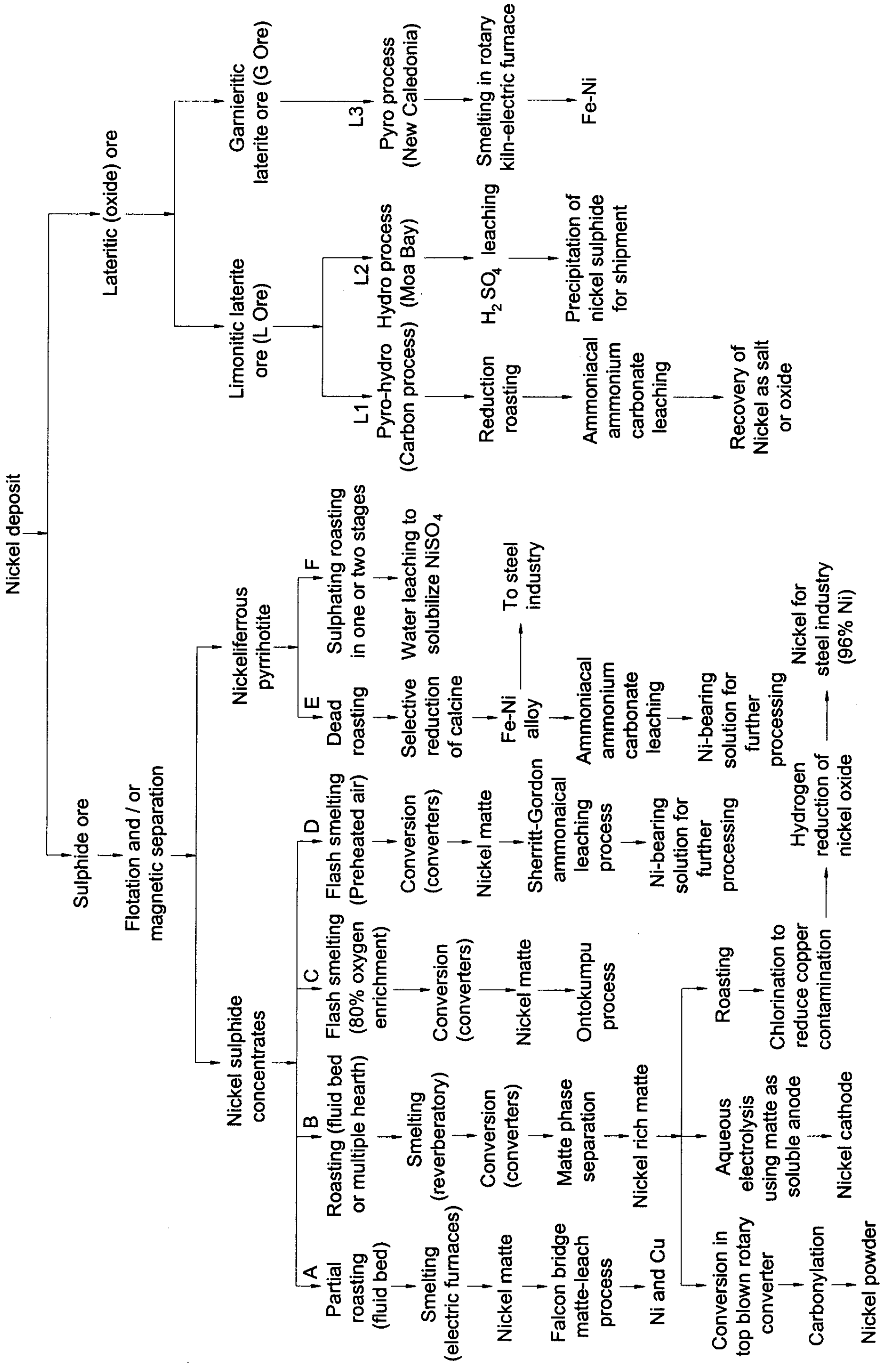


Figure 5.6 The total picture of nickel from its sulphidic and oxidic resources.

5.2.4.2 **Nickel Ores**

It has been mentioned in an earlier chapter that nickel deposits are basically of two types: sulfidic and lateritic (oxide). The scenario of nickel extraction from nickel sulfide concentrates and nickeliferrous pyrrhotite (these two are the two products of physical beneficiation of nickel sulfide ores), and from limonitics and garnieritics (these are the common lateritic ores) has been presented in Figure 5.6. It can be seen that nickel is extracted from its various sources by pyro, pyro-hydro and hydroprocessing. The account given here pertains to the latter two processes applied to the various nickel sources.

5.2.4.2.1 **Nickel Sulfide Concentrates**

Nickel sulfide concentrates are first subjected to an oxidizing treatment and then converted to nickel matte which is processed by hydrometallurgical methods. These methods have been indicated as A, C, and D in Figure 5.6.

In the processing scheme A, partial roasting and smelting are carried out first to produce nickel matte. The subsequent processing that is adopted to produce nickel by hydrometallurgical operations is popularly known as the Falcon bridge matte leach process. A simplified flowsheet of the process, which is essentially based on leaching the nickel–copper matte with hydrochloric acid, has been presented in Figure 5.7. The leaching is implemented with hydrochloric acid at about 70 °C; nickel solubilizes as nickel chloride ($NiCl_2$) together with small amounts of iron, copper and cobalt chlorides and sulfur is liberated as hydrogen sulfide. The leach residue contains the bulk of copper and also the precious metals, if present. This residue is roasted and leached with sulfuric acid to yield copper sulfate solution from which copper is electrowon; the spent electrolyte is reused for further leaching of roasted copper. The nickel chloride solution is subjected to purification by solvent extraction. Purification is first accomplished with respect to iron by using tributyl phosphate (TBP) and then with respect to copper and cobalt using tri-*iso*-octylamine (TiOA).

The first step in the processing scheme C involves flash smelting and conversion to produce nickel matte. The subsequent hydrometallurgical operation, popularly known as the Outokumpu process, the flowsheet for which is shown in Figure 5.8, starts with this nickel matte as the source of nickel. The nickel matte consists of three components – Ni-Cu alloy, Ni_3S_2 and Cu_2S – and is subjected to multistage leaching with sulfuric acid. The process combines the atmospheric as well as higher pressures leaching operations. Atmospheric leaching is a simpler, cheaper and more reliable way of leaching the bulk from the matte as compared to pressure leaching. The residue from atmospheric leaching consists mainly of nickel sulfide, cupric sulfide and cuprous sulfide; in pressure leaching nickel and cobalt are selectively dissolved leaving most of the copper. The final residue from the combined atmospheric and pressure leaching process contains very little nickel. Thus, the copper can be removed from the circuit as sulfides, which also contain the precious metals (almost full recovery of the precious metals can be achieved) and fed to the copper smelter. The nickel-bearing solution is purified first with respect to lead by precipitation brought about by the addition of a solution of barium hydroxide, and then with respect to cobalt by precipitation as the Co(III) hydroxide, using the Ni(III) hydroxide produced electrolytically from the Ni(II) hydroxide. Cobalt precipitation also acts as a scavenging step for other elements present in the solution in very low concentrations. Thus, cobalt precipitation moves almost fully, in addition to the cobalt, iron, manganese, arsenic, antimony, and bismuth.

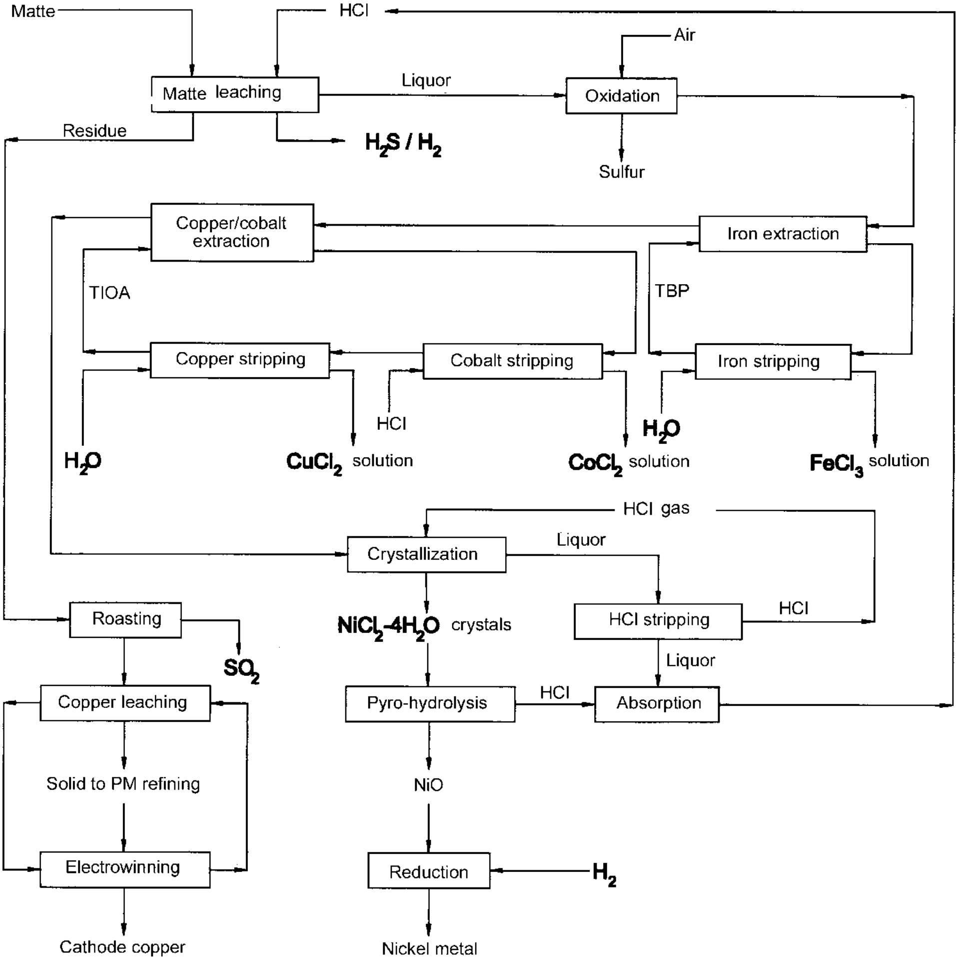


Figure 5.7 Falconbridge matte leach process flowsheet.

Finally, nickel is electrolytically produced from the purified nickel-bearing solution. In electrowinning of nickel, the hydrogen discharge reaction competes with nickel deposition at the cathode. This counterproductive effect is minimized by keeping the acidic anolyte solution separate from the catholyte by means of a diaphragm cloth.

The processing scheme D involves the hydrometallurgical operation popularly known as the Sherritt–Gordon process. The process outline flow diagram is shown in Figure 5.9. The various feed materials for the process can be nickel matte, precipitated nickel sulfide, alloy scrap, and nickel concentrate. The description of the process presented here refers to the use of pentlandite concentrate produced from the ore deposit at Lynn Lake, Manitoba, Canada, in the plant at Fort Saskatchewan, Alberta, Canada. It is pertinent to mention here that this plant no longer uses the Lynn Lake concentrate. The entire operation can be broken down into the following main steps: leaching, solution purification, hydrogen reduc-

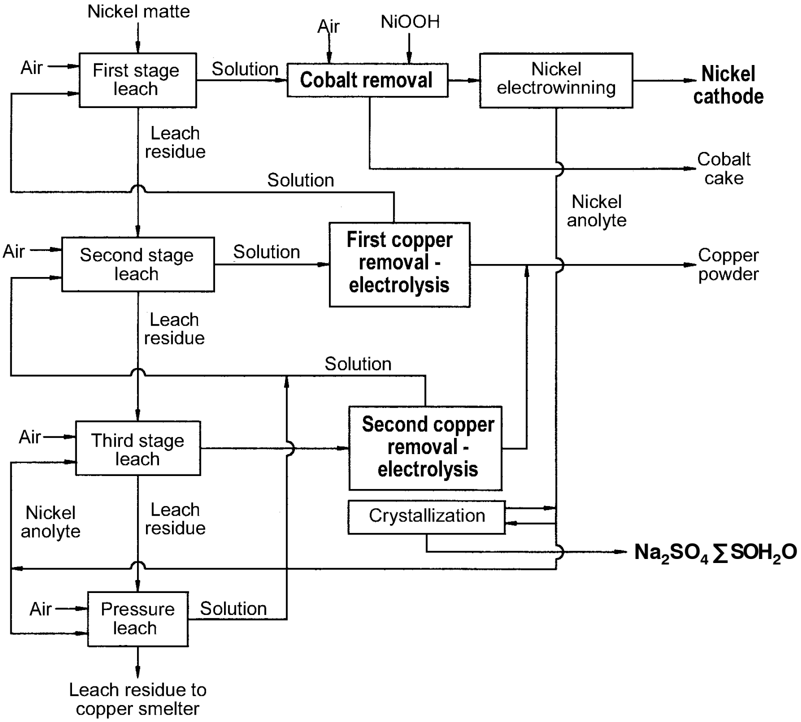


Figure 5.8 Outokumpu process for nickel cathode production.

tion, treatment of nickel reduction end solution, and cobalt-nickel separation. In the leaching process, finely ground matte is mixed with the solution produced in the second stage leaching autoclave to yield a slurry which is treated at about 94 °C in the first stage leaching autoclave with the pressure raised with air. After solid–liquid separation the liquid passes to the purification section while the solid is mixed with water and recycled ammonia and is leached in the second stage autoclave at around 80 °C under pressurized conditions. The solid residue is passed onto the tailings pond. The leach solution from the Lynn Lake concentrate contains nickel, cobalt and copper and much of sulfur from the sulfides. Similar solutions result from leaching matte. In the purification process, excess ammonia is removed from the solution by distillation and is passed to the second stage leaching autoclave. As the ammonia concentration in the solution falls, much of the copper present is precipitated as copper sulfide and the residual amount of copper is removed, together with some nickel sulfide, by precipitation with hydrogen sulfide. The sulfur anions in the solution are oxidized and hydrolyzed to sulfate by heating at 240 °C under air pressure. In the hydrogen reduction step, the purified solution is treated with hydrogen to precipitate nickel. The reduction reaction is stopped when the amount of hydrogen that has reacted corresponds to the removal of nickel from solution to produce a nickel to cobalt concentration ratio at which the amount of cobalt depositing with the nickel becomes too great. Processing of the nickel reduction end solution involves treatment of the solution with hydrogen

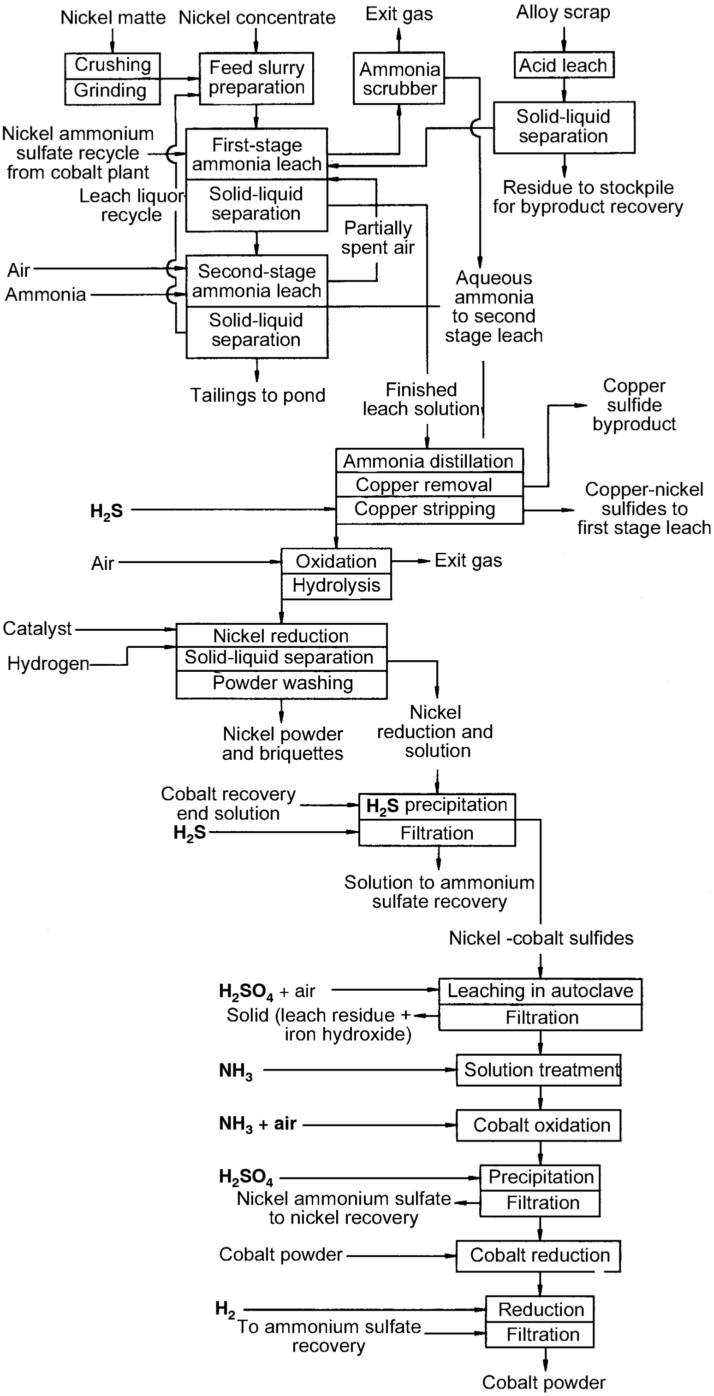


Figure 5.9 Sherritt–Gordon process of nickel production.

sulfide. After filtration, the solution is taken up for ammonium sulfate recovery. The nickel–cobalt sulfide produced in this step is pressure leached in an autoclave with dilute sulfuric acid, with air as oxidant. The solid, consisting of the leach residue and iron hydroxide, is filtered off. The clarified solution finally goes to the nickel–cobalt separation circuit in which the starting operation is the injection of anhydrous ammonia to form nickel and Co(II) amine complexes. The solution is then oxidized in an autoclave at 70 °C, using air under pressure and a free ammonia to nickel plus cobalt molar ratio in the range of 5 and 6. Most of the cobalt forms aquopentamino Co(III) sulfate. The pH of the cooled solution is then adjusted to 2.6 with sulfuric acid; and the nickel ammonium sulfate double salt crystallizes out and is filtered off. The Co(III) pentamine solution is then evaporated to raise the ammonium sulfate concentration from 300 to 500 $g\ l^{-1}$. During this first stage nickel removal, the cobalt to nickel ratio increases from 1.5 : 1 to 35 : 1. To complete the nickel removal, cobalt powder is added to reduce a part of the Co(III) to Co(II); subsequent addition of sulfuric acid precipitates a nickel–cobalt ammonium sulfate which is filtered off and returned to the Co(II) amine oxidation step. The filtrate has a cobalt to nickel ratio greater than 1000; sulfuric acid and cobalt metal powder are then added to reduce all cobalt to Co(II). This is essential because the reduction of a solution of the Co(III) pentamine by hydrogen yields cobalt oxide rather than metallic cobalt.

5.2.4.3.2 **Nickeliferrous Pyrrhotite**

Many sulfidic nickel ores are commonly associated with nickeliferous pyrrhotite containing typically 0.6–1.5% nickel. In such ores, the pyrrhotite is normally separated from the minerals richer in nickel by flotation or magnetic separation to yield a concentrate containing typically 0.8–1.2% nickel. The pyrrhotite was previously being discarded. The resulting environmental problems and the inadvisability of wasting substantial sources of nickel have led to significant developmental efforts for nickel recovery from the pyrrhotite material. The low nickel content of pyrrhotite suggests that additional recovery of iron in useful form is also highly desirable. There are essentially two schemes by which nickeliferrous pyrrhotite can be processed. These have been marked as E and F in Figure 5.6.

The scheme *E* involves dead roasting of the concentrate by which Fe_2O_3 forms and the nickel content is oxidized to nickel ferrite ($NiFe_2O_4$). This material is selectively reduced to produce an iron–nickel alloy which is then leached in an ammoniacal ammonium carbonate solution for nickel recovery, leaving hematite as a leach residue.

The scheme *F* involves sulphating roasting. The conditions are so chosen that iron is converted to its oxidic form (Fe_2O_3) while nickel and copper are converted to nickel sulfate and copper sulfate respectively. The product is subsequently water leached to take the sulfates into solution, leaving the iron oxide in the leach residue.

5.2.4.3.3 **Lateritic (Oxide) Ores**

From the mineralogical description of lateritic (oxide) deposits given in the first chapter, it will be recalled that they are found to contain in all three principal types of ore: limonitic laterite (L ore), serpentinic laterite (S ore) and garnieritic laterite (G ore). Principally on account of the mineralogical differences between L ores and G ores, the two sources are treated by different processes. The G ores are characterized by heterogeneity but are rich in nickel and also in magnesia and silica. They are treated pyrometallurgically. The L ores, on the other hand, are mineralogically quite uniform, being composed principally of goethite. Their high iron and low nickel contents, however, do not lend them to economic processing by pyrometallurgical methods. They are treated by either hydrometallurgical processes or by combined pyro- and hydro-metallurgical processes. Both the pyrometallurgical and the hydrometallurgical schemes can accept the S ore provided it is blended with the respective principal G or L ore feed. The pyrometallurgical processing scheme for the G ores and the combined pyro- and hydrometallurgical, as well as the exclusively hydrometallurgical processing schemes for the L ores have been marked respectively as L3, L1 and L2 in Figure 5.6. The L1 and the L2 scheme will now be described.

The scheme L1 is known as the Caron process. The first commercial plant to use this process was built during the second world war at Nicaro in Cuba. Since then, at least three other similar plants have been built in different parts of the world. Although certain modifications and improvements have gone into the more recent plants, the process still retains the basic concepts developed by Caron in the 1920s. The process consists of four main steps: (i) drying and grinding; (ii) reduction roasting; (iii) leaching with ammoniacal ammonium carbonate solution; and (iv) metal recovery from solution. A detailed flowsheet of the process is shown in Figure 5.10. Since the raw ore contains moisture (usually in the range of 30–50 wt-%), considerable energy is expended in drying which is carried out in rotary kilns. The dried material with about 2–3% moisture is ground to 200 mesh or still smaller sizes. The subsequent reduction roasting is the most critical step in the process. The objective is selectively to reduce nickel and cobalt to the metallic state while minimizing the reduction of iron. The roasting reaction can be represented in idealized form as:

$$\mathrm{NiO + 2\ Fe_2O_3 + 3\ H_2 \rightarrow FeNi + Fe_3O_4 + 3\ H_2O}$$

The Caron process plants universally use multiple-hearth roasters. Strongly reducing conditions are created by burning producer gas in the roasters with stoichiometric amounts of air. The hot reduced ore discharged from the roasters is first cooled to 150–200 °C under a reducing atmosphere and is then put into the quench tanks containing the ammoniacal ammonium carbonate leach solution. The leaching process is carried out in agitated tanks into which air is introduced in order to oxidize and dissolve the iron–nickel alloy. In spite of the high pH of the solution (about 10), hydrolysis of nickel and cobalt is prevented by their strong affinity for dissolved ammonia, which results in the formation of soluble nickel and cobalt complex amine ions. Iron, although initially dissolving in ferrous amine complexes, is rapidly oxidized to the ferric state and hydrolyzes and precipitates as ferric hydroxide, eventually leaving the process in the leach residues:

$$\mathrm{FeNi + O_2 + 8\ NH_3 + 2\ H_2O = Ni(NH)_3)_6^{2+} + Fe(NH_3)_2^{2+} + 4\ OH^-}$$

$$\mathrm{4\ Fe(NH_3)_2^{2+} + O_2 + 8\ OH^- + 2\ H_2O = 4\ Fe(OH)_3 + 8\ NH_3}$$

Following leaching, the pregnant leach liquor is separated from the undissolved barren solids by countercurrent decantation washing in a series of thickeners. The metal recovery process starts with the pregnant liquor overflow from the washing thickeners. The liquor is first filtered to remove suspended solids. Hydrogen sulfide gas or ammonium sulfide is then mixed with the liquor to bring about the precipitation of cobalt sulfide. The latter is somewhat less soluble than nickel sulfide, but because the leach liquor exhibits a high ratio

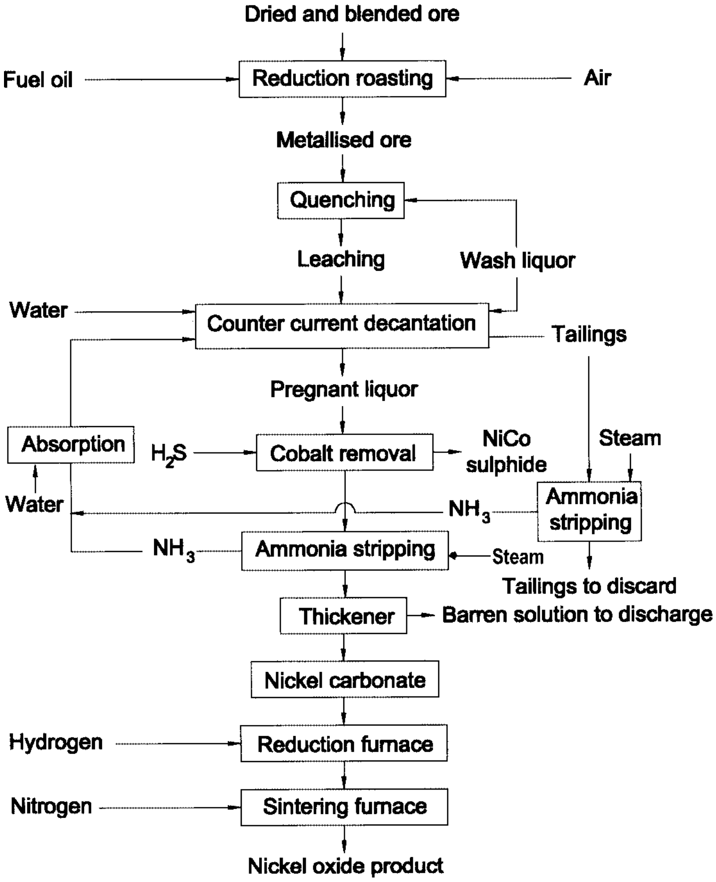


Figure 5.10 Caron process flowsheet.

of nickel to cobalt (typically about 20 to 1), the sulfide precipitate usually contains more nickel than cobalt, the nickel to cobalt ratio usually being about 2 : 1. The precipitated material is thickened, washed and dried and sold as a mixed sulfide by-product. The cobalt-free solution is taken to the nickel precipitation stage, where ammonia and carbon dioxide are removed from solution by steam heating in stripping stills, causing precipitation of basic nickel carbonate. Ammonia and carbon dioxide leaving the top of the stripping are recovered for reuse in the leaching circuit by absorbing the gases in water and returning the ammonium carbonate solution to the countercurrent decantation washing circuit. The dilute slurry of basic nickel carbonate leaving the bottom of the stripping stills is thickened and filtered. The filter cake is finally calcined in a rotary furnace to drive off carbon dioxide and to form nickel oxide. In a variation of the process, the calcined nickel oxide is compacted into pellets before sintering, which is carried out under either inert or reducing conditions. The advantages and the disadvantages of the Caron type processes have been presented in Table 5.6.

Table 5.6 Advantages and disadvantages of Caron-type process.

Advantages	*Disadvantages*
Theoretically speaking there occurs no consumption of leaching reagents, ammonia and carbon dioxide. These are recycled and only process losses are to be made up.	Energy requirements for drying and reduction are high – these front-end operations consume more than 60% of the total energy input to whole processes.
The process is selective for nickel and cobalt, with iron, the major component of the ore, remaining in the leach residue.	Overall metal recovery is low – typically 75–80% recovery of nickel and only 40–50% recovery of cobalt.
The ammoniacal systems do not cause corrosion problems and this allows use of standard materials of construction.	The process is mainly applicable to high iron limonitic laterites. The amount of acceptability of the transition ore (S-ore) is limited due to nickel loss caused by forsterite formation during the roasting process.

The scheme L2 is known as the Moa Bay process. The Moa Bay laterite deposits in Cuba are predominantly limonitic, high in iron, and relatively rich in cobalt. The Moa Bay ore has a much lower magnesium content and as such is suitable for direct attack with sulfuric acid at elevated temperatures and pressures. This approach has two major advantages over the Caron process. The first is the elimination of the energy-intensive drying and reduction steps of the Caron process. Secondly, recoveries of over 90% of both nickel and cobalt can be achieved. The process, however, is not applicable to garniertic laterites because the high magnesia content of these ores leads to excessive acid consumption. The key step in this process is the separation of nickel and cobalt from iron, which is in overwhelming excess, comprising almost 50% of the ore. This separation is achieved by exploiting the tendency of ferric iron to hydrolyze at elevated temperatures to form goethite, hematite and, in sulfate solutions, jarosites. Thus, by leaching with sulfuric acid at 240–260 °C, selective dissolution of nickel and cobalt is achieved, with less than 1 g iron per liter going into the pregnant leach liquor. A flowsheet of the process is shown in Figure 5.11. Leaching is carried out in four vertical autoclaves in series operated under pressure. The leached slurry is then taken through a heat exchanger into a flash tank to be brought down to the atmospheric pressure. Six stages of continuous countercurrent washing are used to separate the solids from the pregnant leach liquor. The liquor is then treated with coral mud for the purpose of neutralization. The high calcium carbonate content and the large surface area make coral mud a rapid and efficient natural neutralizing agent. After the removal of precipitated gypsum, the neutralized liquor at pH 2.4 is preheated and then pumped into a horizontal agitated autoclave where it is treated with hydrogen sulfide gas at elevated temperature and pressure. Under these conditions, the precipitation of nickel and cobalt sulfides takes place; after the reaction, the resulting slurry is cooled and the excess hydrogen sulfide gas is removed by flashing to atmospheric pressure. Thickeners are then used to wash and to concentrate the nickel–cobalt sulfide slurry to 65% slurry ready for shipment.

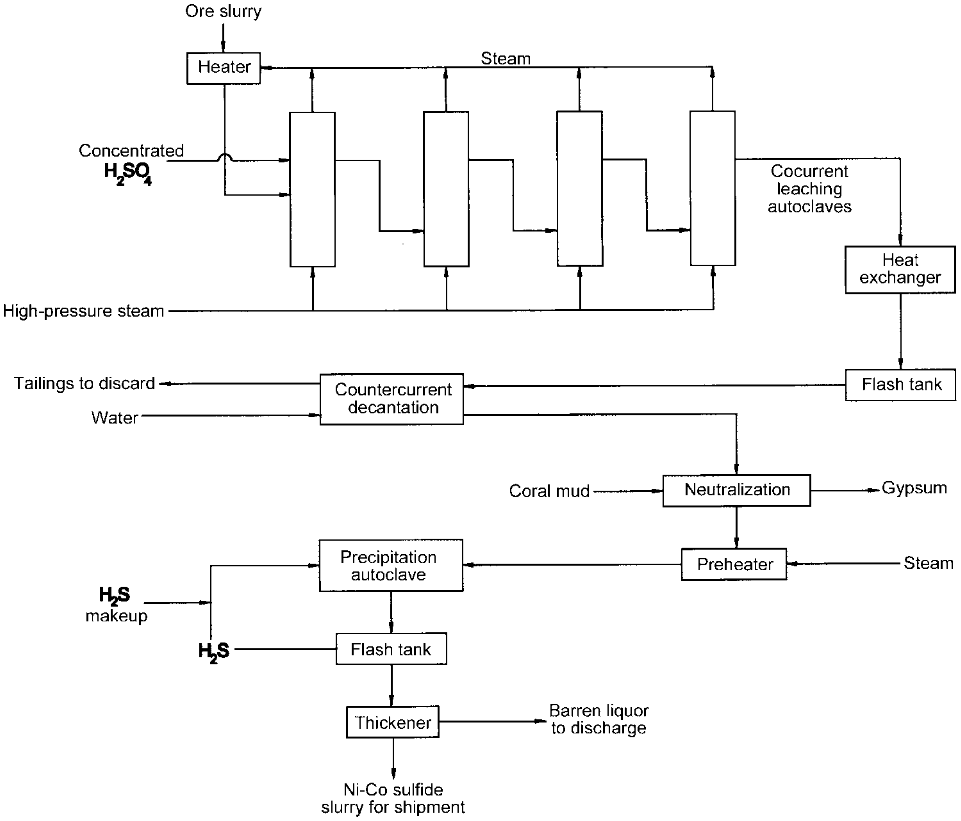


Figure 5.11 Flowsheet for the Moa Bay acid leach process.

5.2.4.4 Zinc Ore

The example being considered under zinc ore pertains to acid pressure leaching of zinc concentrates developed by Sherritt Gordon Mines Ltd. in Canada. The basic reaction involved is

$$ZnS + 0.5\ H_2SO_4 \rightarrow ZnSO_4 + S + H_2O$$

The zinc concentrate is ground well to obtain high zinc extractions. Single-stage, continuous-pressure leaching is carried out in two, three compartment, autoclaves operated in series. The leaching solution is spent electrolyte returned from electrowinning with makeup acid to replace sulfate lost from the process in the leach residues. After leaching, the slurry is cooled by two-stage flashing to atmospheric pressure. After a solid–liquid separation and residue washing step, the liquor is passed to neutralization and the residues to sulfur removal. A two-stage neutralization removes iron from the leach liquor. In the first stage, the liquor at 80–90 °C is neutralized to pH 3.5–4 with limestone. Air is sparged into the agitated neutralization reactor to oxidize iron, which hydrolyses and precipitates. In the second stage, further neutralization to pH 4.5 is carried out by using zinc dross. Copper losses in the second stage residue are significant, and so this is recycled. A purification process involving a treatment of the iron free liquor with zinc dust is carried out before coming to electrowinning. Sulfur removal from the leach residues is accomplished by screening and/or flotation. The composition of the sulfur flotation concentrate decide the subsequent treatment. The suggested methods include melting and pressure filtration or extraction with toluene. According to available reports, the process is known to have been extensively piloted and is close to realization on an industrial scale.

It will be interesting to record some of the evaluatory remarks as regards the process. There is no doubt that the direct acid pressure leach route is an attractive alternative to the conventionally followed process for zinc sulfide processing. Incentives for its adoption on a commercial scale are the reduced capital cost and production of sulfur in its most favored form, the elemental form. Nevertheless, no process is perfect and acid pressure leach process is not an exception. There are at least two aspects of the process which pose some problems. The first is the behavior of impurities, and the second is the disposal of iron.

In the conventional process, certain deleterious impurities are removed during the roasting of the zinc concentrates. In particular, these include Se, Hg, fluoride, and chloride. In the direct leach process, the first three of these are said to be removed either in the leach residues or during the iron precipitation steps. It is known, however, that selenium is difficult to remove from leach liquors produced by leaching copper concentrates. As selenium is very detrimental in the zinc electrowinning step, separate purification procedures may well be necessary to keep its level according to what is acceptable in the electrowinning cells for zinc. Any chloride in the zinc feed will report in the leach liquor and this has to be removed prior to electrowinning by either ion exchange or silver chloride precipitation.

Iron in the feed concentrate is rejected either as unreacted pyrite mixed with elemental sulfur or as jarosites in the leach residue. The pyrite/sulfur mixtures said to be suitable for indefinite storage, but the well known environment effects caused by pyrite weathering are likely to make storage of this material a less than straightforward problem. Besides this, there are problems associated with the disposal of the leach residues from the pressure leach process.

5.2.5
Bacterial Leaching

Bacteria can play an important role in accelerating reactions involving the oxidation of sulfide minerals and of ferrous iron. They are, in effect, catalysts for the oxidation processes. A significant amount of geological weathering is due to microbiological degradation processes, and the most important of these from the hydrometallurgical viewpoint is the dissolution of mineral oxidatively by acidophilic bacteria, *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*. Atmospheric reactions of the type,

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O = 2\ Fe^{2+} + 4\ SO_4^{2-} + 4\ H^+$$

followed by the type,

$$2\ Fe^{2+} + 0.5\ O_2 + 2\ H^+ = 2\ Fe^{3+} + H_2O$$

are very slow. *Thiobacillus ferrooxidans* is capable of promoting the latter reaction at a significantly greater rate. This reaction is a source of energy for the bacteria. The iron (III) ions that result from bacterial oxidation promote the dissolution of a range of sulfide and other minerals. At present, only two metals are recovered by bacterial leaching on a commercial scale – copper and uranium.

Copper sulfide minerals constitute the most significant source of the world's supply of the metal. The primary sulfide, chalcopyrite, is the most important of the sulfides; usually it is initially treated by froth flotation to enhance the copper content from, typically, 0.5–2% to 20–30% in a concentrate. Other copper sulfides are also important sources of the metal, notably the secondary sulfides chalcocite and covellite. The flotation concentrates of these as well as of the primary sulfide are smelted; this continues to be the preferred processing route. Smelting yields high copper and special metal recoveries, but there is also a perceptible swing towards hydrometallurgical processing of copper concentrates. Copper bioleaching is the single largest application of biotechnology in the mining industry. All the copper sulfide ores are amenable to bacterial oxidation, although some oxidize faster and to a greater extent than others. Chalcocite and covellite are particularly amenable to leaching, unlike chalcopyrite which exhibits slow kinetics and often poor recoveries. Copper recovery by dump leaching, in which large tonnages of waste or of marginal ore (which would otherwise be uneconomic to treat) are leached, has very significantly contributed to the total copper produced in the western United States. At present, dump bioleaching is used throughout the world, with significant developments in Chile, which is now the largest producer of copper in the world. In typical operations higher-grade copper ores processed in concentrators yield concentrates for smelting. Lower-grade ores and waste rock are put under leach in dumps in which bacterial activity assists in the oxidation and the solubilization of copper.

In the leaching process, bacteria such as T*hiobacillus ferroxidans* and those belonging to the S*ulfolobus* genera, play a major role in the oxidation reactions at moderate and higher temperatures respectively. The oxidation of sulfides by bacteria is typified by the reactions of pyrite, a common accessory mineral in primary copper ore bodies; this reaction can be considered to proceed through two stages:

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \rightarrow 2\ FeSO_4 + 2\ H_2SO_4$$

The soluble ferrous ions produced are further oxidized rapidly by the bacteria to ferric sulfate:

$$4\ FeSO_4 + O_2 + 2\ H_2SO_4 \rightarrow 2\ Fe_2\ (SO_4)_3 + 2\ H_2O$$

The primary copper sulfide, chalcopyrite, is oxidized in the presence of bacteria in accordance with the following reaction:

$$4\ CuFeS_2 + 17\ O_2 + 2\ H_2SO_4 \rightarrow 4\ CuSO_4 + 2\ Fe_2(SO_4)_3 + 2\ H_2O$$

Sulfide minerals can also be oxidized by the acidic ferric sulfate solutions produced (as shown in the last two equations), with the formation of elemental sulfur:

$$CuFeS_2 + 2\ Fe_2(SO_4)_3 \rightarrow CuSO_4 + 5\ FeSO_4 + 2\ S$$

Although the sulfur so formed can be further oxidized by the bacteria, the presence of surface coatings of sulfur and iron precipitation products on chalcopyrite are implicated for the incomplete reaction usually encountered in this mineral. The ferric sulfate formed during the oxidation of pyrite and chalcopyrite can hydrolyze to form ferric hydroxide, basic ferric sulfate or jarosite, depending on the pH. Under typical dump leaching conditions, jarosite formation is common

$$3\ Fe_2(SO_4)_3 + 14\ H_2O \rightarrow 2\ (H_2O)Fe_3(SO_4)_2(OH)_6 + 5\ H_2SO_4$$

It can be seen, therefore, that ferrous iron and chalcopyrite oxidation are acid-consuming reactions, while pyrite oxidation and iron hydrolysis are acid-producing reactions. Thus, whether the overall reaction in a dump is acid producing or acid-consuming depends on the relative proportions of chalcopyrite and pyrite and on the pH conditions. In practice, sulfuric acid additions to the leach solution applied to the dump are usually required to overcome the acid consuming reactions of the gangue minerals and to keep the pH in a suitable range, typically 2 to 2.4, to optimize bacterial activity and minimize iron hydrolysis.

The commercial processes involving bacterial leaching for copper are applied not only to dump leaching but also to the underground solution mining of copper. The dump containing low-grade copper mineralization is sprayed with an acidic solution containing ferrous iron for leaching. The bacteria are normally indigenous to such sulfide dumps, and grow and multiply as the leaching proceeds. The acidic mine effluent from a nearby mine could be used as an initial or additional source of leach liquor and bacteria. Care must be taken so that the acidity is not allowed to drop and the iron concentration is not allowed to increase much; should this happen, iron precipitates and leaching might suffer. The leaching process can be carried out on material containing both sulfide and nonsulfide copper minerals. The oxide minerals will dissolve in the acid solution without any assistance from the bacteria. However, if the minerals or gangue consume too much acid, a low pH will not be maintained and bacterial leaching of sulfides will not take place. Sulfuric acid can be added to depress the pH provided that the amount required is within economic limits. Bacterial dump leaching of copper is practised at various sites in the United States but the largest undertaking is at the Kennecott Corporation's Utah Copper Division, Bingham Canyon Mine, where daily mine production averaged 97,000 tons of ore and 32,000 tons of wastes in 1980.

A process called thin-layer bioleaching is a recent application originally developed for oxide copper ores by Sociedad Minera Pudahuel in Chile. This technology is being commercially used by Quebrada Blanca (Cominco) and by Cerro Colorado (Rio Algom) in Chile. The Quebrada Blanca plant will process 17,300 tons per day with projected recoveries of 80–90% from sulfide ores (primarily containing chalcocite) to produce 75,000 tons of copper per year. In this process, secondary copper sulfide ores are finely crushed, agglomerated by adding water and sulfuric acid, piled in low heaps and bioleached. The process is suitable only for copper recovery from secondary sulfides such as chalcocite. This is due to the relatively rapid oxidation kinetics and the more complete reaction obtainable with this mineral as compared to chalcopyrite leaching. The ores can also contain a good amount of oxide copper minerals which are rapidly leached under the acidic conditions. Pyrite is either absent or present in only small amounts so that the pyrite oxidation and iron hydrolysis reactions, which play a significant role in the performance of a dump leach operation, are of minor importance here. There are two stages through which bacterial oxidation proceeds. Chalcocite is readily converted to covellite by direct bacterial attack:

$2\ Cu_2S + O_2 + 2\ H_2SO_4 \rightarrow 2\ CuS + 2\ CuSO_4 + 2\ H_2O$

The covellite is then oxidized more slowly by the bacteria to the sulfate:

$CuS + 2\ O_2 \rightarrow CuSO_4$

Chalcocite and covellite are also oxidized by ferric sulfate, with the resulting ferrous sulfate reoxidized back to the ferric form. This mechanism is termed indirect bacterial oxidation. Ferric oxidation of chalcocite can also be seen to proceed through two stages, with very quick conversion to covellite in the first stage, and the completion of the oxidation in the second stage:

$Cu_2S + Fe(SO_4)_3 \rightarrow CuS + CuSO_4 + 2\ FeSO_4$

$Cu_2S + Fe(SO_4)_3 \rightarrow CuSO_4 + 2\ FeSO_4 + S$

The sulfur formed as a result of the last reaction is oxidized by bacteria in the following manner:

$2\ S + 3\ O_2 + 2\ H_2O \rightarrow 2\ H_2SO_4$

The sulfuric acid needed to solubilize copper from chalcocite is balanced by the acid recovered from the copper electrowinning step; this acid is recycled to the heaps. The overall acid requirements for the process are, therefore, dependent on the acid consumption by the gangue minerals in the ore and the acid production by pyrite oxidation. If the pyrite associated with the ore is significant and the acid consumption by the ore is low, excess sulfuric acid can be neutralized by lime.

The bacterial leaching of uranium minerals is complex. This is because of the fact that uranium minerals are not sulfides and are not, therefore, directly attacked by the bacteria. However, the uranium sources usually have a substantial pyrite content which can be bacterially oxidized to give an acidic ferric sulfate solution which is an effective leaching medium for uranium minerals. The reactions involved in the system can be shown in a simplified form as:

Pyrite oxidation:	$2\ FeS_2 + H_2O + 7.5\ O_2 \rightarrow Fe_2(SO_4)_3 + H_2SO_4$ (Bacteria-assisted reaction)
Uranium oxidation: (U^{4+} to U^{6+})	$UO_2 + Fe_2(SO_4)_3 \rightarrow UO_2SO_4 + 2\ FeSO_4$ (Chemical reaction)
Reoxidation: (Fe^{2+} to Fe^{3+})	$2\ FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O$ (Bacteria-assisted reaction)

The last reaction cited above as shown is very effectively catalyzed by bacterial action but is very slow chemically; by recycling the spent ferrous liquors and regenerating ferric iron bacterially, the amount of iron which must be derived from pyrite oxidation is limited to that needed to make up losses from the system, principally in the uranium product stream. This is important if the slow step in the overall process is the oxidation of pyrite. The situation is different in the case of bacterial leaching of copper sulfides where all the sulfide must be attacked to obtain copper with a high efficiency. A fourth reaction which may occur is the hydrolysis of ferric sulfate in solution, thus regenerating more sulfuric acid the ferrous-ferric oxidation consumes acid.

5.3
Solution Purification

Leaching processes are seldom, if ever, completely discriminative. Consequently, the resulting leach liquors contain impurities and almost invariably require purification prior to recovery of the recoverables. The purpose of solution purification is to remove undesirable impurities as well as to increase the metal concentration in certain cases, and this usually involves chemical separations. Enrichment of dilute solutions may bear out particularly useful in the subsequent metal recovery process in that much smaller volumes have then to be processed. Lower capital equipment costs may be the outcome. A more effective metal recovery may be the result. The range of methods used or potentially useful is very large indeed, and comprises in fact most of the procedures used in qualitative and quantitative analysis. However, the solution purification can be stated to be achieved by using any one or a combination of the following processes: (i) ion exchange; (ii) carbon adsorption; and (iii) solvent extraction. This grouping must include precipitation processes. They are, however, used for a variety of purposes. A later section devotes on the precipitation processes for metal separation and recovery aspects from solutions.

5.3.1
Ion Exchange

Ion exchange (IX) is a very useful technique for the concentration, the purification and the separation of chemically similar metallic elements present in an aqueous solution. In its most popular form of application, the metal-bearing aqueous solution is passed through a bed of solid organic resin in a particulate form wherein the sorption of the metal ions on the resin takes place by ion-exchange reactions. The pregnant resin is washed free of the entrapped feed solution and then brought into contact with an eluant of suitable composition and volume so that the resin releases the metal ions back to the eluant. The ratio of the volume of the feed and that of the eluant determines the extent of concentration that can be achieved. Purification and separation are achievable if the resin is selective or specific with respect to the metal ions of interest in comparison to impurity ions.

5.3.1.1 Ion-Exchange Equilibria

An ion exchanger is an insoluble solid, carrying accessible cations, anions or amphoteric ions. It differs from a strongly sorbing solid in that stoichiometric action takes place, the ions captured by the exchanger from the ambient solution being replaced in that solution by an equivalent number of similarly charged ions. Thus, ion-exchange involves a preferential, selective electrostatic interaction between the ions and the ion exchange leading to the capture of an ion by the ion-exchanger solid in accordance with their relative ionic sizes, valence and concentrations of the ions displaced by this capture.

Solid ion exchangers are solid electrolytes with inert matrices (M) to which are attached special polar groups (P) balanced by oppositely charged ions (I) which are available for exchange. These can be represented by the formula $M(PI)_n$. When the balancing ion I is removed, $M(PI)_n$ is sometimes represented as R^+ or R^-, depending on the nature of I. If P is negative, I is a cation and the material is a cation exchanger; if P is positive, I is an anion

Table 5.7 Types of ion-exchange resins.

Resin type		***Functional group***	***Mobile ion***	***PH range for exchange***	***Resin (regeneration, preparation) wash with***	***Trade names of market products***
Cationic exchanger	Strong acid	$-SO_3^-\ H^+$ $-SO_3^-\ Na^+$	H^+ Na^+	0–14 0–14	Dil. H_2SO_4, HCl, NaCl (brine)	Dowex 50, Dowex 50W, Amberlite IR 120, Duolite, C20, Permutit Q
	Weak acid	$-COO^-H^+$	H^+	4–14	Dil. HCl	Amberlite IRC-50, Amberlite IRC-84, Amberlite Xe-318
Anionic exchanger	Strong base	$-N^+(CH_3)_3Cl^-$ $-N^+(CH_3)_3OH^-$	Cl^- OH^-	1–14 1–14	NaCl NaOH	Amberlite IRA 400, Amberlite IRA 425, Dowex 1, Dowex 21K, Permutit SK
	Weak base	$-N^+H(CH_3)_2Cl^-$	Cl^-	1–8	Dil. HCl	XE-270, XE-299
	Chelating	CH_2COOH $-CH_2N$ CH_2COOH	H^+	4–14	Dil. H_2SO_4, HCl	Dowex XF-4195, Dowex XF-4196, Duolite ES-63, Duolite CS-346

and the material is an anion exchanger. The IX reaction with a specie, S, in an aqueous medium to be exchanged with a resin is

$$M(PI)_n + n\ S \pm = M(PS)_n + n\ I \pm$$

In precise terms, ion-exchange resins can be stated to consist of two principal parts – a polymeric organic network and ionized functional group which enter into exchange reactions. The different types of ion-exchange resins that are made are the various formulations of these two parts to provide the desired exchange and physico-chemical properties. There are five types of ion-exchange materials which are classified accordingly to their functional groups. As shown in Table 5.7, these are: (i) strong acid, (ii) weak acid, (iii) strong base, (iv) weak base, and (v) miscellaneous types of nonspecific structures, such as the chelating resins. The last one in the list is a specific exchanger in which the functional group has the property of a specific reagent. The specificity should, however, not be confused with selectivity. Because of its specificity, an ion exchanger can absorb one ionic species to the exclusion of others over a broad range of conditions. Some of the basic requirements of an effective ion-exchange material are presented in Table 5.8.

The selectivity of an ion-exchange resin means its ability to discriminate among different ionic species. A cation-exchange reaction can be represented by an equation of the form

$$P^-\ I^+ + M^+ = P^-\ M^+ + I^+$$

Table 5.8 Some of the basic requirements of an effective ion-exchange material.

1. High capacity.
2. Good equilibrium characteristics and capabilities of regeneration.
3. Very low solubility, so that it can be reused, and resistance to chemical attack by strong acids, bases, and oxidizing agents.
4. Physical stability and resistance to osmotic and hydraulic shock.
5. Particle size, shape, and density to give low pressure drops when operated as a filter bed as well as good backwash characteristics.

where M^+ is the metal cation which takes part in the exchange. The fractions of exchange sites occupied by I^+ and M^+ are respectively $[P^-I^+]$ and $[P^-M^+]$. For dilute solutions,

$$K = \frac{[P^-M^+][I^+]}{[P^-I^+][M^+]}$$

When the resin loading $[P^-M^+]$ is small and $[P^-I^+]$ and $[I^+]$ are large and their ratio is relatively constant, the ratio $[P^- M^+]/[M^+]$ is termed the distribution co-efficient (D_M). D_M is thus the ratio of the concentration of the metal in the resin to that in the solution. In a dilute solutions when two metal ions X^+ and Y^- are competing for adsorption sites at the same pH, then

$$\frac{[P^-X^+][I^+]}{[P^-I^+][X^+]} = K_x \quad \text{and} \quad \frac{[P^-Y^+][I^+]}{[P^-I^+][Y^+]} = K_y ,$$

so that

$$\frac{[P^-X^+][Y^+]}{[X^+][P^-Y^+]} = \frac{K_x}{K_y} = \frac{D_x}{D_y} = K_y^x$$

The quantity K_y^x is called the selectivity coefficient and indicates the ability of the resin to adsorb X^+ in preference to Y^+. When K_y^x equals unity, the exchanger shows no preference for X^+ over Y^+ and, consequently, for every separation it is important that the value of the selectivity coefficient should be as far away from unity as possible. The selectivity coefficient is not a true constant as it takes no account of activity coefficients. The selectivity coefficient value for a given ion is therefore influenced by its own concentration in, and the ionic strength of, the aqueous phase. It will also be dependent upon the nature of the ion exchanger. In general terms, for solutions of low concentrations, the selectivity coefficient increases with increasing atomic number and increasing valency of the metal ion. The affinity of metal ions for an ion-exchange resin may be expressed alternatively by distribution coefficient (D_M) defined earlier in the present paragraph. Distribution coefficients for two metals may be compared and ratio of the two is the separation factor (α). The separation factor is thus an expression for the selectivity of one ion relative to another and is analogous to the selectivity coefficient. In selecting ion-exchange resins, besides selectivity, a number of other chemical and physical properties must be considered. The ion-exchange capacity of a resin is a measure of the number of ions which are exchangeable in a given amount of the resin. This is commonly defined in terms of equivalents, eq (kg resin)$^{-1}$, where one equivalent is the ratio of the gram mole weight of ions exchanged to the charge on the ions. The exchange capacities of commercial resins range typically from 0.5 to 10 eq kg^{-1}.

Ion-exchange processes are strictly heterogeneous reactions that involve two phases. They, however, mostly comply with homogeneous, second-order reaction kinetics. An exchange reaction represented by

$$RA + M^+ = RM + A^+$$

can be considered to take place as a series of steps: (i) transport of M^+ ions from the bulk of solution across the diffusion layer enclosing the resin bead; (ii) diffusion of M^+ into the resin interior; (iii) exchange between A^+ ions and M^+ ions; (iv) diffusion of A^+ ions outwards to the surface of the resin bead; and (v) diffusion of A^+ ions across the diffusion layer into the bulk of solution. The diffusion processes taking place through the Nernst diffusion layer (steps (i) and (v)) may be termed film diffusion, while the processes taking place inside the resin phase are commonly referred to as particle diffusion (steps (ii) and (iv)).

The film diffusion stages (i) and (v) are similar to the external mass transfer stages in leaching and may be dealt similarly (see Section 2.1.3). Solution flow conditions for resin touching the fixed beds are likely to be in the laminar flow range.

Diffusion is not straightforward inside the resin phase, and this is due to the restrictive influences of the polymer network and because of the charge distribution connected with the fixed ions of the functional groups. The resin phase is consequently related to a porous solid. The effectual diffusivities of metal ions in the resin phase may differ but are largely less than those in the aqueous phase external to the resin phase. If Fick's law is applied to diffusion in a resin bead of radius, r, it may be represented as

$$J = \frac{dn}{dt} = -4\,\pi\,r^2\,D\,x\left(\frac{dC}{dr}\right)_R$$

where D_C is the effective diffusivity of a metal ion in the resin phase. The effective diffusivity, D_C, takes into account the tortuosity (τ) and the porosity (ε) of the resin in addition to the normal molecular diffusivity of the diffusing ion. The tortuosity factor is a measure of the increased diffusion path distance in the resin phase and is difficult to ascertain. The degree of cross-linkage in the resin structure is related to both tortuosity and porosity. Particle diffusion as the rate-controlling process is likely to be favored by a higher cross-linkage.

In hydrometallurgical processing, the rate-controlling process in the beginning stages of the ion-exchange reaction is likely to be film diffusion. However, as the actual zone of reaction moves interior from the surface of the resin bead, the diffusion path increases progressively. At some stage, particle diffusion probably takes over as the rate-controlling process.

5.3.1.2 **Familiarization**

It will be useful to become familiar with the commonly used terms associated with ion exchange practice. In the process, a resin contained in a column and the metal-rich solution is fed through it slowly enough to permit exchange to take place; this operation is called the *sorption step*.

The *total capacity* of the column is an indication of the total number of exchange groups it contains in terms of ion equivalents. In column, however, the *breakthrough capacity* is also an important parameter; this can be determined from a breakthrough curve. This curve is obtained by checking metal ion concentration in the effluent during the sorption step, and scheming this as a ratio of the effluent metal concentration versus the volume of influent-solution clearing through the column or versus the quantity of metal it holds. A series of breakthrough curves showing decreasing flow rate ($P_1 \rightarrow P_3$) are shown in Figure 5.12. The breakthrough capacity, as shown by the curves, is the quantity of ions that can be retained by a column under the particular conditions prior to leakage taking place into the effluent. Decreasing flow rate gives rise to a steeper curve and a higher breakthrough capacity. The breakthrough capacity is identical to the total capacity only when the flow rate is infinitely slow (Figure 5.12, curve P_3). The total capacity is denoted by the point of inflexion of a breakthrough curve. Consequently, in practice the breakthrough capacity is always less than the total capacity and parameters influencing its value include, in addition to flow rate, resin bead size, column dimensions, and temperature.

The *elution* or *regeneration* involves displacement from the resin of the ions retained on it by passing an excess of an electrolyte, termed the regenerant or eluant, through the column holding the resin. An elution curve of the type shown in Figure 5.13 (A) is obtained by scheming metal ion concentration versus the volume of solution coming out of the column (the eluate). In situations where two or more metals have simultaneously sorbed with the separation factors close to unity, selective elution may often be obtained by using an appropriate complexing agent. Thus, A may be separated from B, following cosorption on a cation resin column from say a sulfate solution, by elution with say hydrochloric acid (of a suitably chosen concentration) as shown in Figure 5.13 (B). The differential behavior is due to the

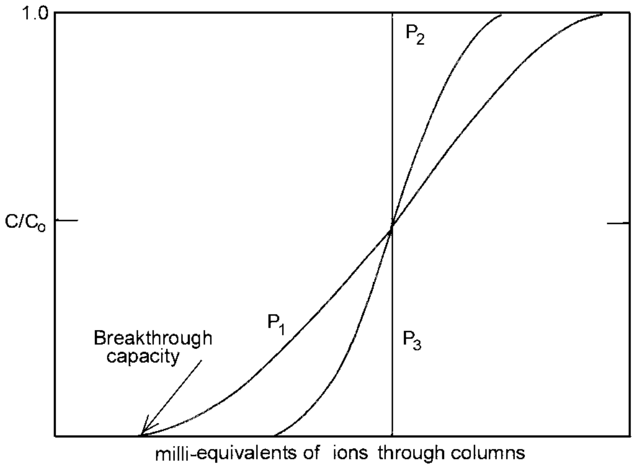


Figure 5.12 Sorption breakthrough curves – effect of flow rate of breakthrough capacity (C_0 = influent concentration; C = effluent concentration).

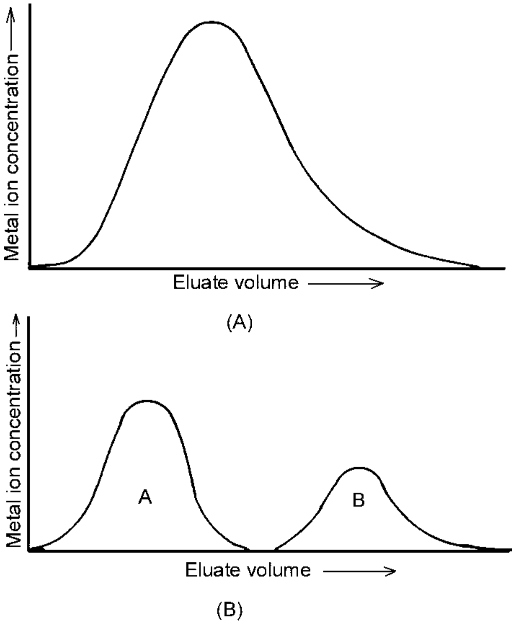


Figure 5.13
(A) Elution curve.
(B) Differential elution of A from B.

strong tendency of A to form an anionic chlorocomplex in the chosen acid concentration, whereas B remains essentially cationic. Elution of B may be represented by

$$R_2A + 4\ HCl = 2\ RH + HACl_4 + H^+$$

Hence, once a B ion is freed from the resin, it is immediately complexed and there is much less tendency for it to be resorbed lower down the column as would happen with a stable cationic species. This is an illustration of separation by elution analysis. Its most important application is in the separation of rare earths. When used on a laboratory scale in chemical analysis, this separation technique is known as ion-exchange chromatography.

Frontal analysis is the terminology used to the more usual ion-exchange separation technique where the desired metal is accepted on the resin column. The undesirable elements pass out unsorbed. The separation of a single metal in the cationic form on a cationic exchange resin column is not commonly very selective unless the undesirables are in the anionic form or uncharged. In contrast, frontal analysis using an anion exchanger provides much greater versatility. A number of metals form soluble anionic complexes with a wide range of complexing agents, and different systems have been found in terms of their characteristics or behaviors towards anion exchangers. The chloride ion complexes with many metal ions and may give rise to a series of complex ions with eventual anion formation. Thus in the case of Fe^{3+}

$$FE(H_2O)_6^{3+} \xrightarrow{Cl^-} Fe(H_2O)_5Cl_2^{2+} \xrightarrow{Cl^-} Fe(H_2O)_4Cl_2^+$$
$$\xrightarrow{Cl^-} Fe(H_2O)_3Cl_3 \xrightarrow{Cl^-} Fe(H_2O)_4Cl_4^-$$

A comprehensive survey is available in literature on the sorption behavior of elements over a range of hydrochloric acid concentrations. The compiled data show the following: (i) a number of elements exhibit no sorption tendency at all; (ii) many exhibit a change of behavior with hydrochloric acid concentration; and (iii) several cases exhibit high distribution coefficients over at least some part of the concentration range. It can be found out that there is a possibility of separating certain metal combinations not easily obtainable by conventional chemical means.

Study of anion exchange of metal ions in sulfuric acid shows that many metals are not significantly sorbed from sulfate solution. An exception to this is uranium, and this has been of paramount importance in the hydrometallurgical extraction of uranium following the leaching of uranium ores by sulfuric acid. Uranium is similarly strongly sorbed from carbonate solutions and face little competition from other metals, and this characteristic has been used in the separation of uranium following carbonate leaching. These areas have figured in the description on uranium resource processing given later in the chapter.

5.3.1.3 Process Description

In this section only one among the many ways in which the ion-exchange process is put to operation will be described. The pregnant liquid is first separated from the solid residue in the pulp after leaching is complete by decantation or filtration. This may be followed by further clarification. The liquor with its load of say C-type ions now percolates downward through what is called an IX column. This column is packed with resin beads loaded with ions of say type B. As the solution enters the column it deposits some of its C ions in a narrow zone near the entry point, and takes up an equivalent number of B ions. As the solution moves down, the resin becomes progressively loaded with C ions and the zone of exchange travels through the column until the resin bed approaches saturation. This stage is termed the "break-through point", and once this stage is reached, C ions begin to appear in the effluent, though the lowest zone is not yet fully loaded. In order to check the loss of C ions, a series of three IX columns is usually put on stream. The first column is isolated when the breakthrough point is reached. New pregnant solution is then led to the second column, the original third column now becomes the second column, and a freshly prepared column is introduced in behind it. This arrangement allows three in-line columns to be continuously loading while a fourth one is being regenerated (unloaded and re-activated).

When loading of the first column is stopped, its resin is usually not fully saturated. Some channelling of the bed may also have taken place, leading to an incomplete contact between the resin beads and the liquor, and if clarification has been incomplete then some surfaces may have been marked by slime. The next stage is usually a stirring of the bed by rising water, sufficient to scrub the beads without flushing them out. At the same time, the deposited slimes are detached and flushed out. This operation, called "backwashing", which also removes any residual undrained pregnant solution, is sometimes omitted.

The next stage is elution, in which the captured ions are displaced from their sites when a suitable chemical solution, called the eluant, is flushed through the column. With the completion of this operation, the resin sites are restored to their original state and the beads are stated to be regenerated. The new pregnant eluate is either stored or is administered a precipitating treatment; the column is subjected to a further backwash to remove its residual eluant. It is then fit to go on stream once more.

The chemical constituents of the backwash water (which may be acidified) and of the various eluants (recycling, new and special) are specific to the problem of displacing the captured ions from the resin and reactivating its sites. The final stage of IX, namely, the recovery in a solid form of the values from the eluting solution, is effected by chemical methods which yield the desired precipitate. This is settled out, filtered and dried for despatch.

5.3.2
Adsorption on Carbon

The process making use of adsorption on carbon involves first contacting a pregnant leach liquor with the adsorbent (activated carbon) and then stripping the species adsorbed on it. Activated carbon is a widely recognized as a metallurgical reagent that has found a number of industrial applications.

The adsorption process, in principle, is an anion-exchange process which is restricted only to the surface of the activated charcoal. This fact makes the loading or the exchange capacity of activated charcoal to be relatively smaller in comparison with ion-exchange resins, and it is for this reason that charcoals are quite often treated suitably to improve their loading capacities. The surface and the pore structure characteristics of activated carbon are the important factors upon which its industrial applications depend.

5.3.2.1 Surface and Pore Structure Properties

The adsorption action of activated carbon may be explained in terms of the surface tension (or energy per unit surface area) exhibited by the activated particles whose specific surface area is very large. The molecules on the surface of the particles are subjected to unbalanced forces due to unsatisfied bonds and this is responsible for the attachment of other molecules to the surface. The attractive forces are, however, relatively weak and short range, and are called Van der Waals forces, and the adsorption process under these conditions is termed as a physical adsorption (physisorption) process. In this case, the adsorbed molecules are readily desorbed from the surface. Adsorption resulting from chemical interaction with surface molecules is termed as chemisorption. In contrast to the physical process described for the adsorption on carbon, the chemisorption process is characterized by stronger forces and irreversibility. It may, however, be mentioned that many adsorption phenomena involve both physical and chemical processes. They are, therefore, not easily classified, and the general term, sorption, is used to designate the mechanism of the process.

The absorption property exhibited by active carbon certainly depends on the large specific surface area of the material, though an interpretation that it is based solely on this is incomplete. This is borne out by the fact that equal amounts of two activated carbon specimens, prepared from different raw materials or by different processes and having the same total surface area, may behave differently with regard to adsorption. Such differences can be partly explained in terms of the respective surface properties of the carbon samples and partly in terms of their relative pore structure and pore distribution. Every activated carbon particle is associated with at least two types of pores of distinctly different sizes. They are the macropores and the micropores. The macropores completely permeate each particle and act as wide pathways for the diffusion of material in and out of carbon, but they contribute very little to the total surface area. The micropores are more important since they contribute nearly all the available surface area for adsorptive action. The micropores result from the process of activation. It is thus seen that the overall contribution of the macropores to the total surface area and to the adsorptive capacity of activated carbon is negligible. The presence of macropores in carbon, therefore, can become a disadvantage in certain cases, since their excessive occurrence can lead to an undesirable loss of density. However, in situations where diffusion is the rate-controlling mechanism for adsorption, it is desirable that large macropores should be present in the material.

5.3.2.2 Mechanism

An electrochemical theory has been applied to explain the mechanisms of adsorption of metal ions on activated charcoal (carbon). According to this theory, oxygen in contact with an aqueous suspension of charcoal is reduced to hydroxyl groups with the liberation of hydrogen peroxide:

$$O_2 + 2\,H_2O + 2\,e^- = H_2O_2 + 2\,OH^-$$

Since carbon is a supplier of electrons, it acquires a positive charge in the process. In order to maintain electrical neutrality, carbon attracts the hydroxyl (OH^-) ions. When the aqueous solution contains metal anions that have a greater affinity towards carbon, the hydroxyl ions are exchanged. In support of this theory, mention may be made of the observation that no adsorption takes place in the absence of oxygen and that hydrogen peroxide is liberated when oxygen is bubbled through an aqueous slurry of charcoal.

5.3.2.3 Preparation

There are two main varieties of carbon: (i) crystalline (e.g., graphite and diamond), and (ii) amorphous. The amorphous variety consists of carbon blacks and charcoals. Carbon blacks are nonporous fine particles of carbon produced by the combustion of gaseous or liquid carbonaceous material (e.g., natural gas, acetylene, oils, resins, tar, etc.) in a limited supply of air. Charcoals are produced by the carbonization of solid carbonaceous material such as coal, wood, nut shells, sugar, synthetic resins, etc. at about 600 °C in the absence of air. The products thus formed have a low porosity, but when activated by air, chlorine, or steam, a highly porous material is produced; this porous product is called activated charcoal. Chemically speaking carbon blacks and charcoals are similar, the difference being only in physical aspects. Carbon blacks find use in the rubber industry and in ink manufacture. An important use of charcoals is as adsorbents.

The preparative process for activated charcoal as mentioned in the previous paragraph, involves a carbonization step which is followed by activation. In the carbonization step, for example, for making wood charcoal, wood pieces are mixed with a concentrated solution of zinc chloride (which serves as a dehydrating agent) and dried. Zinc chloride causes the hydrogen and the oxygen of the source to form water vapor rather than hydrocarbons or oxygenated organic compounds. The dried material is carbonized in the absence of air in the temperature range of 400 to 900 °C until all the zinc chloride is expelled. The carbonized product is then subjected to activation, which is usually carried out with steam or with air for a limited time at a temperature between 400 and 800 °C. The activation process carried out for charcoals at around 400 °C yields products known as L-charcoals; when the process is carried out at 800 °C, H-charcoals are produced. In the case of H-charcoals, cooling must be carried out in an inert atmosphere after the conclusion of the activation process, otherwise their conversion to L-charcoals takes place. H-charcoals are convertible to L-charcoals on heating in air at around 400 °C. Activated charcoals are produced both in a finely divided state and in a porous granulated form. The granulated products with sizes ranging from 3.35 to 1.18 mm, are used extensively in hydrometallurgical applications. In the carbon adsorption technique, the adsorbing power of activated charcoal for any given metal ion is expressed in terms of the loading capacity, which is the amount of metal in grams that can be adsorbed by each gram of activated charcoal. The maximum loading capacity of fine charcoal is 0.04 g Au g^{-1} charcoal for gold and 0.02 g Ag g^{-1} charcoal for silver. The activity of charcoal is a measure of the rate at which it adsorbs metals such as gold and silver irrespective of its ultimate loading capacity.

5.3.2.4 **Techniques**

The three different ways by which the carbon adsorption process can be implemented are: (i) carbon-in-column (CIC); (ii) carbon-in-pulp (CIP); and (iii) carbon-in-leach (CIL).

The CIC process is carried out much in the same way as the ion-exchange process. A series of large-sized cylindrical tanks are arranged in the descending order of their heights. Activated charcoal granules are placed over a multinozzle distribution plate provided at the bottom of each tank. The leach liquor is allowed to enter the first tank that is placed at the highest elevation from the bottom, travel through the bed at a desired rate, decant, and then flow by gravity through each of the successive carbon columns. In the countercurrent system, high-grade metal solutions comes in contact with the carbon that is almost fully loaded. Carbon removed from the first column is eluted is freed of metal ions and is returned to the last column. The solution overflow from the last column free of metal value and is pumped to the barren storage pond for reagent make-up and subsequent recycle back to the leaching stage.

The CIP process is the most widely used among the three popular method. This technique involves contacting the leached pulp with granular carbon in a series of gently agitated tanks with a sufficient retention time. The loaded charcoal is then easily separated from the pulp by screening and washing, and is then eluted for metal recovery. Both mechanically and pneumatically agitated tanks are used in a CIP circuit.

In the CIL process leaching and adsorption are not carried out separately but are combined into one operation. In this process the first tank is used only for leaching, while leaching and adsorption occur simultaneously in the remaining tanks. Since it is not necessary to build a separate adsorption section, there is an advantage in terms of savings in capital investment associated with the CIL systems.

The employment of charcoal adsorption in hydrometallurgical processes offers several advantages: (i) the process flowsheet is simplified, since thickening, washing, and filtration steps are avoided; this implies a reduction in the capital as well as the operating costs, and (ii) charcoal adsorption makes it possible to treat ores which are difficult to settle or filter.

5.3.3
Solvent Extraction

Solvent extraction (SX) is a separation/transfer procedure; if it is to be used it is required at first to identify the separation(s) desired, the main separation as well as the secondary ones.

If a constituent has the disposition to transfer from one liquid to another across the liquid–liquid boundary by whatever mechanism, then separation of the liquid phases will comprise also a separation of the constituent that has transferred.

If X is to be separated from Y, one must firstly assess, thoughtfully, whether X should be transferred away from Y or vice versa. Secondly, one must define the disparities in characters between X and Y which can be used for achieving the desired separation. Clearly, the more X discords from Y the more likely will it be that a high degree of separation can be attained. Next, it is necessary to identify the character or feature which is to be used for achieving the separation(s). For example, if an acid is to be separated from other acids, one needs to have some scale of comparison of the acids, so as to see whether separation can be anticipated from this scale, e.g., strong acids versus weak acids, or the tendency to complexation, hydrogen-bonding, etc.

Once it is known that what is to be separated from what, and how one hopes to foster the separation, one can consider solvent extraction. The attributes of the solvent, which must interlock with the chosen attributes of the solute being separated, need to be identified. Once the attributes of the solvent have been stipulated, it is viable to determine what the constituents of the solvent will be.

Solvent extraction (SX) separation serves the same purpose and relies on similar principles as does ion exchange, but here the nonaqueous phase is a liquid substance instead of a solid substance. Hence the process is often called liquid–liquid extraction. The process, as used in hydrometallurgy, consists of contacting an organic solvent with an aqueous solution containing the desired metal constituent. During the contact, for chemical reasons, the desired metal is transferred preferentially from solution in the aqueous phase to solution in the organic phase. Because the organic solvent and aqueous phase are immiscible, they separate when the mixing ceases. This initial process is called the extraction stage.

The products of the extraction stage are the organic solvent, loaded with the desired metal or metals, and the aqueous extraction raffinate. Originally, the term raffinate indicated a refined product but now it refers to a residual aqueous phase after the extraction of some specified solute. The extraction raffinate could either go to waste or to further processing. The loaded solvent from the extraction process may be scrubbed by treatment with a fresh aqueous phase in order to remove the contaminating impurities. The scrubbed organic solvent is then stripped in order to remove the desired solute or solutes. Scrubbing and stripping are two entirely different processes which, unfortunately, are often considered synonymous. The organic solvent, after stripping, is recirculated back into the extraction process. The net result of the technology involving the three principal stages, namely, extraction, scrubbing and stripping, is the separation of an impure aqueous stream into two aqueous streams, one containing most of the impurities and the other containing most of the valuable metal ions.

To provide a more generalized picture for achieving separations by solvent extraction one can consider a number of possibilities, according to direction of transfer. Such possibilities are: (i) pre-extraction (aqueous → solvent); (ii) extraction (aqueous → solvent), scrubbing (solvent → aqueous); (iii) stripping/back extraction (solvent → aqueous); and (iv) solvent clean up (solvent → aqueous → solvent). The direction of transfer has been shown in the parentheses of the four possibilities that have been listed. A reference to Figure 5.14 is relevant in this premise.

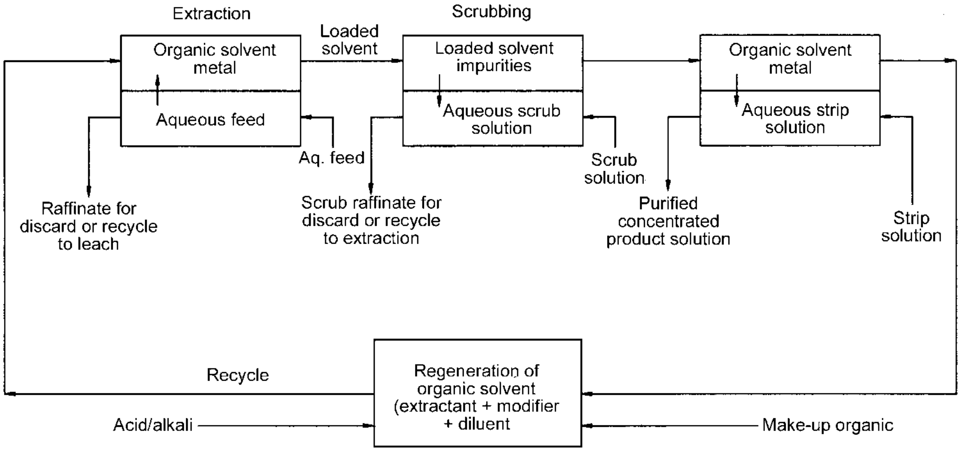


Figure 5.14 Generalized solvent extraction process flowsheet.

Solvent extraction owes its origin to analytical chemistry in which dilute aqueous solutions are concentrated by using an extractant reagent in the organic phase. Solvent extraction is no longer what it started out as, whence it was an unit operation of very limited applicability, justifying only the smallest fraction of cognizance directed to other unit operations of more major interest such as distillation, heat transfer and the like. However, separation and recovery from solution constituted a very fundamental need in chemical processing – in all its variations and branches – so the potential for applying solvent extraction was in fact unlimited, so to say. It was the nuclear industry which pioneered the industrial use of solvent extraction for the separation and purification of nuclear metals and materials. The preparation of plutonium for nuclear weapons in 1942 used the solubility of uranyl nitrate in diethyl ether, and this was the forerunner of a large number of applications of solvent extraction in the nuclear industry and elsewhere. At the present time, solvent extraction is in commercial use for a wide range of metals including copper, nickel, cobalt, chromium, uranium, vanadium, molybdenum, tungsten, zinc, the rare earths, the platinum group metals, tantalum/niobium, zirconium/hafnium, and gold.

5.3.3.1 Technical Aspects

In the simplest cases, the solvent may consist of one specified component, although in fact in a steady-state cyclic process it is highly unlikely that the solvent will ever come back to the initial composition at time zero. Rather, perhaps, one can say that make-up will entail addition of one material only. Again, clearly this need not be a pure compound, but its composition should be consistent. The single solvent offers limited scope for manipulating the system since it alone must meet all process and operational requirements. In other words, it must satisfy all aspects that will lead to an overall viable system. These aspects include selectivity, capacity, solubility, mass transfer, phase separation, costs, among others. The solvent is, therefore, a mixture components. The solvent components are: extractant, (ii) diluent, (iii) modifier, and (iv) synergist.

5.3.3.1.1 **Extractants**

The extractant is the vital, the active and the central component or ingredient of the organic solvent phase. In principle, choice of extractants would seem to be limitless in scope, but in fact, of course, this is not so. There are a number of general features which are essential for an extractant if it is to achieve the extraction of the desired metal. These are: (i) to have the ability to extract the metal at the required pH; (ii) to be selective for the required metal and to reject undesired metals; (iii) to have acceptable rates of extraction, scrubbing and stripping; (iv) to be soluble in the organic phase and to have a very restricted solubility in the aqueous phase; and (v) to be stable throughout the principal stages. Very often, these criteria are mutually incompatible so that it is important to achieve a balance between them. Examples of situations where these criteria are in conflict with each other are to be found throughout the solvent extraction literature.

According to the principle of extraction, the organic extractants can be classified into four classes: (i) solvating (neutral); (ii) cationic (acidic); (iii) anionic (basic); and (iv) chelating. The trade names and chemical names of the various extractants have been presented in the figures illustrating the classification.

Solvating extractants are organic liquid extractants which are used to extract metals from an aqueous phase by the solvating action. The process involves the formation of an addition complex comprising undissociated, electrically neutral molecules and the organic extractant. The addition complex thus formed is more soluble in the organic phase than in the aqueous phase. This obviously leads to the transfer of the neutral species from the aqueous to the organic phase. As an example, reference may be drawn to iron in the form of ferric iron. This is soluble in aqueous but not in organic solutions; however, high chloride concentrations, such as those provided by hydrochloric acid solutions, brings about anion formation:

$$Fe(H_2O)_6^{3+} + 4\ Cl^- = Fe(H_2O)_2Cl_4^- + 4\ H_2O$$

This is followed by solvation with diethyl ether molecules to yield $Fe[(C_2H_5)_2O]_2Cl$. Diethyl molecules may become protonated by reaction with oxonium ions:

$$(C_2H_5)_2O + H_3O^+ = (C_2H_5)_2OH^+ + H_2O$$

and electrostatic attraction between the two types of ions results in the formation of an ion association compound:

$$(C_2H_5)_2OH^+ \cdot Fe[(C_2H_5)_2O]_2Cl_4^-$$

Thus, dehydration and charge neutralization are obtained favoring transfer to the organic phase.

As examples of a number of solvating extractants of various types, mention may be made of phosphoric and phosphonic acid esters; phosphine oxides; various alcohols, ethers, ketones; and alkyl sulfides. Among these solvents, tributyl phosphate (TBP) is the most widely used solvating extractant. It is preferred over amine extractant in processes for recovering acids from pickling liquors because of higher loadings and better phase separation behavior. It also competes with methyl isobutyl ketone for niobium–tantalum and zirconium–hafnium separations, as it has the advantages of lower losses and a much lower flammability.

Cationic extractants are organic liquid extractants in which the transfer of metallic species from aqueous to organic phase takes place through ionic interaction. Cationic-exchange processes involve the exchange of metal cations with the hydrogen ions of the reagent dissolved in the organic phase. A cationic extractant is also called acidic extractant, the exchange process being represented by the following equation:

$$M^{n}+ \text{ (aq)} + n \text{ RH (org)} \rightleftharpoons MR_n \text{ (org)} + n \text{ H}^+ \text{ (aq)}$$

where M is an n-valent metal cation, RH is an organic species with an ionisable H^+ ion (the organic acid representing a cationic extractant), and MR_n is the organometallic molecule. The liquid cationic extractants are classified into two broad groups: carboxylic compounds, and organophosphorus compounds. As examples of carboxylic compounds, mention may be made of versatic and napthenic acids. The dissociation of carboxylic acids is weak in highly acidic solutions, and they are therefore the most effective in the pH range of 7 to 7.5, the pH being a critical factor in their full utilization. As indicated in the above equation, the extraction of the metal is associated with the liberation of an equivalent amount of H^+ ions with the result that the pH goes down so that further extraction is progressively impeded. To overcome this problem, a continuous neutralization of the liberated acid by the addition of an alkali such as sodium hydroxide is necessitated. During such neutralization, sodium salts of the reagent form and these are highly soluble in the aqueous phase. This leads to a significant loss of the extractants and this is the reason why carboxylic acids are not very popular reagents in metal extraction. As examples of organophosphorus compounds mention maybe made of di(2-ethylhexyl) phosphonic acid (D2EHPA); octyl pyrophosphoric acid (OPPA); octyl phenyl acid phosphate (OPAP); dialkyl phosphinic acid (Cyanex 272); di-alkyl phosphonic aicd mono-2 ethylhexyl ester (PC 88A, P-507, Ionquest 801). Of the organophosphorus compounds, which constitute the second variety of acidic extractants, D2EHPA is the most widely used extractant, though during recent years other reagents such as di-alkyl phosphonic and phosphinic acids are also being made available commercially. In fact, phosphonic acid, marketed under several trade names (PC 88A, P-507 and Ionquest 801), has been proved to be a better extractant for separation of nickel and cobalt, and has replaced D2EHPA in rare earths separation technology.

Anionic exchange extractants are frequently termed liquid anion exchangers. These function essentially in the same way as cationic extractants except that they extract anionic species from the aqueous phase. These are also called basic extractants. Since only limited number of metals can form anionic species (also under specific conditions), anionic extractants can selectively recover and purify certain metallic elements. Liquid anion exchangers are essentially long-chain alkalyamines and are classified as being of primary (RNH_2), secondary (R_2NH), and tertiary (R_3N) varieties. In addition, quaternary ammonium halides also find applications as extractants of the anionic type.

The amines require protonation before they can act as anion exchangers and thus show acid extraction properties in the free base form. For example, a tertiary amine has to react with an inorganic acid in accordance with a reaction of the type:

$$R_3N \text{ (org)} + H^+ + A^- \rightleftharpoons R_3NH^+A^- \text{ (org)}$$

prior to its participation with a metal-bearing anion, say B^-, in the following way:

$R_3NH^3A^-$ (org) + $B^- \rightleftharpoons R_3NH^+B^-$ (org) + A^-

In the case of a dibasic acid such as sulfuric acid, the normal as well as the acid salts of the amine are formed as shown by the reactions:

$2\ R_3N$ (org) + $H_2SO_4 \rightleftharpoons (R_3NH)_2SO_4^{2-}$ (org)

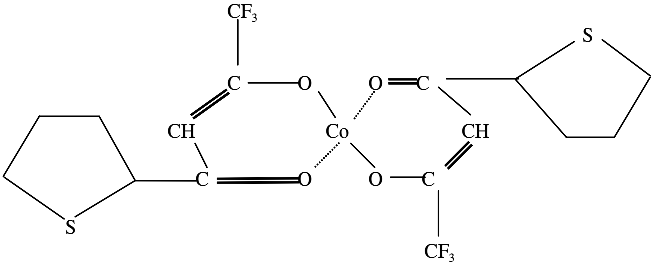
$(R_3NH_2)_2SO_4^{2-}$ (org) + $H_2SO_4 \rightleftharpoons 2\ R_3NHHSO_4^-$ (org) + $2\ H^+$

In contrast, quaternary amine salts can participate in an exchange reaction directly with the aqueous solution as indicated below:

$R_4N^+A^-$ (org) + B^- (aq) $\rightleftharpoons R_4N^+B^-$ (org) + A^- (aq)

It is interesting to note that some metal ions may exist in solution partly as cationic and partly as anionic species. The uranyl ion is a good example. From sulfate solution it is possible to extract species such as $UO_2(SO_4)^{2-}$ with amines. The uranyl cation, on the other hand, can be extracted with acidic extractants such as D2EHPA.

Chelating extractants (the liquid organic extractants) by virtue of the manner of their extractant action, are said to belong to the category of acidic extractants. These reagents are essentially hydroxyoximes or oxine derivatives or ketones. The examples under hydroxyoxime group include ketoxime (LIX 63, LIX 70, LIX 84), aldoxime (LIX 65, LIX 860), aldoxime + ketoxime (LIX 64N (LIX 65N + LIX 63) + LIX 984 (LIX 860 + LIX 84)), aldoxime + modifier (acorga P 5100 (modifier: nonylphenol), acorga PT 5050 (modifier: tridecanol), acorga M5640 (modifier: ester), LIX 622 (modifier: tridecanol); those under oxime derivates include alkalyted 8-hydroxy quinoline (kelex 100, LIX 26); those under diketones include betadiketone (LIX 54, X 151, hostarex DK 16, Hoechst AG). The essential feature of these extractants is that they show chelation behavior; that is, the formation of ring structures involving the extractant molecule as a ligand to the metal ion. In order to illustrate the point, mention may be made of cobalt forming a complex with thenoyltrifluoro acetone (TTA), a betadiketone. The structure of the cobalt–TTA complex is shown below:



The given structure shows two molecules of TTA to have reacted with a cobalt ion to form the cobalt–TTA complex, in which the cobalt atom forms a valence bond solid lines) with one, and a coordinate bond (broken lines) with the other, oxygen atom of each TTA molecule. Thus, in the cobalt–TTA complex there is a six-membered ring formed by each TTA molecule with the cobalt atom. Metal chelate complexes of this type have good stability, they are nonpolar and soluble in the organic phase. The usefulness of the chelating extractants in solvent extraction is therefore obvious.

5.3.3.1.2 **Diluents**

The diluent, or carrier solvent, is mainly required as an diluting medium to lower the viscosity of the organic extractant and make it more mobile. The following properties of the diluent should all be low: cost, stability in the aqueous phase, viscosity, vapor pressure, flammability, rate of evaporation, and toxicity. It should be stable and should have good solubility for the complexed and the uncomplexed extractant. A low flammability, or in other words, a high flash point and a consistent low rate of evaporation, are especially important properties in plants erected in countries having high ambient temperatures, or where it is proposed to run the solvent extraction process at a high temperature. Many diluents have been considered and used in the extractive metallurgical field. Diluents may be purely aliphatic compounds such as carbon tetrachloride or chloroform, purely aromatic such as xylene or toluene, or could be mixtures of these compounds. Commercially available diluents are generally mixtures. It is noteworthy that, apart from the complex composition of commercial diluents, their aromatic-to-aliphatic content remains a major feature.

5.3.3.1.3 **Modifiers**

Sometimes a third phase or emulsion tends to form during the extraction stage. Invariably it is the organic phase that splits into two to yield a metal complex-rich phase at the aqueous interface and a diluent-rich phase above. To overcome this problem, after the extractant and diluent, a third component known as a modifier is added to restore these organic phases into a single phase. The commonly used modifiers are: (i) long-chain alkyl alcohols like isodecanol and 2-ethylhexanol; (ii) nonylphenol; and (iii) extractants of the neutral category like TBP. The example given for solvent extraction of copper earlier has illustrated a typical role of a modifier.

5.3.3.1.4 **Synergists**

Sometimes it so happens that two solvents, belonging to different categories or to the same category of solvents, are mixed together to yield a mixed solvent that may have properties which are orders-of-magnitude different vis-à-vis what could be expected by considering the properties of the individual solvents. This phenomenon is known as synergism. In a synergistic situation, properties are not simply additive in nature. When two extractants (A and B) are mixed together, the distribution ratio of the mixture (D_{AB}) is different from the sum of the distribution ratio of A(D_A) and of B(D_B), each acting individually. Thus, $D_{AB} = D_A + D_B + \Delta D$. If the extraction increases (ΔD is positive), the effect is called synergism, and if extraction decreases (ΔD is negative) it is called antisynergism. The component which normally exhibits a low or practically no extraction for the metal is said to be a synergistic agent and enhances the extraction power of the second component which is the primary extractant. A well-known synergistic combination is that of D2EHPA, and neutral organophosphorus compounds like tri-octyl phosphine oxide, TOPO, for the recovery of uranium from phosphoric acid. In this case, D2EHPA is the primary extractant and TOPO is the synergistic agent.

5.3.3.2 **Solvent Extraction Terminologies**

In addition to those already described, a number of other terminologies have been used to delineate quantitatively solvent extraction. The text that appears hereunder describes (in sequence) transfer coefficients, phase ratio, percent extraction, separation factor, enrichment factor, and multiple extractions. This listing represents largely the main language used to convey various aspects of solvent extraction process. Transfer coefficients in solvent extraction are the distribution coefficient and stripping coefficient. The distribution coefficient, D, which measures the transfer of metal ions from an aqueous phase to the organic phase, is defined as:

$$D = \frac{\text{Concentration of metal in organic phase}}{\text{Concentration of metal in aqueous phase}}$$

It is clear that the greater the value of D at equilibrium, the greater the extractability of metal ions in question by the extractant concerned. The stripping coefficient, E, is the inverse of D; hence, the greater the value of E at equilibrium, the greater the tendency of metal ions to be shifted to the aqueous phase. The different ways by which stripping is carried out are: (i) back-washing the organic phase; (ii) selectivity, when the extractant is weighed with more than one metal (in this instance different stripping agents are deployed consequently); and (iii) precipitation of metal values directly from the organic phase. The two golden purposes of the stripping process are: (i) to retrieve the metal values weighed into the organic phase; and (ii) to provide the extractant a rejuvenation for recycle.

Phase ratio is given by the volume ratio of the two phases, and its significance is in the solvent extraction process. A small organic to aqueous ratio although beneficial ideally, it is sometimes unwelcome because it may result in high solvent losses. A raised organic to aqueous ratio, on the other hand, needs a large reservoir of solvent, and this may imply a financial burden.

In the extraction process it may so happen that volume changes occur of the organic and aqueous phases. This change in volumes must be taken into account in the calculation of D. The volume change owes due to the relocation of metal species from one phase to the other or due to the mutual solubility of the phases concerned. The volume changes attributed to solubility of phases mutually may be cut down by adopting the practice of equilibration of the organic phase with water prior to extraction.

Percent extraction as the term implies provides directly a measure of effectiveness a solvent or a strippant used in solvent extraction. The mathematical expression of percent extraction is quite simple to derive simply from elementary considerations. This fact, therefore, spares the need to deduce. The expression for percent extraction, P, is shown as:

$$P = \frac{D}{D + V_a / V_o} \cdot 100$$

where D is the distribution coefficient, V_a is the volume of the aqueous phase, and V_o is that of the organic phase.

Separation factor, as the terminology implies, concerns the accomplishment of separation of say one metallic species from the other. When two metal ions, X and Y, are required to be extracted from an aqueous solution, the separation factor, S, of the two metal ions is given by:

$$S = \frac{D_X}{D_Y}$$

where D_X and D_Y are the distribution coefficients of the two metals. It is implicit in the given relationship that separation tends to be greater and greater as S tends to departs further and further from 1. There is no separation when S equals 1.

The enrichment factor, F, is given by:

$$F = \frac{P_X}{P_Y}$$

Where P_X and P_Y represent respectively percent extractions X and Y. Working further on the expression of F given above, the following may be written:

$$F = \left(\frac{D_X}{D_X + V_a / V_o} \cdot 100 \right) \div \left(\frac{D_Y}{D_Y + V_a / V_o} \cdot 100 \right)$$

$$= S \cdot \frac{D_X + V_a / V_o}{D_y + V_a / V_o}$$

From the expression provided above it may be pointed out that to have a high enrichment it is necessary to have not only the separation factor, S, high but that the volume of organic phase must also be as small as possible in comparison to aqueous phase. It can be left as a simple exercise to the reader to examine the fact that enrichment factor, F, enhances with enhanced V_a/V_o.

Multiple extractions expression may be derived by considering a certain volume, V_a, of the aqueous phase containing m_a grams of solute and a certain volume, V_o, of the organic phase. With first extraction concluded, the weight of solute left in the aqueous phase is considered to be m_1. The equilibrium concentration in aqueous phase is then equal to m_1/V_a and the equilibrium concentration in organic phase is equal to $(m - m_a)/V_o$. The process so far permits the following expression:

$$D = \frac{(m_a - m_1)/V_o}{m_a / V_a}$$

Rearrangement of the expression above leads finally to:

$$m_1 = m_a \cdot \frac{1}{1 + D\, V_o / V_a}$$

A second extraction is considered, and in that case the weight of the solute left in the aqueous phase is taken to be m_2. Like those while on first extraction, the equilibrium concentration in aqueous phase is equal to m_2/V_a and the equilibrium concentration in organic phase is equal to $(m_1 - m_2)/V_o$. The expression for D in the second extraction process carried out is as follows:

$$D = \frac{m_1 - m_2 / V_o}{m_2 / V_a}$$

Rearrangement of the above expression, like the preceding case of the first extraction, leads the final expression to:

$$m_2 = m \cdot \left(\frac{1}{1 + D\, V_o / V_a} \right)^2$$

It is thus possible to record the expression for m_n, the weight of solute left behind in the aqueous phase after n extractions. Such an expression is:

$$m_n = m \cdot \left(\frac{1}{1 + D\, V_o / V_a} \right)^n$$

Replacing weight by concentration terms,

$$C_n = C_i \cdot \left(\frac{1}{1 + D\, V_o / V_a} \right)^n$$

where C_n is concentration after n extractions and C_i is initial concentration in aqueous phase.

Certain practically interesting facts ensue from the expression given above. In order to keep the concentration of metal staying in the aqueous phase minimum (or in other words to enhance efficiency of extraction) for a given value of distribution ratio, D, n should be large. The total volume of the extracting liquid is equal to $n \cdot V_o$, which is a constant. Hence, it is more beneficial to keep n large and V_o small. Thus, for a given volume of solvent to be used, a large number of extractions, each using a small volume of the solvent, will yield the lowest residual metal concentration in the raffinate.

Besides solvent extraction, there are other examples where benefits accrue by resorting to the mode of separation described above. In washing of precipitates, for example, the distribution of the impurity between water and the precipitate is known, and for the reason given it would be more effective to use small quantities of water and repeat the process a number of times. As another example, Parke's process may herein be recalled. The process, it may be reaccounted, is used for desilverization of lead. In this process, zinc is used to extract silver from argentiferrous lead. Zinc and lead, in their molten conditions, are not miscible with each other and silver is more soluble in zinc than in lead, the distribution ratio being 300 : 1 in favor of zinc at 800 °C. Therefore, when argentiferrous lead is heated to 800 °C and made to come in contact with zinc, silver transfers from the lower lead layer to the upper zinc layer and by repeating this operation with fresh batches of zinc, most of the silver associated with lead can be removed. It must be realized that it is impossible to extract the entire amount of a dissolved substance, however large the number of extractions may be. Each time, the substance in question distributes itself between the two solvents and an amount, howsoever small, must always remain unextracted or, in other words, be left behind.

5.3.3.3 Countercurrent Extraction

An infinitely large volume of solvent is needed to achieve complete extraction of a solute in a single stage. This necessitates application of multistage extraction. It allows essentially complete recovery deploying a limited volume of the solvent. In the countercurrent process, the organic phase and the aqueous feed course in opposite directions. Thus, the nearly infertile raffinate establishes contact with the fresh extractant, while fresh aqueous feed establishes contact with the nearly saturated extractant.

The countercurrent extraction is shown schematically in Figure 5.15. The organic course volume is denoted by O, and the corresponding aqueous flow volume is designated by A. The concentration of the extractable species are x and y in the aqueous and organic phases, respectively. There are n stages, and mass balance over them is:

$$\mathrm{A}x_0 + \mathrm{O}y_{n+1} = \mathrm{A}x_n + \mathrm{O}y_1$$

The relationship above may be arranged to provide finally the following:

$$y_1 = \frac{\mathrm{A}}{\mathrm{O}}(x_0 - x_n) + y_{n+1}$$

The equation above is a straight line of gradient, A/O. The composition of the organic phase going out of the first stage (y_1) is a linear function of the composition of the aqueous phase leaving the nth stage (x_n). The values x_0 and y_{n+1}, composition of aqueous and organic phases prior to countercurrent contacts, are constants.

A diversion from the present content is taken to refer to representation of extraction data. They may be represented in two ways. One representation is through bringing out of percentage extraction as a function of variable such as concentration, pH, etc.; the other is in the form of extraction isotherms. The extraction isotherms are the layout obtained of the concentration of the metal's ion in the aqueous phase as a function of its concentration in the organic phase at the point of time when equilibrium between the two phases becomes established. Such a layout or chart is helpful, since at each point it directly conveys the concentrations in both phases and this readily allows calculation of distribution coefficients. The construction of distribution isotherms may be carried out in two ways, and in view of their availability in a good many of elementary texts on hydrometallurgy, this presentation does not include their descriptions. With an addition of an operating time based on the volume ratio of the aqueous and organic phases, the distribution isotherms offers a McCabe-Thiele diagram for carrying out a stage-wise analysis of extraction in the solvent extraction system working countercurrently.

A McCabe–Thiele diagram is helpful for assessing the number of theoretical stages needed to achieve specified results in a solvent extraction system. Since the operating line is based on mass balance, the concentration of solute in the aqueous feed going into any stage and the organic phase going out of any stage, are coordinates of points on the operating line. Since the operating line is straight, it is settled by any two points. Alternatively, it can be settled by only one point and the ratio of aqueous to organic feed that decides the gradient of the line.

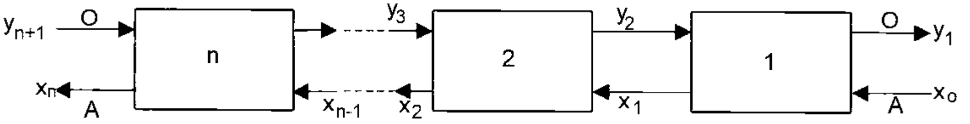


Figure 5.15 Countercurrent extraction.

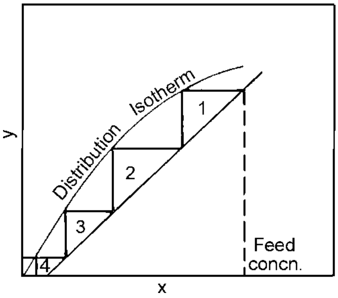


Figure 5.16 Extraction equilibrium diagram.

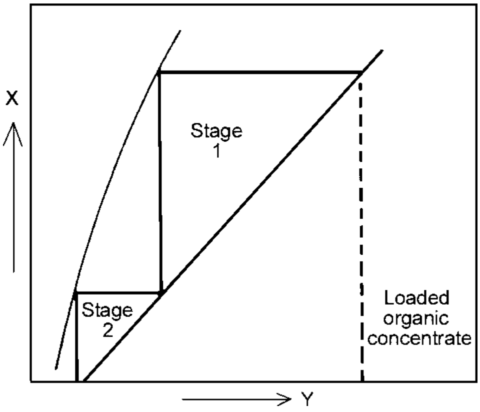


Figure 5.17 Stripping equilibrium diagram.

A McCabe–Thiele diagram (Figure 5.16) indicates how to determine the construction bound between the operating line and the distribution isotherm. The intersection of each pair of vertical and horizontal lines with the operating line implies the amount of the solute of the aqueous raffinate going out of an ideal stage, and the organic feed entering that stage.

It is by now well known that stripping is as a important phase of operation in solvent extraction as the extraction phase of operation. A stripping equilibrium diagram can be produced analogous to the diagram for extraction but with the axis reversed (Figure 5.17), and the number of stages needed to reduce the organic phase to a specified amount of solute may be assessed in a similar manner to the procedure describe for the extraction stage. Also included in the figure is a diagram showing the aqueous and organic flows, in what is called a continuous countercurrent solvent extraction circuit.

5.3.3.4 Metal Extraction

A knowledge of the extraction equilibria between the organic and aqueous phases helps to identify the operational variables that can control the solvent extraction process. An example – the extraction of copper from a copper sulfate solution using a chelating reagent (HR) – is considered. This is one of the best studied examples of solvent extraction. Normally, the system would not be described as a "water–hydrocarbon" dual-phase system, as it is in fact the Cu^{2+}, SO^-, H^+, R^-, and R^-, and the equation

$$Cu^{2+}\,(aq) + 2\,HR\,(org) \rightleftharpoons CuR_2\,(org) + 2\,H^+\,(aq)$$

which describes the system. That is, the tendency for the equilibrium to proceed to the right by virtue of the possibility of the CuR_2 thus formed dissolving in a suitable selected second phase, provided that the H_2SO_4 level in the aqueous phase is low enough not to reverse the reaction. Hence, the second phase is the HR/diluent mixture, certainly not the diluent as such, nor HR alone. If for any reason a modifier is added to the second phase, this must be treated as an integral part of the system, and the distribution of Cu^{2+}, or in practical terms its extraction efficiency, must be pertained to the second phase as a whole.

The thermodynamic or extraction equilibrium constant (K) for the reaction is given by

$$K = \frac{[\mathrm{CuR_2}]_{\mathrm{org}}\,[\mathrm{H^+}]^2_{\mathrm{aq}}}{[\mathrm{Cu^{2+}}]\,[\mathrm{HR}]^2_{\mathrm{org}}} \cdot F$$

where F is the ratio of the molar activity coefficients. Usually, F is unknown and is combined with K to give another constant K':

$$K' = \frac{[\mathrm{CuR_2}]_{\mathrm{org}}\,[\mathrm{H^+}]^2_{\mathrm{aq}}}{[\mathrm{Cu^{2+}}]_{\mathrm{aq}}\,[\mathrm{HR}]^2_{\mathrm{org}}} = \frac{K}{F}$$

At this stage, it will be appropriate to introduce the term "distribution coefficient" (K_D) which is defined as

$$K_\mathrm{D} = \frac{\text{Concentration of the metal in the organic phase}}{\text{Concentration of the metal in the aqueous phase}}$$

In this case,

$$K_\mathrm{D} = \frac{[\mathrm{CuR_2}]_{\mathrm{org}}}{[\mathrm{Cu^{2+}}]_{\mathrm{aq}}}$$

So that

$$K' = \frac{K_\mathrm{D}[\mathrm{H^+}]^2_{\mathrm{aq}}}{[\mathrm{HR}]^2_{\mathrm{org}}}$$

Therefore,

$$\log K' = \log K_\mathrm{D} - 2\log[\mathrm{HR}] + 2\log[\mathrm{H^+}];$$

$$\log K_\mathrm{D} = \log K' + 2\log[\mathrm{HR}] - 2\log[\mathrm{H^+}];\quad \log K_\mathrm{D} = \log K' + 2\log[\mathrm{HR}] + 2\,\mathrm{pH}$$

The above expression suggests that a high value of K_D, which is desirable for solvent extraction, is achievable if the equilibrium pH is maintained at higher values and higher concentrations of the extractant. It also indicates that at a constant concentration of the extractant, log K_D will vary linearly with log [HR] and the slope of the line will confirm the charge carried by the metal species (e.g., 2 in this case).

Solvent extraction is often applied to separate two chemically similar metals such as nickel/cobalt, adjacent rare earths, niobium/tantalum, zirconium/hafnium, etc. For the purpose of elaboration, the example of the separation of two chemically similar elements such as zirconium and hafnium from their nitrate solution, using TBP as an extractant is considered. The solvent extraction process in this case is chemically constant (K) is given by:

$$\mathrm{ZrO^{2+}\,(aq) + 2\,H^+\,(aq) + 4\,NO_3^- + 2\,TBP\,(org) \rightleftharpoons Zr(NO_3)_4 \cdot 2\,TBP\,(org) + H_2O}$$

so that

$$K = \frac{[\mathrm{Zr(NO_3)_4} \cdot 2\,\mathrm{TBP}]_{\mathrm{org}}}{[\mathrm{ZrO_{2+}}]_{\mathrm{aq}} \cdot [\mathrm{H^+}]^2_{\mathrm{aq}} \cdot [\mathrm{NO_3^-}]^4_{\mathrm{aq}} \cdot [\mathrm{TBP}]^2_{\mathrm{aq}}}$$

The expression for the equilibrium constant can further be written as:

$$K = \frac{K_{D_{Zr}}}{[H^+]_{aq}^2 \cdot [NO_3^-]_{aq}^4 \cdot [TBP]_{aq}^2}$$

where $K_{D_{Zr}}$ is the distribution coefficient of zirconium and is given by

$$K_{D_{Zr}} = \frac{[Zr(NO_3)_4 \cdot 2\ TBP]_{org}}{[ZrO_{2+}]_{aq}}$$

Therefore,

$$K_{D_{zr}} = K[H^+]^2 \cdot [NO_3^-]^4 \cdot [TBP]^2$$

Similarly,

$$K_{D_{Hf}} = K[H^+]^2 \cdot [NO_3^-]^4 \cdot [TBP]^2$$

with the separation factor β given by the following relationship:

$$\beta = \frac{K_{D_{Zr}}}{K_{D_{Hf}}}$$

It can be seen from Figure 5.18 that the K_D values for zirconium are higher than those for hafnium at all nitric acid concentrations. This is because the dissolution of zirconium nitrate ($Zr(NO_3)_4$) into zirconyl (ZrO_2^{2+}) and nitrate (NO_3^-) ions takes place to a lower extent as compared to the corresponding dissolution of hafnium nitrate in an aqueous medium. Hence, separation is feasible. However, at higher nitric acid concentrations the separation factor is reduced significantly because the dissociation of hafnium nitrate ($Hf(NO_3)_4$) decreases sharply with increasing nitric acid concentration, with the result that the separation factor, β, falls off rapidly. Hence, the separation process calls for the adjustment of the nitric acid concentration to a suitably low value.

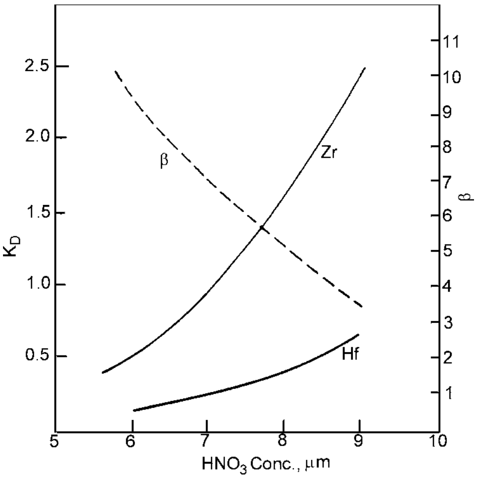


Figure 5.18 Plot of K_D of Zr and Hf and β against HNO_3 concentration.

5.3.3.5 **Solvent Extraction Equipment**

There is a broad range of equipment available for contacting the organic and the aqueous phases to achieve mass transfer. The simplest way of achieving contact is in unagitated column contactors. However, these have not seen widespread use in solvent extraction in hydrometallurgy. The most widely used stage-wise contactor in extractive metallurgy is the mixer–settler device in which the aqueous and the organic phases flow countercurrent to one another between the different stages. Usually these devices are large (perhaps the size of a swimming pool) and expensive to construct. The size and expense can be maintained at reasonable levels if there is no insistence that equilibrium must be reached. The use of a mixer–settler for loading would then result in the organic phase containing less valuable metal than predicted by equilibrium experiments, and a second (or a third) mixer–settler might be necessary in order to obtain the degree of loading. This then is another incentive to use stage operations in hydrometallurgy besides the advantages pointed out earlier. The mixer-settlers are reliable and flexible, and are attractive because of their mechanical sim-

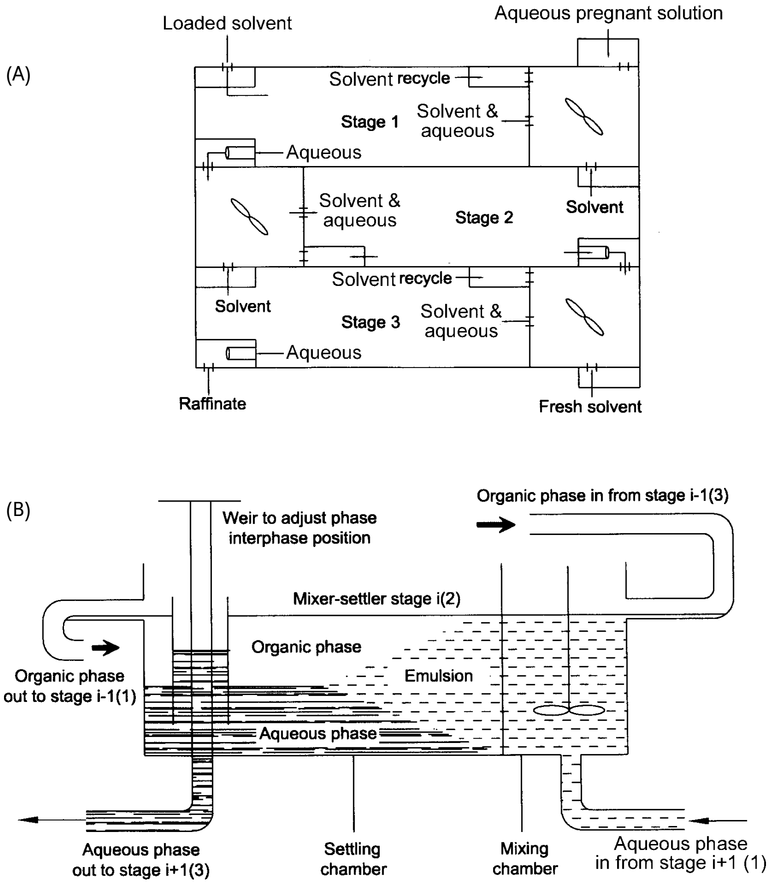


Figure 5.19 (A) Flow diagram for three stages of mixer settlers; (B) Aqueous and organic solution flow control to a mixer.

plicity. Figure 5.19 (A) shows a common mixer–settler arrangement, where the flow of the organic and aqueous phases through three stages of the mixer-settler unit is depicted. An arrangement for controlling the flow of the phases to a mixer is illustrated in Figure 5.19 (B). The solution inlet to the mixer is placed below the impeller at a point of low pressure in order to ensure a rapid and continuous flow through the mixer.

5.3.3.6 Applications

5.3.3.6.1 Copper

The present description pertaining to copper refers to solvent extraction of copper at the Bluebird Mine, Miami. When the plant became operational in the first quarter of 1968 it used LIX 64, but LIX 64N was introduced in to its operation from late 1968. The ore consists of the oxidized minerals, chrysocolla and lesser amounts of azurite and malachite. A heap leaching process is adopted for this copper resource. Heap-leached copper solution is subjected to solvent extraction operation, the extractant being a solution of 7–8% LIX 64N incorporated in kerosene diluent. The extraction process flowsheet is shown in Figure 5.20. The extraction equilibrium diagram portrayed in Figure 5.21 (A) shows the condi-

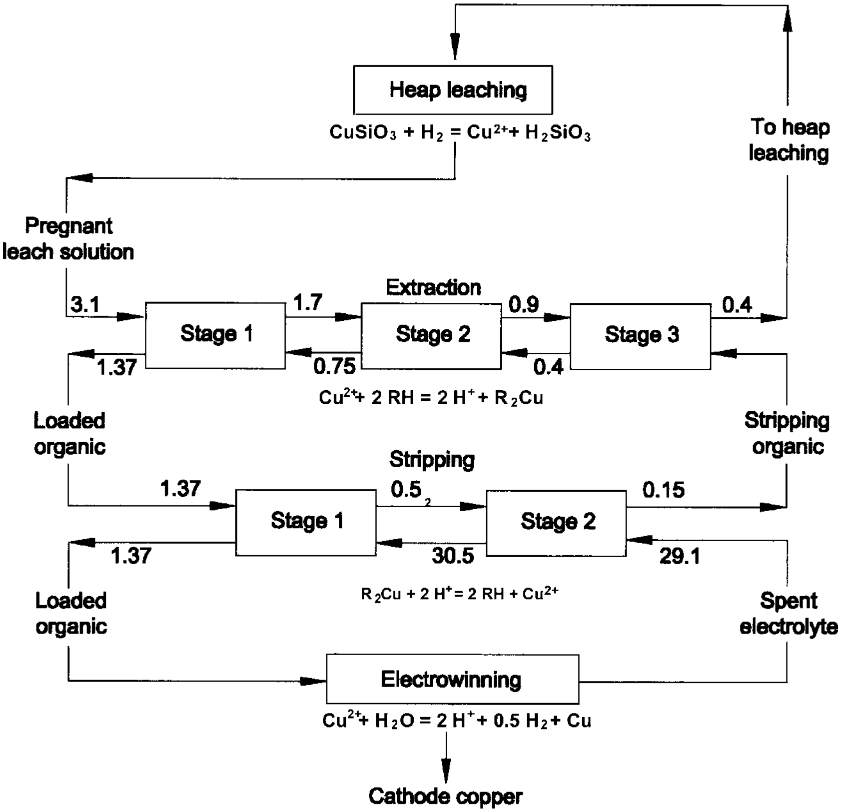


Figure 5.20 Bluebird mine copper solvent extraction process.

tions in the three-stage, multiple contact extraction circuit. The final raffinate copper concentration is 0.4 g l^{-1}. Stripping of the organic phase is readily achieved, with only two stages being required to provide an adequate circulating level (Figure 5.21 B), and a phase ratio of 6 : 1 (o/aq) assures large enhancement resulting in a feed copper concentration of roughly 34 g l^{-1} for electrolysis that follows. This plant verges on the ideal metal extraction process in that it involves three reaction stages in which the reagent of the preceding stage is reborn for reuse (these are called closed cycles), as incorporated in Figure 5.20. It may also be noted that the numerical data shown in the flowsheet show concentration (in g l^{-1}) of copper in phases that are in-coming and out-going each stage.

In the extraction stage, the 2 H^+ ions that are generated go back to the leaching stage, whilst in the stripping stage the 2 RH generated go back to the extraction stage. In the electrolysis, the 2 H^+ ions that are produced similarly go back to the previous stage involving stripping. The process is a reagent-eternalizing one in which there arises no need for replenishment of reagent. In practice, however, there is one dominant exception to this in

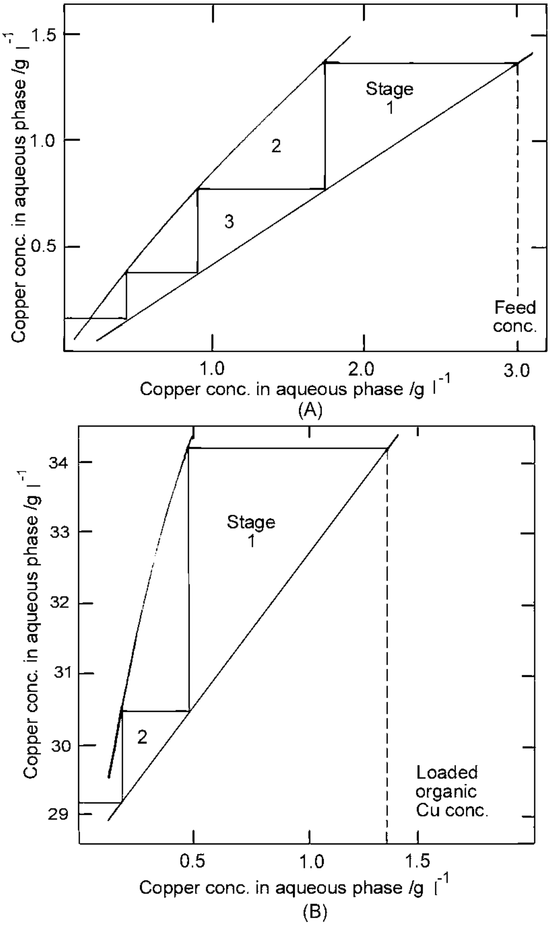


Figure 5.21 (A) Copper extraction equilibrium diagram; (B) copper stripping equilibrium diagram.

that acid make-up is needed at the leaching stage due to acid consumption in the dissolution of gangue materials associated with the copper source. Some losses of solvent also occur, these being principally due to solubility or entrainment in the aqueous phase. The present description of a copper plant involving solvent extraction is typical of many others that have been reported and described succinctly in the open literature.

5.3.3.6.2 **Zirconium–Hafnium**

In an earlier section, the separation of zirconium from hafnium in a nitrate medium using TBP as an extractant was described with a view to explaining the principle involved. While this is an established commercial method, another method which involves separation of the two elements in a sulfate medium has also gained commercial acceptance. The economic incentive of the process is the use of sulfuric acid instead of nitric acid. The system involving separation of zirconium from hafnium from a sulfuric acid leached solution is an important example of the application of basic extractants such as amines. The process flowsheet is shown in Figure 5.22. The process commences with the reaction of zircon sand with fused caustic soda, and this is followed by leaching in water and digestion with sulfuric acid at about 200 °C by which zirconium and hafnium are brought into solution in their sulfate forms. This is the feed solution for the SX circuit. An organic solvent, composed of 10% tri-n-octyl amine (TNOA) as the extractant, 7% tridecanol as the modifier and 83% n-paraffin as the diluent, extracts zirconium in preference to hafnium according to the reaction:

$$2\ R_2N\ (org) + 2\ H_2SO_4\ (aq) \rightleftharpoons 2\ (R_3NH)HSO_4\ (org)$$

$$4\ (R_3NH)HSO_4\ (org) + Zr(SO_4)_2\ (aq) \rightleftharpoons (R_3NH)_4Zr(SO_4)_4\ (org) + 2\ H_2SO_4\ (aq)$$

After extraction, the loaded solvent contains 6 g l^{-1} zirconium as zirconium oxide with 0.2% hafnium oxide. The raffinate is left with 0.2 to 0.3 g l^{-1} of the oxides of zirconium and hafnium; of this, 70–90% is hafnium oxide. This raffinate can act as a feed solution for the recovery of pure hafnium oxide. The loaded extractant, on the other hand, is subjected to a scrubbing operation with pure zirconium sulfate solution to eliminate any co-extracted hafnium. This scrubbing operation is essentially a displacement reaction:

$$(R_3NH)_4Hf(SO_4)_4\ (org) + Zr(SO_4)_2\ (aq) \rightleftharpoons (R_3NH)_4Zr(SO_4)_4\ (org) + Hf(SO_4)_2\ (aq)$$

and results in the transfer of an equivalent amount of zirconium sulfate to the extractant which now contains less than 50 ppm hafnium and is stripped with a 3 M sodium chloride solution to yield a pure zirconium sulfate solution according to the reaction:

$$(R_3NH)_4Zr(SO_4)_4\ (org) + 4\ NaCl\ (aq) \rightleftharpoons 4\ (R_3NH)Cl\ (org) + 2\ Na_2SO_4\ (aq) + Zr(SO_4)_2\ (aq)$$

The barren organic in its chloride form is treated with sodium carbonate to convert the amine to its free base form, as indicated in the reaction given below:

$$2\ (R_3NH)Cl\ (org) + Na_2CO_3\ (aq) \rightleftharpoons 2\ R_3N\ (org) + 2\ NaCl\ (aq) + CO_2\ (g) + H_2O$$

The pure product solution, which on analysis is shown to contain 80–100 g l^{-1} zirconium oxide, is treated with ammonia to precipitate zirconium hydroxide which, upon calcination at 850 °C, yields pure zirconium oxide.

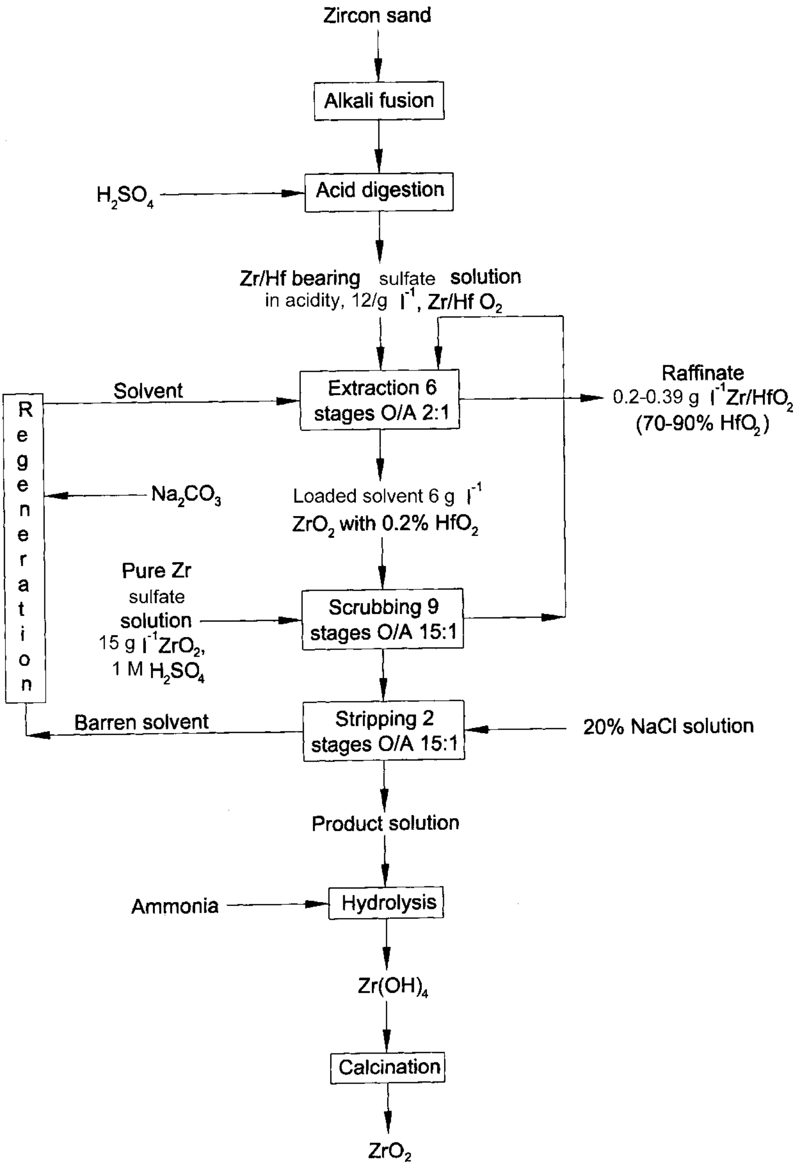


Figure 5.22 Flowsheet for the production of nuclear pure ZrO_2 by amine–sulfate route.

5.3.3.6.3 **Niobium–Tantalum**

Commercial-scale application of solvents coming under the category of neutral reagents is largely found as applied to the nuclear industry materials, as in example, for the separation and refining of uranium, plutonium, thorium, zirconium, and niobium. A process flowsheet for extracting niobium and tantalum from various resources is shown in Figure 5.23. It will

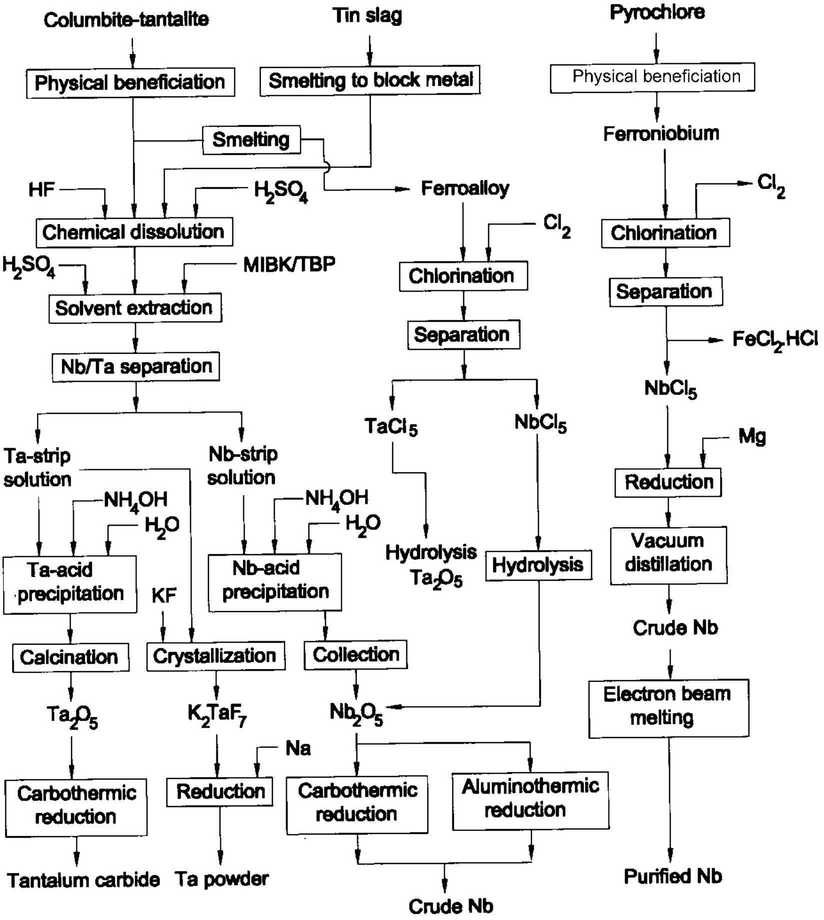


Figure 5.23 Processing flowsheet for various niobium–tantalum bearing sources.

be seen that the solvent (MIBK/TBP) is the central figure as a reagent that accomplishes separation of the two elements in the flowsheet. When the niobium–tantalum values are solubilized in an acid mixture of hydrofluoric and sulfuric acids, tantalum remains in solution as fluorotantalic acid (H_2TaF_7) at all acidities whereas niobium exists as different forms, fluoroniobic acid (H_2NbF_7) and oxyfluoroniobic acid (H_2NbOF_5). Of these, the former is stable at high acidities. The leaching reactions for columbite-tantalite are given below:

$$(FeMn)Nb_2O_6 + 16\ HF = 2\ H_2NbF_7 + (FeMn)F_2 + 6\ H_2O$$

$$(FeMn)Nb_2O_6 + 12\ HF = 2\ H_2ONbF_5 + (FeMn)F_2 + 4\ H_2O$$

$$(FeMn)Ta_2O_6 + 16\ HF = 2\ H_2NbF_7 + (FeMn)F_2 + 6\ H_2O$$

In solvent extraction with TBP, the fluoride complexes form solvated complexes with TBP. The stabilities of such complexes depend on the acidity/concentration of hydrofluoric acid. At low acidities there is practically no transfer of niobium from the aqueous phase to organic phase because niobium is present as oxyfluoroniobic acid, whereas the transfer of tantalum to organic phase is quite good due to the formation of solvation complex according to the reaction:

$$H_2TaF_7 + 3\ TBP = H_2TaF_7 \cdot 3\ TBP$$

At high acidities, niobium is present as fluoroniobic acid, and this forms a solvation complex given by the reaction:

$$H_2NbF_7 + 3\ TBP = H_2NbF_7 \cdot 3\ TBP$$

The extractability of such a complex is quite good. Thus, if the feed solution is low in its acidity only tantalum is extracted, while niobium remains in the raffinate. The niobium-bearing raffinate is then separately contacted with TBP after adjusting its acidity to higher values so that niobium is than transferred from aqueous to the organic phase.

5.3.3.6.4 Nuclear Fuel Reprocessing

Nuclear fuel reprocessing was first undertaken with the sole purpose of recovering plutonium, for weapons use, from uranium irradiated in nuclear reactors. These reactors, called the production reactors, were dedicated to transmuting as much of the uranium as possible to plutonium. From its original scope of recovering exclusively plutonium, with no attempts to either recover or recycle uranium, nuclear fuel reprocessing has since grown into a much more sophisticated and complex operation with expanded scope. It is now called upon to separate uranium and plutonium from the fission products, and to purify these elements to levels at which these fissile materials can be conveniently recycled for reuse. The present scope also extends to fission products separation and concentration.

Solvent extraction is now the universal choice in this field. As an example, the Purex (**P**lutonium **U**ranium **R**eduction **Ex**traction) process for nuclear fuel reprocessing will be described here. The process has gained wide acceptance, and is currently the only process used for reprocessing light water reactor spent fuel. The fuel rods used in these reactor systems consist of sintered uranium oxide pellets clad in zircaloy (zirconium alloyed with 1.5% tin and small quantities of iron, nickel and chromium) tubes. The first step in the reprocessing scheme is to chop the fuel rods into small pieces. The plutonium bearing spent uranium fuel matrix is leached in a nitric acid solution; the zircaloy cladding does not dissolve in this and becomes a part of the waste stream. The solution from the dissolver is centrifuged to remove fine particles. The clarified solution is then conditioned by hydroxylamine (N_2O_4) which brings the dissolved plutonium to its most extractable state, Pu(IV). The extractant used is TBP, diluted with odourless kerosene (OK). An outline flowsheet for the Purex process is shown in Figure 5.24. The clarified and conditioned solution of the spent fuel is first contacted with the extractant, TBP. Both U(VI) and Pu(IV) nitrates are extracted from the aqueous solution and are transferred to the organic phase. The organic phase is scrubbed with concentrated nitric acid. Most of the fission products, which have passed into the organic solvent, are now back-extracted by the aqueous phase. The nitric acid used performs the important function of keeping the uranium and plutonium in their extractable valence forms by providing nitrate ions and thereby inhibiting any tendency for their reversal from the organic to the aqueous phase in the scrub section. The raffinate

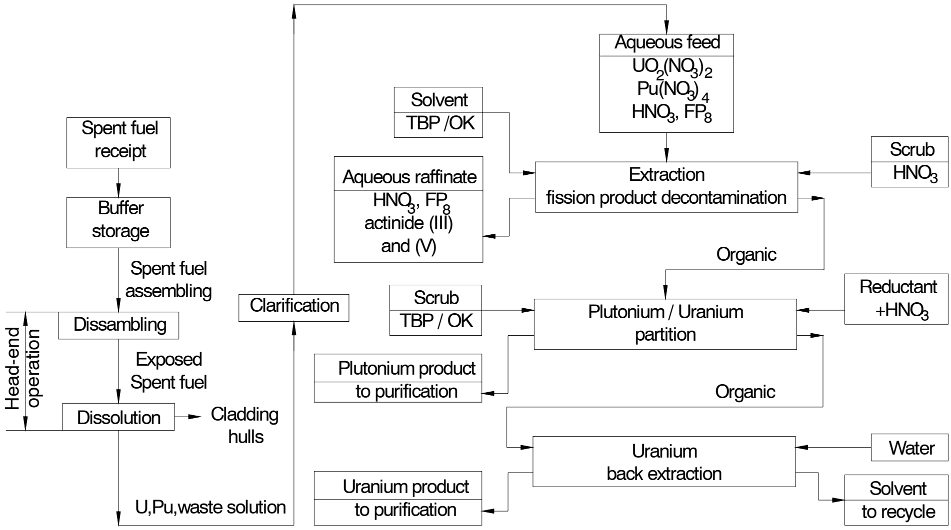


Figure 5.24 Purex process flowsheet.

from the scrub section thus contains all the fission products with very little or no uranium or plutonium. The organic phase containing the uranium–plutonium mixture is next contacted with an aqueous phase containing ferrous sulfamate ($Fe(NH_2SO_3)_2$) and nitric acid. The ferrous ion reacts according to the reaction: Fe(lI) + Pu(IV) → Pu(III) + Fe(III). The sulfamate component reacts with nitrous acid, which is always present in the nitric acid solution, converting it to water and nitrogen and thereby stops it from acting as an oxidizing agent, which would otherwise reoxidize Pu(II) back to Pu(IV). The Pu(II) product gets extracted into the aqueous phase. Thus, the partitioning between uranium and plutonium takes place. The aqueous solution after partitioning has Pu(III) nitrate in solution. The uranium-bearing organic phase is stripped with nitric acid, while the U(VI) and Pu(III) nitrate-bearing aqueous solutions generated respectively from the stripping and the partitioning operations are subjected to a second cycle for further purification.

5.3.4
Membrane-Based Solvent Extraction

Solvent extraction carried out in conventional contactors like mixer-settlers and columns has certain limitations, including: (a) controlling optimum dispersion and coalescence, (b) purifying both phases to ensure that stable emulsions are avoided; (c) temperature control within a narrow band; (d) high entrained solvent losses and related environmental and process economic effects; and (e) large equipment dimensions and energy requirements when the density differential or selectivity is low.

The introduction of a third phase – the membrane phase – between the two conventional phases (i.e., the aqueous and the organic phases) helps in overcoming many of the problems of solvent extraction. The membrane phase is a thin film, immiscible with the aqueous and the organic phases, which allows the transport of ions or molecular complexes selectively. It is the membrane phase via which the metal is transferred from the feed solution to stripping agent solution, with the extraction and stripping reactions taking place simultaneously on opposite faces of the membrane. Conventional polymeric membranes have low flux rates and selectivities, and new membrane techniques have been developed for solvent extraction. These include emulsion or liquid surfactant membrane systems, electrostatic liquid membranes systems, microporous or supported liquid membranes systems and electro-dialysis membrane systems. In fact, membrane-based technology is the only industrial-scale technology capable of removing toxic effluents without involving precipitation on a continuous basis. Since the literature abounds in the field of membrane-based solvent extraction systems no attempt is made here to describe them in detail. The present text serves only as an introduction to the subject

5.4
Precipitation Processes

Although precipitation constitutes the concluding part of the hydrometallurgical process flowsheet, the process is also put to use as a purification step in order to separate impurities. The different methods of precipitation are shown in Figure 5.25. The crystallization process is probably the simplest method to remove metals from solutions as compounds. No reagents are added, and the process simply involves the complete dissolution of the metal salt at a suitable temperature and pressure to obtain as high a metal content as possible. As the temperature is raised or lowered, depending on the particular system, the solubility of the metal salt in solution is exceeded and the salt precipitates or crystallizes

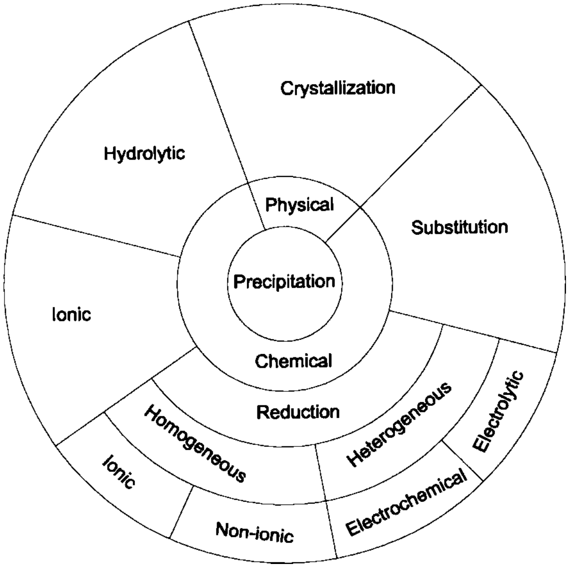


Figure 5.25 Precipitation processes from an aquatic solution.

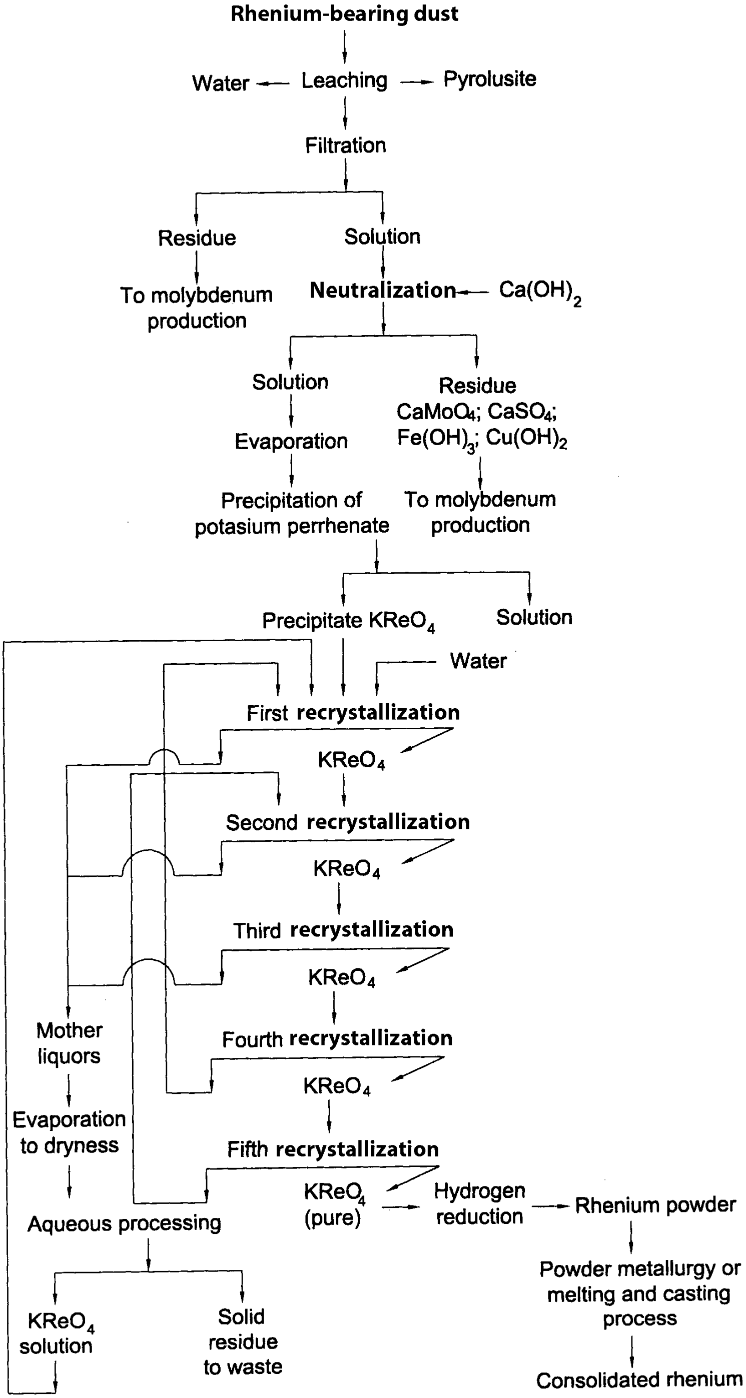


Figure 5.26 Flowsheet rhenium metal production.

from the solution. If several salts are dissolved in the solution, then as long as the solubilities of the salts are different, selective crystallization may be carried out. This feature has led to the separation of one constituent from another in a solution of the two. In this context, the classical method of Marignac which makes use of the difference in solubilities of K_2TaF_7 and K_2NbOF_5 to separate niobium from tantalum is worth mention. The slurry containing the metal oxides is dissolved in 70% hydrofluoric acid, diluted, and heated to near boiling. A potassium salt is added in sufficient amount to form the complex fluorides of the niobium and tantalum present, after which the solution is filtered and allowed to cool. Most of the tantalum salt crystallizes from the solution, leaving niobium in solution at room temperature. A single crystallization step cannot give rise to complete separation. The precipitates are, therefore, removed from the solution, redissolved and subsequently recrystallized. At each successive crystallization the chemical purity of the crystals is increased. In this context reference may be drawn to Figure 5.26, which shows how fractional crystallization is carried out to produce purified rhenium salts. Fractional crystallization on this basis can be stated to depend on small differences in salt solubilities which are magnified by repeated operations.

The crystallization process in any particular situation is strongly influenced by complexing agents, and this is demonstrated by beryllium resource processing to the beryllium fluoride intermediate that forms the starting compound which is chemically reduced to beryllium metal, using magnesium as the reductant. The preparation of beryllium fluoride cannot be accomplished by dissolving BeO or $Be(OH)_2$ in HF solution because when is the solution evaporated a tetrahydrate ($BeF_2 \cdot 4H_2O$) crystallizes and this, when dried, hydrolyzes to oxyfluoride ($5\,BeF_5 \cdot 2\,BeO$). For this reason, an aqueous solution of BeF_2 with intentionally added equimolar quantity of an alkali fluoride (e.g., NH_4F) is taken and subjected to evaporation. The process yields ammonium fluoroberyllate ($(NH_4)_2BeF_4$) which is thermally decomposed to obtain beryllium fluoride:

$$BeF_2 \cdot (NH_4)_2\,BeF_2 \rightarrow BeF_2 + 2\,NH_4F$$

5.4.1
Chemical Precipitation Processes

Chemical methods of precipitation from aqueous solution are much more common, both in number and variety, than physical methods. The presentation hereunder briefly outlines the processes grouped under chemical methods.

5.4.1.1 Hydrolytic and Ionic

Hydrolytic precipitation process is accomplished only by adding water, and the addition of this exclusive reagent usually causes the precipitation of oxides, hydrated oxides, hydroxides, or hydrated salts. For instance, the precipitation of hydroxides can be depicted as:

$$M^{a+} + a\,H_2O \rightarrow M(OH)_a + a\,H^+$$

Ionic precipitation process is accomplished by adding a reagent instead of water to a metal ion-containing solution, leading to the formation of a compound whose solubility is very low so that it readily precipitates. The added reagent functions by contributing anionic species.

Interaction of anions with cationic metal in the solution forms the compound. The anionic species, depending upon the reagent deployed, can be Cl^-, SO_4^{2-}, PO_4^{3-}, S^{2-}, OH^- or CO_3^{2-}.

The chlorides of most metals have a very good water solubility, though there are exceptions in the case of some metals. A typical example of the latter is silver which can be very efficiently separated by forming insoluble silver chlorides. Although, the separation of silver as the chloride is rarely used as a method for bulk precipitation, it is certainly useful for the removal of relatively small amounts of the metal when present as a minor constituent. In the case of cuprous and cupric chlorides, the former has a low solubility in water; hence, if the leach liquor contains cupric chloride, a suitable reducing agent such as sulfur dioxide can be introduced to convert cupric chloride to cuprous chloride so that precipitation occurs.

The separation of impurities such as calcium, barium and radium can be effected by the precipitation of their sulfates. In the case of sulfuric acid leaching of uraninite ore, the leach liquor contains radium which is removed if barium chloride is added since barium sulfate acts as a carrier for radium sulfate.

If an acidic leach liquor is associated with phosphate ion a gradual neutralization of the free acid and raising the pH can result in the precipitation of impurities like zirconium, thorium, beryllium, aluminum, zinc, manganese, calcium, and magnesium. Zirconium phosphate starts precipitating at a pH of 1.57, and magnesium phosphate at a pH of 9.76. As another example, mention may be made of the separation of thorium from the sulfuric acid leach solution of monazite sands by gradually decreasing the acidity of the solution such that all the thorium phosphate precipitates, but most of the rare earths and uranium remain in solution. The acidity control in this case can be accomplished by dilution or by neutralization. In dilution, large volumes of water are required to complete thorium precipitation. Precipitate recovery from dilute solutions entraps the rare earths, and so the method is not very successful. In neutralization, the use of a neutralizing agent eliminates the problem of handling large volumes of water. The thorium phosphate precipitate is washed with dilute sulfuric acid (pH 1.3) to reduce the rare earth content of the cake. Phosphate precipitation is particularly suited for the removal of trivalent metal impurities from a divalent metal. From the solubility diagram of iron-nickel-chromium-phosphate system (Figure 5.27) it can be seen that in a solution analyzing 15 $g\,l^{-1}$ nickel, iron can be brought down to 0.6 $mg\,l^{-1}$ at pH 3 by the precipitation of ferric phosphate, ($FePO_4$). Similarly the equilibrium concentration of chromium can be brought down to 0.5 $mg\,l^{-1}$ in a solution containing 4.2 $g\,l^{-1}$ nickel by the precipitation of chromium phosphate ($CrPO_4$) at pH 3.5. An additional feature in favor of phosphate precipitation is the precipitate morphology. The phosphate precipitates are small, dense, and spherical in shape and can easily be separated from the leach liquor without surface adsorption and contamination.

A popular source of sulfide ions is hydrogen sulfide gas. This is a versatile reagent capable of precipitating a number of metal sulfides, some of which can be precipitated selectively from solution by suitably adjusting the solution pH. In the aqueous medium the following reactions take place by which hydrogen sulfide releases, in two stages, sulfide ions to the medium:

$$\mathrm{H2S\ (aq)} \rightarrow \mathrm{HS^- + H^+};\quad \mathrm{HS^-} \rightarrow \mathrm{S^{2-} + H^+};\quad K = \frac{[\mathrm{S^{2-}}]\cdot[\mathrm{H^+}]^2}{[\mathrm{H_2S}]}$$

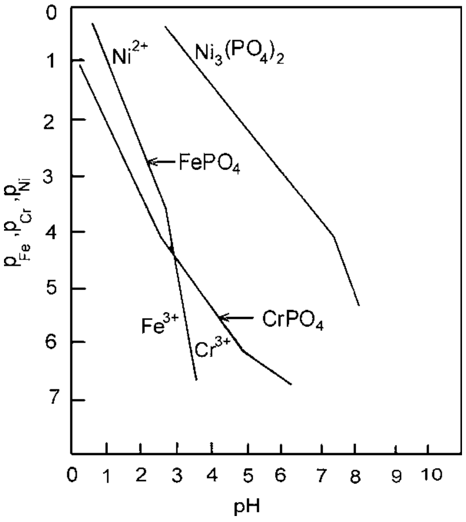


Figure 5.27 Stability diagram of phosphates of Fe, Cr and Ni $p_M = -\log a_M$ where M = Fe/Cr/Ni.

Taking logarithms:

$$\log K = \log [S^{2-}] + 2 \log [H^+] - \log [H_2S]$$

or

$$\log [S^{2-}] = \log K + \log [H_2S] + 2\ \mathrm{pH}$$

Taking the available data into account this equation for 90 °C and a pressure of 1 atm of H_2S takes the form,

$$\log [S^{2-}] = \log 1.2 \cdot 10^{-20} + 2\ \mathrm{pH}$$

The above equation brings out the effects of temperature, solubility of H_2S and pH. At a given temperature and solubility of H_2S, when pH is increased by one unit, the sulfide ion concentration increases by two orders of magnitude. Increasing P_{H_2S} increases the solubility of H_2S and thus the sulfide ion concentration. However, to produce the same effect as a single unit increment of pH, a hundred-fold increase of P_{H_2S} would be required. Among the three main factors that influence the sulfide ion concentration, pH, P_{H_2S} and temperature, the pH of the solution has, by far, the maximum influence. A higher P_{H_2S} is advantageous in that it permits use of temperatures more than 100 °C and leads to fast reactions.

The solubility product (K_{sp}) for the precipitation of metal sulfide (MmSn) from a solution containing m M^{z+} and n S^{2-} ions is

$$K_{sp} = [M^{z+}]^m \cdot [S^{2-}]^n$$

or

$$[M^{z+}]^m = \frac{K_{sp}}{[S^{2-}]^n}$$

Taking logarithms:

$$m \log [\mathrm{M}^{z+}] = \log K_{\mathrm{sp}} - n \log [\mathrm{S}^{2-}]$$

The equation above is the basis of the curves shown in the sulfide precipitation diagram (Figure 5.28). For unit metal ion concentration, $\log K_{\mathrm{sp}} = n\log [\mathrm{S}^{2-}]$ and hence the $\log [\mathrm{S}^{2-}]$ values corresponding to zero $\log [\mathrm{M}^{z+}]$ along the top of the diagram directly gives the $\log K_{\mathrm{sp}}$ values for both uni- and bivalent metal sulfides. The point on a specific curve for a given metal ion concentration yields on the x-axis the sulfide ion concentration point below which precipitation of the metal sulfide thermodynamically cannot take place, but above which it can. Superimposed upon the log sulfide ion concentration scale are the corresponding pH values for standard conditions obtained from the relationship,

$$\log [\mathrm{S}^{2-}] = \log 1.2 \cdot 10^{-20} + 2\,\mathrm{pH}$$

This incorporation permits a direct thermodynamic evaluation of precipitation tendency in terms of the solution pH. The diagram bespeaks that the K_{sp} values for sulfides CuS, $\mathrm{Cu_2S}$, $\mathrm{Ag_2S}$, HgS, $\mathrm{Bi_2S_3}$ are so low that they tend to precipitate at any pH. Thermodynamically, any of these metal sulfides can be selectively precipitated from $\mathrm{Co^{2+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Fe^{2+}}$ and $\mathrm{Mn^{2+}}$ at pH zero. While the information furnished by the precipitation diagram is utilized in the purification of leach solutions, it can also be useful in analyzing leaching conditions. For example, in the leaching of sulfidic resources of metals in acidic, nonoxidizing conditions, hydrogen sulfide may be generated during the reaction. The presence of hydrogen sulfide can cause the precipitation of secondary metal sulfides which are intended to be coextracted from the resource. These precipitated sulfides would then be lost in the discarded leach residues.

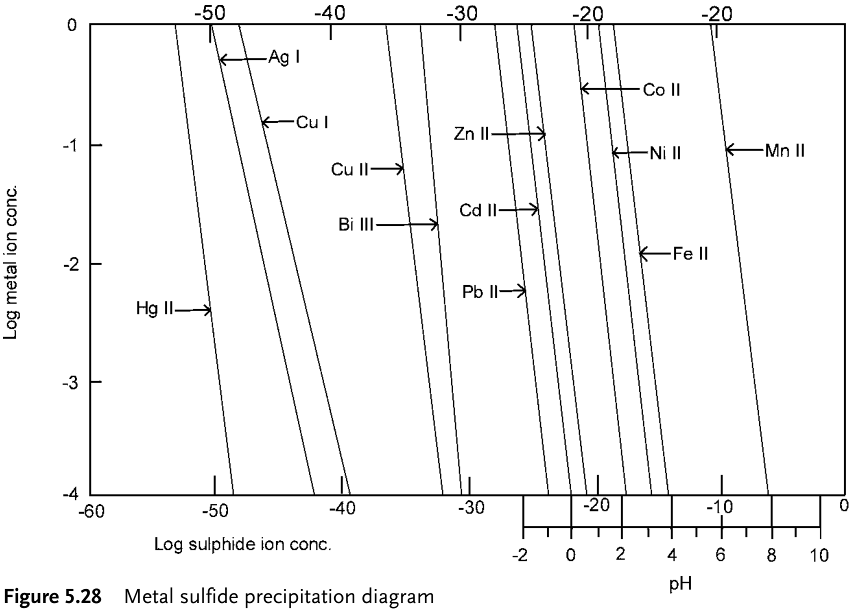


Figure 5.28 Metal sulfide precipitation diagram (based on data for 25 °C and 1 atm pressure of hydrogen sulfide).

Ionic precipitation involving addition of reagent contributing to the anionic species, OH^- ions, in the aqueous medium and interaction with the cationic species, the metal ions, to result in the formation of a compound which, on account of its poor solubility in the medium, precipitates rapidly and is generically alternatively embodied in the description on hydrolysis.

Hydrolysis may thus be said to be the most popular example of chemical precipitation wherein the metal is separated as its hydroxide. When a metal hydroxide is equilibrated with water it partially dissociates into ions

$$M(OH)_n \rightleftharpoons M^{z+} + n\, OH^-$$

and the solubility product (K_{sp}) is expressed by

$$K_{sp} = [M^{z+}] \cdot [OH^-]^n$$

Taking logarithms, one gets:

$$\log [M^{z+}] = \log K_{sp} - n \log [OH^-]$$

and using pH + pOH = log k_w the final equation takes the form:

$$\log [M^{z+}] = \log K_{sp} - n \log k_w - n\, \text{pH} \quad (k_w \text{ is the ionic product of water})$$

The equation above is the basis of the curves shown in the hydroxide precipitation diagram (Figure 5.29). It is seen from the above equation that each line in Figure 5.29 has a gradient of $-n$, where n is defined by the equation appeared earlier ($M(OH)_n \rightleftharpoons M^{z+} + n\, OH^-$). The precipitation process is dependent on both the metal concentration and the solution pH. As in the case of the metal sulfides, hydroxide precipitation will occur in solutions whose compositions lie to the right of the lines on this diagram. The diagram demonstrates the

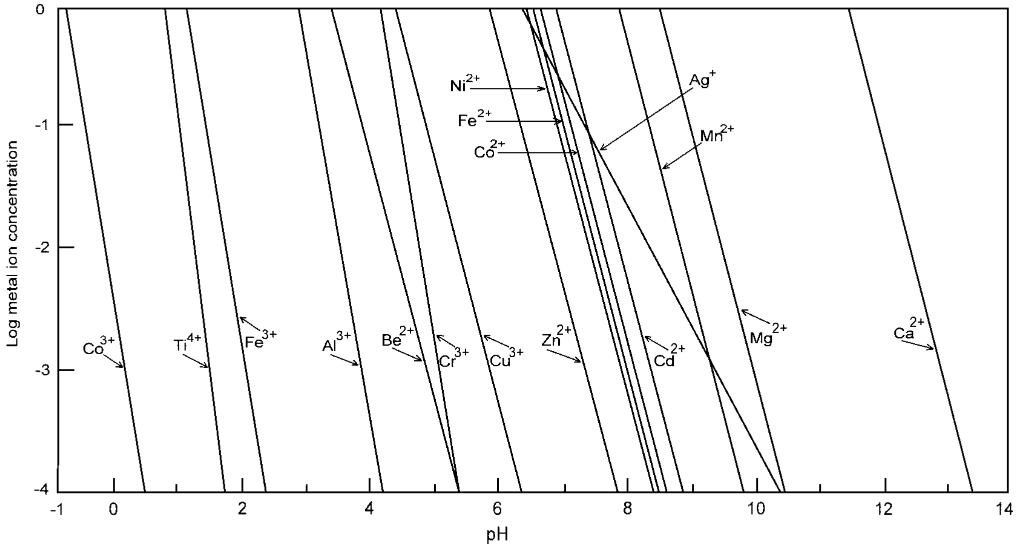


Figure 5.29 Precipitation diagram for metal hydroxides (based on data for 25 °C).

considerable range of pH over which the different metals precipitate as hydroxides. As a result, the selective precipitation of several metal hydroxides by appropriate control of the solution pH becomes theoretically possible. The diagram indicates that higher valent metal ion like Ti^{4+}, Zr^{4+}, and Co^{3+} tend to hydrolyze even in acidic solutions. Separation of cobalt and nickel by hydrolysis is not possible as the lines corresponding to them are quite close to each other on the diagram.

Iron is omnipresent. It is one of the most common impurities found in many leach liquors in small or much larger concentrations. It may be present in ferrous and/or ferric forms which show quite different behaviors in their tendency to hydrolyze. A pH of the order of about 8 and beyond is required to precipitate iron present in the ferrous state, while a pH of 3.5 is sufficient to precipitate iron present in the ferric state. The occurrence of the two oxidation states of iron offers alternative selective hydrolysis avenues for the separation of iron from other metals. Thus, a number of metals can be precipitated preferentially as hydroxides in the presence of Fe^{2+}. It has been seen from the hydroxide precipitation diagram that hydrolysis of titanium occurs in acidic conditions under which condition Fe^{2+} will not precipitate. This plan is utilized in the extraction of titanium by sulfate process where Ti^{4+} is selectively hydrolyzed at pH 2 with Fe^{2+} kept back in solution. Alternatively, Fe^{3+} in lesser amounts can be precipitated selectively as hydroxides from various other metals. For example, in the extraction of nickel, iron is subjected to oxidation and separation as $Fe(OH)_3$ using nickel hydroxide as the hydrolysing agent. The service of a nickel compound has the advantage in these incidents of excluding the addition of any foreign ions, the nickel cations generated merely upsurging to the nickel concentration in the solution. The reaction between ferric iron and nickel hydroxide may be shown as:

$$2\ Fe^{3+} + 3\ Ni(OH)_2 = 2\ Fe(OH)_3 + 3\ Ni^{2+}$$

A general note can be injected on iron precipitation. The precipitation calls for a prior oxidation of ferrous iron to ferric iron. The precipitation of the former occurs at high pH of the order of 8 and above. Simple hydrolysis at pH 3.5 at room temperature yields a voluminous and gelatinous ferric hydroxide ($Fe(OH)_3$) precipitate which not only settles and filters slowly but also acts as a good trapper for the values present in a leach liquor. Repeated dissolution of the hydroxide precipitate in acidic water and reprecipitation, at extra cost and time, is inevitably to be carried out to gain back the lost values that remain untrapped. It may also be pointed out that the iron hydroxide can have a vital scavenging role and can remove any deleterious impurities, such as As, Sb and Ge, from leach liquors. Hydrometallurgists certainly welcome iron hydroxide performing this function. A more practical and better approach is to separate iron in one of the following forms: (i) goethite – $FeO \cdot OH$; (ii) jarosite – $MFe_3(SO_4)_2(OH)_6$, where M represents a monovalent cation from the group comprising Na^+, NH, K^+, Ag^+, Rb^+, 0.5 Pb^{2+}, H_3O^+; and (iii) hematite – Fe_2O_3; all these compounds possess excellent filtration characteristics. While the formation of goethite and hematite is a function of the solution pH and the temperature, the separation of iron as jarosite requires the addition of cationic species like Na^+, and NH_4^+ according to following reactions:

$$2\ FeSO_4 + 0.5\ O_2 + 3\ H_2O \rightarrow 2\ FeO \cdot OH\ (\alpha\ \text{form}) + 2\ H_2SO_4$$

$$Fe_2(SO_4)_3 + 3\ H_2O \rightarrow Fe_2O_3 + 3\ H_2SO_4$$

$$3\ Fe_2(SO_4)_3 + 2\ (NH_4,Na)OH + 10\ H_2O \rightarrow 2\ (NH_4,Na)Fe_3(SO_4)_2(OH)_6 + 5\ H_2SO_4$$

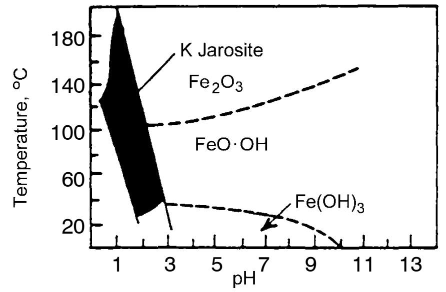


Figure 5.30 Stability field for hydrolysis production of 0.5 M $Fe(SO_4)KOH$ solution.

The stability diagram shown in Figure 5.30 gives a general idea about the conditions under which the precipitation of various iron compounds can take place from a 0.5 M $Fe_2(SO_4)_3$ solution. It suggests that at any pH value beyond 3.5, the hydroxide precipitate is first converted to goethite ($FeO \cdot OH$) and then to hematite (Fe_2O_3) as the temperature is raised from room temperature to more than 110 °C. It also indicates that goethite, hematite and potassium jarosite can precipitate from acidic solutions. A comparison of the various precipitation processes involving iron is presented in Table 5.9. This particular area which has been described as regards iron precipitation is amply illustrated in the zinc solution purification described later.

The presentation finally descends on the very last of the listed chemical precipitation processes, and this pertains to precipitation implemented by carbonate anions (CO^-). The dissolution of carbon dioxide takes place with the formation of the weak diabasic acid, H_2CO_3. The overall dissociation of this acid (dissociation constant, K_D) is represented by:

$$H_2CO_3 \rightleftharpoons 2\,H^+ + CO_3^{2-}$$

The overall tie-in between the carbonate concentration and pH is given by:

$$\log\,[CO_3^{2-}] = 2\text{ pH} + \log K_D + \log\,[H_2CO_3]$$

Table 5.9 Comparison of various ionic precipitation processes for iron removal.

Parameters	*Type of iron precipitate*		
	Goethite	*Jarosite*	*Hematite*
Compound formed	α, β $FeO \cdot OH \cdot Fe_2O_3$	$RFe_3(SO_4)_2(OH)_6$	Fe_2O_3
pH	2–35	1.5	Up to 2% H_2SO_4
Temperature, °C	70–90	90–100	~ 200
Anion	Any	SO_4^{2-} only	SO_4^{2-} only
Cation to be added	Not necessary	Na^+, K^+, NH_4^+	Not necessary
Cationic impurities	Medium	Low	Low
Anionic impurities	Medium	High	Medium
Filterability	Very good	Very good	Very good
Fe left in filtrate after precipitation, g l^{-1}	< 0.05	1–5	3

For a sparingly soluble metal carbonate, $M_m(CO_3)_n$:

$$M_m\,(CO_3)_n \rightleftharpoons m\,M^{z+} + n\,CO_3^{2-}$$

and the solubility product (K_{sp}) is given by:

$$K_{sp} = [M^{z+}]^m \cdot [CO_3^{2-}]^n$$

From the data available on the solubility product values of some common metal carbonates at 25 °C the values are observed to fall within a much smaller range than those in the case of the sulfides, and this is reflected in terms of pH in the carbonate precipitation diagram (Figure 5.31) the curves of which are based on the relationship involving K_{sp} in the logarithmic form. None of the carbonates is stable below pH 1.5, and the chances of securing neat, selective precipitation of metal carbonates by exercising control over pH is, as a result, much diminished. The diagram, however, shows that preferential precipitation should be workable in some cases. Thus, cadmium carbonate should precipitate preferentially to manganese carbonate, zinc carbonate to nickel carbonate, and cobalt carbonate to nickel carbonate. Such reactions may be used for purification purposes in cases where the second metal is the minor component.

The precipitation diagrams can be of help when considering leaching processes. They can give an indication of the dissolution behavior of particular minerals. They may be treated as adjunct to Eh–pH diagrams which are available for a somewhat limited range of systems. An examination of the carbonate (Figure 5.31) and sulfide (Figure 5.28) precipitation diagrams suggests that a nonoxidizing acid of pH 1 should dissolve any metal carbonate and also the sulfide of nickel, iron, and manganese (NiS, FeS and MnS). The highly stable

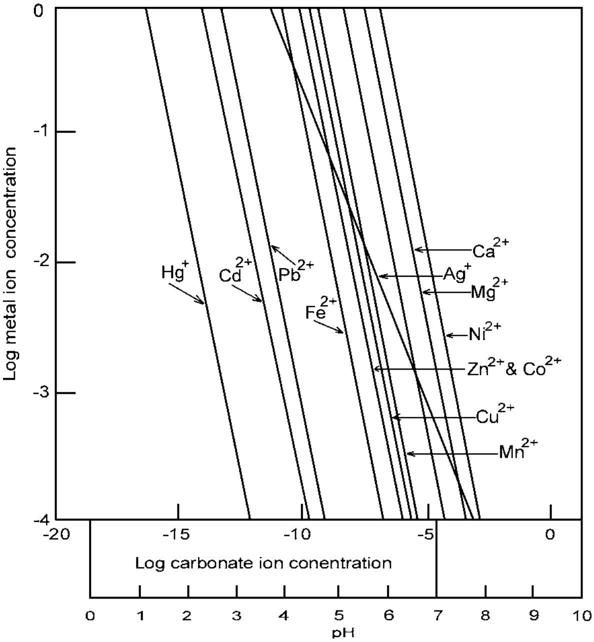


Figure 5.31 Metal carbonate precipitation diagram (based on data for 25 °C).

sulfides (e.g., Ag_2S, Cu_2S, CuS) would remain inert. Thus, in the sulfuric acid leaching of a heterogeneous source containing sulfides of iron and copper and oxidized copper carbonate minerals, the component, CuS, would remain insoluble whilst the other minerals would be likely to dissolve. This would result in a secondary reaction, the H_2S produced from the dissolution of the FeS reacting with the Cu^{2+} ions to precipitate CuS.

Chemical precipitations which are not dependent on pH are used in various processes. Sometimes the reagent is reasonably set for a certain metal and this is the situation in the precipitation of silver as silver chloride. The only other insoluble common metal chlorides of significance are lead chloride, cuprous chloride, and mercurous chloride. This implies that precipitation of cuprous and mercurous chlorides generally may be avoided by ensuring that the metals occur in their higher oxidation states, cupric and mercuric states. The separation of silver in its chloride form is rarely employed for bulk precipitation, but is quite useful for removing relatively small amounts of the metal when it occurs in minor amounts.

5.4.1.2 **Reductive Precipitation Processes**

The penultimate categorization of the chemical precipitation processes detailed in this chapter is reduction. The process basically involves electron transfer from different ions. The reductive precipitation may be either *homogeneous* (which may be ionic or non-ionic), or *heterogeneous* (which may be electrochemical or electrolytic). Electrolytic processes are described in Chapter 6, and no account of these need be given here.

5.4.1.3 **Homogeneous Processes**

In cases of both the ionic and non-ionic homogeneous reduction processes, a reducing agent figures which oxidizes itself and, consequently, results in the precipitation of a metal. This description may wholesomely be conveyed by the following scheme:

$$M^{a+} + \text{Reduced breeds} \rightarrow M + \text{Oxidized breeds}$$

As a typical example of an ionic reducing agent, mention may be made of precipitation of silver nitrate by ferrous ion:

$$Fe^{2+} \text{ (reduced breeds)} + Ag^{+} \rightarrow Ag + Fe^{3+} \text{ (oxidized breeds)}$$

In the given example, Fe^{2+} oxidizes to Fe^{3+} (de-electronation) and Ag^+ reduces to Ag (electronation), and this as a whole is then an oxidation reduction process. The examples of nonionic reducing agents are hydrogen, carbon monoxide, formaldehyde and hydrazine. Their action may representatively be described for hydrogen:

$$H_2 \rightarrow 2\,H^+ + 2\,e^-$$

Gaseous hydrogen is well reputed for its industrial use as the reductant to precipitate metals or oxides from solutions under high temperature and pressure. As some leading examples of this method of precipitation, mention may be made of cobalt, nickel, copper, and uranium dioxide. The process is implemented in horizontal autoclaves made of stainless steel provided therein with agitators, baffles, heating/cooling coils, required connections for feed, and gas entry and exit provisions. High-purity powder yields which can be directly used in the condition produced. In the case of metals, however, powder metallurgy processes need to be applied to produce usable products. It should be pointed out that precipitation can occur from aquatic as well as from non-aquatic media.

The reaction between hydrogen and an aquatic medium holding say a copper metal ion, Cu^{2+}, can be shown as:

$$Cu^{2+} + H_2 \rightarrow Cu + 2\ H^+$$

The equilibrium constant, K, for the above reaction can be written as:

$$K = \frac{[H^+]^2}{[Cu^{2+}]\,P_{H_2}}$$

The following relationship results by taking logarithm of the equation above:

$$\log\,[Cu^{2+}] = 2\ pH - (\log K + \log P_{H_2})$$

The relationship obtained finally as above implies that when precipitation is implemented at a constant H_2 pressure and constant temperature, then log $[Cu^{2+}]$ and the pH of the solution bear linear functional relationship at the point of equilibrium, and the slope of this straight line corresponds to 2.

It is clear from the foregoing equation that there will be deposition of more metal, provided that the resulting hydrogen ions are eliminated as quickly as they are produced. Copper, together with certain other metals such as nickel, and cobalt, form a group of metals in which hydrogen ion removal is conveniently accomplished by working in an ammoniacal medium. Precipitation in this case of copper can be shown by the following set of equations:

$$[Cu(NH_3)_2]^{2+} \rightarrow n\ NH_3 + Cu^{2+}$$

$$Cu^{2+} + H_2 \rightarrow Cu + 2\ H^+$$

$$H^+ + NH_3 \rightarrow NH_4{}^+$$

It may be noted that enhancement of the concentration of ammonia gives rise to two opposing effects. Precipitation is encouraged on account of destruction of the liberated acid, but at the same time, precipitation is retarded on account of the reduction of the availability of reducible metal ions, Cu^{2+}, due to the prevalent complexing action by ammonia. It is for this reason that an optimum $[NH_3]/[Cu^{2+}]$ ratio must be maintained so that the opposing effects are at balance.

An additional means of eliminating hydrogen ions as quickly as they are produced during reduction is to carry out precipitation in an alkaline medium. The following set of equations represents this particular case:

$$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2\ (OH)^-$$

$$Cu^{2+} + H_2 \rightarrow Cu + 2\ H^+$$

$$OH^- + H^+ \rightarrow H_2O$$

There are often instances when one encounters a metal-bearing organic phase, and the attraction may be to recover the metal loaded into the organic. This is made possible by using hydrogen at elevated temperature and pressure in an autoclave, wherein the metal precipitates in powder form, and the organic regenerates. The process may be reported as precipitation by substitution, though ionic species take no part in the reaction. The process is unlike precipitation by hydrogen from an aqueous medium. The substitution reaction of a typical example of precipitation of metallic copper powder from hydroxyquinoline–kerosene organic phase holding copper by hydrogen is portrayed by the following scheme:

$$H_2\ (\text{gas}) \rightarrow H_2\ (\text{org})$$

$$R_2Cu\ (\text{org}) \rightarrow 2\ RH\ (\text{org}) + Cu\ (s)$$

where R stands for the hydroxyquinoline–kerosene organic phase and copper is the bivalent metal considered in the example taken.

5.4.1.4 **Heterogeneous Processes**

The text now turns to the heterogeneous precipitation processes which, as depicted in Figure 5.25, are grouped into two types: electrochemical and electrolytic.

The electrochemical reduction and its heterogeneity feature may be described by considering two reducing agents, one is the activated charcoal, the other a metal.

The use of activated charcoal dates back to ancient times when it was acclaimed as the reductant for precipitating gold from solutions generated by leaching gold ores with chlorine water. The reactions can be shown as:

$$AuCl_4^- \rightleftharpoons Au^{3+} + 4\ Cl^-$$

$$Au^{3+} + 3\ e^- \rightarrow Au$$

$$C + 2\ H_2O \rightarrow CO_2 + 4\ H^+ + 4\ e^-$$

$$\text{Overall reaction: } 4\ Au^{3+} + 3\ C + 6\ H_2O \rightarrow 4\ Au + 3\ CO_2 + 12\ H^+$$

The precipitation of gold occurred on the surface of the reductant charcoal. The charcoal was subsequently burnt and the gold recovered. This process was used successfully for some time until it was withdrawn in favor of using cyanide solution because of the ineffectiveness of chlorine water to dissolve silver, which more often than not co-occurs with gold ores.

The process of precipitation of a metal from an aqueous solution of its salt by another metal is the well-known *cementation process*, so named because the precipitated metal is usually cemented on the metal introduced into the system. The process prediction stems from consideration of electrode potentials of metals. The metal positioned with greater (oxidation) potential in the electromotive series will pass into solution and remove a metal positioned with a less positive potential. The larger the spread of the positions of the two metals in the series, the greater is the possibility or feasibility of cementing out one by the other.

The cementation process in a general fashion may be represented as:

$$M_1^+M_2^0 \rightarrow M_1^0 + M_2^+$$

where M_1^+ represents metal ions in an aqueous medium and M_2^0 is the suitable metal in the solid state introduced to precipitate the aquatic metal (M_1^+) in the metallic form (M_1^0) while itself going into the aquatic state (M_2^+). The reaction is obviously associated with a free energy charge, ΔG, whose value must be negative in order for the cementation reaction to be feasible. Alternatively, as has already been pointed out, the terms of reference for feasibility of any proposed cementation process are the electrode potentials of the metals concerned or, in other words, their positions in the electrochemical series. The overall process of cementation consists of a number of steps, namely, diffusion of the M^+ species to the surface of M_2, surface adsorption of M^+, chemical reaction between M_2 and M^+, desorption of the M^+ species, and diffusion of M^+ into the bulk solution. The kinetics of the whole process is controlled by the slowest of the sequential steps mentioned above. A diffusion-controlled cementation process, like the recovery of copper from sulfate or chloride solutions, is characteristically associated with a low activation energy. Cementation of lead from its chloride solution with iron, on the other hand, is associated with a high activation energy. The rate of cementation is directly proportional to the effective depositing surface area of the precipitating metal. The rate of cementation also depends upon the morphology of the depositing metal; if the deposit is nonporous in nature, the rate of cementation is likely to be slow, whereas dendritic or powdery deposits are associated with fast cementation rates.

Some applications of the cementation processes are:

(1) Recovery of copper from solutions generated in heap/dump leaching with sulfuric acid by cementation with iron.

(2) Recovery of gold and silver from cyanide solutions – the largest gold producing mines of the US, namely those at Newmount (Carlin), Placer Amex (Golden Sunlight), and Louisiana Land (Round Mountain), make use of the Merrill Crowe zinc precipitation process for the recovery of gold from the cyanide leach liquor. This process essentially involves bringing together a clarified deaerated gold cyanide solution (dissolution is by potassium cyanide solution) and zinc dust to cement out gold according to the reactions:

$$KAu(CN)_2 + 2\ KCN + Zn + H_2O \rightarrow Au + K_2Zn(CN)_4 + 0.5\ H_2 + KOH$$

$$Zn + 4\ KCN + 2\ H_2O \rightarrow K_2Zn(CN)_4 + H_2 + 2\ KOH$$

This process has been extensively elaborated in a later section.

(3) Purification of leach liquors – as an example, mention may be made of the removal of cadmium and thallium from a zinc sulfate solution. In this case it is very convenient to use metallic zinc as a cementing metal, since the zinc that enters into solution is recovered subsequently.

(4) Separation of two metals from a leach solution – as examples, mention may be made of solutions containing cobalt and copper, and nickel and copper. The former solution is treated by metallic cobalt to precipitate copper, and the latter by metallic nickel to precipitate copper. In both cases, the metal added to cement the copper is recovered afterwards.

5.4.2
Uranium

The present account on uranium begins with some of the basic elements of chemistry used in the hydrometallurgy of uranium. Although the inorganic chemistry of uranium, is quite involved, the processes used in recovering the element from its resources are straightforward. Although there is a U(III) species which can exist in aqueous solutions, the consequential valency states are U(IV) and U(VI). U(IV) can exist in aqueous solutions as U^{4+} ions, whereas U(VI) exists as the uranyl ion UO_2^{2+}. In the context of leaching uranium minerals it is, in the first instance, very useful to refer to the relevant potential–pH diagram which depicts the regions of pH and oxidation potential in which simple uranium oxides, ions in solution, and insoluble uranates exist.

A metal can exist in more than one oxidation state, and the lower state forms a sparingly soluble compound; reduction of ionic species of the higher state with hydrogen may influence precipitation of the compound. The possibility of reductive precipitation of a metal oxide may be determined by referring to the metal–water system diagram available for uranium. Inspection of this diagram brings out the fact that hydrogen line maintains a potential more negative than that of the

$$UO_2^{2+} + 2\,e \rightleftharpoons UO_2$$

system over the entire pH range. However, the pH of the solution should not come down to the value of 2 for hydrolysis to occur. This is because of the indication of the formation of the soluble U^{4+} species. The precipitation reaction is:

$$UO_2^{2+} + H_2 = UO_2 + 2\,H^+$$

The acidity generated as a result of the reaction must be neutralized to maintain the pH at the correct level. The precipitation of UO_2 may be implemented even in the case when uranium is present as a complex such as the sulfate or carbonate complexes. The chemical equation shown below represents the latter case:

$$UO_2(CO_3)^{4-} + H_2 = UO_2 + CO_3^{2-} + 2\,HCO_3^-$$

Hydrogen reduction to form metallic uranium is simply an impossibility. This readily follows from the potential–pH diagrammatic portrayal for uranium.

The leaching process essentially involves selecting a region of pH and oxidation potential where the solids are not stable and ions containing uranium are stable in solutions. The potential–pH diagram for the uranium system readily predicts the acidic conditions as to be necessary to dissolve uranium oxides and oxidizing conditions lead to formation of soluble uranyl salt. In practice, it is necessary to use an oxidizing agent in order to cause minerals containing U(IV) to react and dissolve. The uranyl minerals do not need an oxidizing agent, but the pH of the leached solution must be outside the area over which they are sparingly soluble. It may also be seen from the uranium diagram that if the pH of a uranium-laden liquid is increased, then an insoluble uranate precipitates; such solids are well known as "yellow cake", and it is in this commercial form that uranium is delivered by an uranium mine and mill.

The sum and substance is that there are two available process routes for leaching uranium from its ores; acid leaching, usually under oxidizing conditions, and alkali leaching over the restricted range of pH, usually realized using sodium carbonate bicarbonate or, in the case of in-situ leaching, the ammonium salts. Thus, all processes for recovering uranium from ores involve leaching, and this step is of fundamental importance to the overall flowsheet as it involves a choice between using acid or alkaline conditions. Sulfuric acid leaching is used when workable because it is most productive with most ores and does not demand the ore to be comminuted as finely as does carbonate leaching. This is because the acid acts on other minerals as well as on those containing uranium and so earns entry to uranium-containing grains inside individual ore particles. Carbonate leaching, on the other hand, is marked by more selectivity than acid leaching. In particular, the alkaline leaching is useful for working ores which are associated with acid-consuming constituents such as calcareous material.

In most uranium ores the element is present in several, usually many diverse minerals. Some of these dissolve in sulfuric acid solutions under mild conditions, while others may require more aggressive conditions. Thus, while it may be comfortable to recover 90–95% of the uranium present, it may be tough or impractical to win the balance amount of a few percent economically. Some of the most difficult uranium minerals to leach are those of the multiple oxide variety, most commonly brannerite and davidite. These usually have U(IV) as well as U(VI), together with a number of other elements such as titanium, iron, vanadium, thorium, and rare earths. To extract uranium from these sources is not as easy as other relatively simpler commonly occurring sources.

In a common acid-leaching works in which ore is churned with acid in the presence of an oxidizing reagent in pachuca tanks, the main need is to keep a free acid concentration adequate enough to attack the uranium minerals without dissolving undue amount of the associated gangue minerals. The leaching must conclude with sufficient acid remaining to prevent uranium from precipitating out. In the operational sequence, the maintenance of correct oxidizing conditions during leaching is next in importance to acid concentration in achieving a high recovery of uranium. The two oxidizing agents most commonly deployed in uranium leaching are manganese dioxide (as pyrolusite) and sodium chlorate. Neither, however, oxidizes the U(IV). They both oxidize ferrous to ferric ions which bring about the oxidation action – a clear example of indirect action.

It has been seen that one set of leaching systems is that in which the reaction of H^+ and OH^- species are involved. In case an adequate leaching is not obtained by deploying these situations, the introduction of another anionic species may be required for the formation of new and more appropriate soluble metal species. The leaching of uranium minerals represents one of the fine examples which makes use of this stated provision.

The dissolution of uranium minerals which may contain U(IV) and U(VI) in U-H_2O systems is only achieved with the difficulty through the reactions as shown below:

$$UO_2\ (s) + 4\ H^+\ (aq) \rightarrow U^{4+}\ (aq) + 2\ H_2O$$

$$UO_2\ (s) + 2\ H^+\ (aq) + 0.5\ O_2\ (g) \rightarrow UO_2^{2+}\ (aq) + H_2O$$

The incorporation of anions, as for example, SO_4^{2-}, CO_3^{2-}, etc., makes leaching possible through the formation of stable uranyl (VI) oxyanions. In sulfate leaching, an observation of the potential–pH diagram for the uranium system reveals that uranium species in solution may be in the form of cations UO^{2+}, neutral species $UO_2(SO_4)_2$ or anions $UO_2(SO_4)^{4-}$. The oxidation of uraninite, UO_2, in acid solutions, transforming U(IV) to U(VI), yields soluble uranyl sulfate through the reaction as shown below:

$$UO_2\ (s) + 2\ H^+\ (aq) + 0.5\ O_2\ (g) + 2\ SO_4^{2-}\ (aq) \rightarrow UO_2(SO_4)_2^{2-}\ (aq) + H_2O$$

In the reaction cited above, the oxidizing agent is oxygen gas; however, other reagents, for example, MnO_2 and others, are normally used. The reaction of the oxidant MnO_2 (this is not soluble in dilute acid) with ferrous iron is as follows:

$$MnO_2\ (s) + 2\ Fe^{2+}\ (aq) + 4\ H^+\ (aq) \rightarrow Mn^{2+}\ (aq) + 2\ Fe^{3+}\ (aq) + 2\ H_2O$$

The solution potential is then controlled by the ratio of ferric to ferrous ions.

Alkaline leaching is carried out by using sodium carbonate solution. In this case any U(IV) present in the ore must also be oxidized to U(VI). The uranium species soluble in carbonate leach solutions in the uranyl tricarbonate ion. The formation of this ion by solubilization of a hexavalent uranium mineral such as carnotite, or a tetravalent uranium mineral such as uraninite, may be represented by the following reactions:

$$K_2(UO)_2)_2(VO_4)_2 \cdot 3\ H_2O + 6\ CO_3^{2-} = 2\ K^+ + UO_2(CO_3)_3^{4-} + 2\ VO_3^{\ -} + 4\ OH^- + H_2O$$

$$2\ UO_2 + 6\ CO_3^{2-} + O_2 + 2\ H_2O \rightarrow 2\ UO_2(CO_3)_3^{4-} + 4\ OH^-$$

The above reactions show hydroxyl ion formation in the dissolution. Uranates will precipitate when the hydroxyl ion concentration becomes sufficiently high, according to the reaction:

$$2\ UO_2(CO_3^{4-}) + 6\ OH^- + 2\ Na^+ \rightarrow Na_2U_2O_7 + 6\ CO_3^{2-} + 3\ H_2O$$

Some bicarbonate or other acid cation, therefore, is required to be present in a leach solution, and the sole purpose is to buffer the hydroxide produced and prevent thereby uranate formation.

Following the acid or the alkali leaching, the two important techniques which take over for concentration and purification of the uranium are ion exchange and solvent extraction. Acid leaching, in particular, takes into solution (besides uranium) many elements which are present in the ore. Based on the control exercised on the concentration of sulfate, carbonate or nitrate in the uranium-bearing solution the uranium can be made to occur as cation, uncharged species, or an anion. Removal from solution as an anion by an ion-exchange resin or by solvent extraction, generally provides an excellent separation of uranium from most impurities. Solvent extraction is used to treat clarified acid liquors, and has also been used after resin ion exchange, as a second stage of purification, to obtain very high-grade products.

The ion exchange process involves the ability of hexavalent uranium as the uranyl ion, UO^+, to form anionic complexes with sulfate ions, SO_4^{2-}, and carbonate ions, CO_3^{2-}. In a general way, it may be mentioned that the uranyl ion exits in dynamic equilibrium with its sulfate complexes,

$$UO_2^{2+} + n\ SO_4^{-2} \rightleftharpoons UO_2(SO_4)_n^{2-2n}$$

where $n = 1, 2$, or 3. In alkaline carbonate solutions, the uranyl ion is complexed strongly to form well-defined species.

$$UO_2^{2+} + 3\ CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-}$$

The ion-exchange process consists of adsorbing these anionic complexes selectively and quantitatively on an anion-exchange resins as illustrated in the following reactions:

$$4\ R^+X^- + UO_2(SO_4)_3^{4-} \rightarrow (R^+)_4UO_2(SO_4)^{4-} + 4\ X^-$$

$$4\ R^+X^- + UO_2(CO_3)_3^{4-} \rightarrow (R^+)_4UO_2(CO_3)^{4-} + 4\ X^-$$

where R^+ = fixed ion-exchange sites of the resin and $X^- = NO_3$ or Cl^-. The reactions shown above are reversible, and the uranium may be divorced from the resin by shifting the reactions to the left. This is usually accomplished by contacting the uranium-loaded resin with solutions containing either nitrate or chloride salts.

Focusing attention on the acid solution in whose case the distribution coefficient is very high, the competitive sorption of most of the impurities present in solutions from sulfuric acid leaching of uranium ores (e.g., Ca, Mg, Al, Cu, Mn, Fe(II)) is quite negligible. Iron is unfailingly present, often in concentration larger than uranium. It may be pointed out that Fe(III) present as species such as $Fe(OH)(SO_4)^{2-}$ shows some affinity for the anion resin. The separation factor, however, is over 1000. For a representative acid leach solution, breakthrough of iron takes place ahead of the uranium, and uranium dislodges sorbed iron due to much greater affinity for the resin of the $UO_2(SO_4)^{4-}$ ion. This results in a crest in the iron breakthrough curve (Figure 5.32 A). Uranium may be retrieved from the resin by elution by sulfuric acid or by a nitrate solution. An acidic ammonium nitrate (NH_4NO_3) is found to be generally very economic. With this eluting reagent, the remaining sorbed iron elutes before uranium (Figure 5.32 B), and advantage is taken of this to further ameliorate the uranium solution by using a split eluate technique. The first portion (x) containing the principal part of iron is taken back to the pregnant liquor holding tank, whilst the dominant uranium portion (y) is treated ammoniacally:

$$2\ UO_2^{2+} + 2\ NH_3 + 3\ H_2O = (NH_4)_2U_2O_7 + 4\ H^+$$

The final portion (z), holding a relatively small quantity of uranium is taken back to the eluant-containing section in readiness for redeployment in the first stage of the next elution cycle, two-stage elution having been practised to upgrade efficiency. The concentration of uranium in the mid portion (y) may be up to 100 times the concentration of the initial pregnant leach solution. An anion exchange is, of course, reasonably specific for the take up of uranium from sulfate solution. However, some other ions co-sorp and certain of these are not completely removed during the elution cycle. Any substance that reduces the ion exchanger capacity in this manner can be regarded as a resin "poison". The poison occupies an increasing proportion of the exchange sites with each cycle, and the capacity becomes progressively reduced. The development of this situation is particularly severe with molybdenum. In the ion exchange of uranium from carbonate solution, the resin poisoning phenomenon is not generally as disturbing as in sulfate media. Iron does not contest disposition with uranium for sorption as it remains an insoluble species at the carbonate leaching stage.

In dealing with solvent extraction as applied to uranium, it may at first be pointed out that uranium can exist in aqueous solution either as a neutral complex, a complex anion, or a cation. The organic solvents used in solvent extraction can accordingly be divided into three classes, according to the type of uranium complex extracted.

The principal member of the first class is tributyl phosphate (TBP). It is convenient to use this organic reagent in the refining of yellow cake consequent to nitric acid dissolution. After dilution, the solution is subjected to filtration through vacuum filters prior to intro-

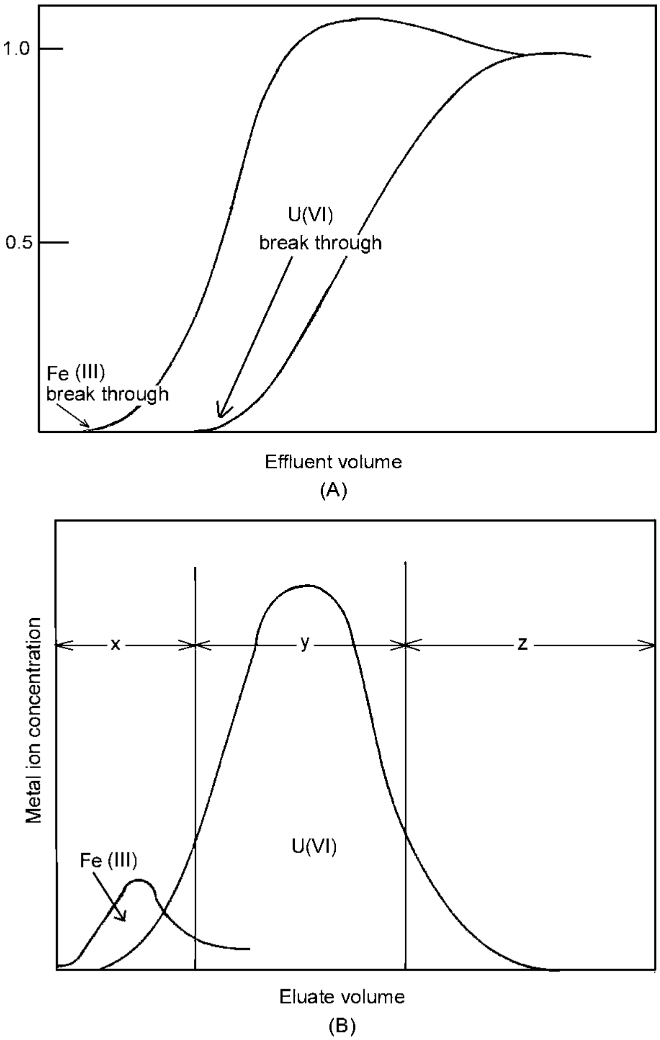


Figure 5.32
(A) Sorption breakthrough curves for U(VI) fouled with Fe(III) on an anion-exchange resin column.
(B) Elution curve for U(VI) involving Fe(III) fouling.

duction to the solvent extraction circuit. The uranyl cation (UO_2^{2+}) forms a series of breeds with the nitrate anion in aqueous solution, and one of these is neutral. Uranium is extracted from nitric acid leach liquors of concentrates by the following reaction:

$$UO_2^{2+}\ (aq) + 2\ NO_3^-\ (aq) + 2\ TBP\ (O) \rightleftharpoons UO_2(NO_3)_2 + 2\ TBP\ (O)$$

for which

$$K_1 = \frac{UO_2(NO_3)_2 \cdot 2\ TBP\ (O)}{UO_2^{2+}\ (aq) \cdot (NO_3^-)^2\ (aq) \cdot (TBP)^2\ (O)}$$

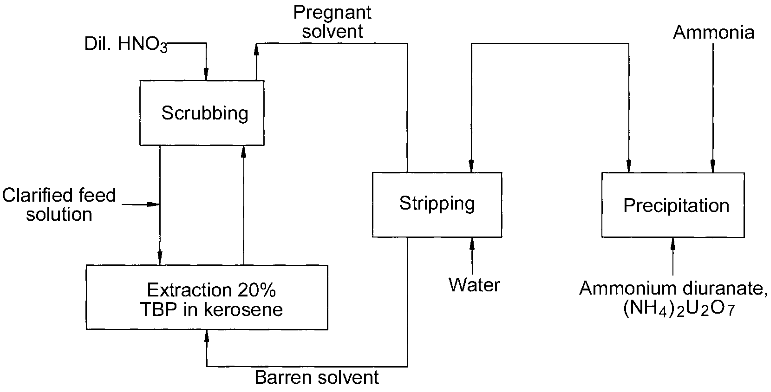


Figure 5.33 Uranium purification process by tributyl phosphate (TBP).

But

$$\text{Distribution coefficient,} \quad D = \frac{\mathrm{UO_2(NO_3)_2 \cdot 2\,TBP\,(O)}}{\mathrm{UO_2^{2+}\,(aq)}}$$

Therefore,

$$D = K_1\,(\mathrm{NO_3^-})^2\,(\mathrm{aq}) \cdot \mathrm{TBP}^2\,(\mathrm{O})$$

The above relationship shows that a high distribution ratio can be achieved by maintaining a high nitrate ion and TBP concentrations. The process based on TBP is outlined in Figure 5.33.

The principal members to belong to the anion-exchanger group are the various primary, secondary, and tertiary amines. The wide range of amines have been proven to extract uranium from sulfate solution, and in general they show better selectivity than di-ethylhexyl phosphoric acid (DEHPA) which is one of the most extensively used reagents to belong to cation exchanger group. This selectivity is found to increase from the primary through to the tertiary varieties. Earlier secondary amines were being used. These have, however, given way to tertiary amines which generally feature higher distribution ratios and higher uranium up-takes. The most commonly used solvent extraction process for the recovery of uranium from leach liquors is the Amex process. The extractant is customarily trioctylamine which is usually used as a 5% solution in kerosene, or some other mainly aliphatic hydrocarbon, with 2% isodecanol present to enhance the solubility of the amine salts in the diluent. The relevant reactions involved with the process are as follows:

$$2\,\mathrm{R_3N\,(O) + H_2SO_4\,(aq) \rightleftharpoons (R_3NH_2)_2SO_4\,(O)}$$

$$\mathrm{R_3\,(NH)_2SO_4\,(O) + H_2SO_4 = 2\,(R_3NH)HSO_4\,(O)}$$

$$2\,\mathrm{(R_3NH)_2SO_4\,(O) + UO_2\,(SO_4)_3^{4-}\,(aq) \rightleftharpoons (R_3NH)_4\,UO_2(SO_4)_3\,(O) + 2\,SO_4^{2-}\,(aq)}$$

Normally, a number of stages of extraction work in a countercurrent cascade, with mixer-settlers. A generalized flowsheet for the Amex process is shown in Figure 5.34. Stripping may be implemented by any one of the reagents, as indicated in the figure. Alternatively,

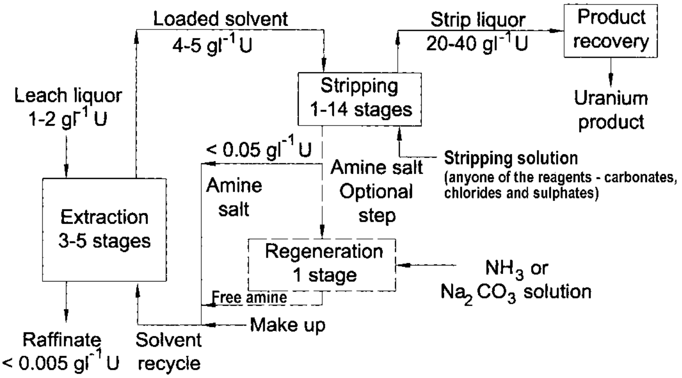


Figure 5.34 Amex process for uranium extraction.

regulated pH stripping may be accomplished by using a sulfate solution adjusted to pH of about 4 with ammonia:

$$(R_3NH)_4UO_2(SO_4)_3(O) + 4\ NH_4OH\ (aq) =$$
$$4\ R_3N\ (O) + UO_2SO_4\ (aq) + 2\ (NH_4)_2SO_4\ (aq) + 4\ H_2O$$

The uranium is later precipitated and recovered in the diuranate form by introducing gaseous ammonia which causes the pH to rise to about 7. The amine is transformed from the sulfate form to free base by regeneration with sodium carbonate before returning to the extraction step.

The three familiar phosphatic raw materials are phosphate rock, monazite sand, and xenotime. Among these, the phosphate rock is the most important and reputed as the major source of phosphorus in nature. There are two main types of phosphate rock, sedimentary and igneous. The rock of sedimentary origin carries 100–200 ppm of uranium, while that of igneous origin carries much less to (< 10 ppm). Phosphate rock is the main raw material used for the production of phosphatic fertilizers, and the rock of sedimentary origin when used for this purpose opens the possibility of recovering associated uranium. Since the cost of mining and processing of phosphate rock is already borne by the operating phosphatic fertilizer industry, the price of the uranium yielded as a byproduct should be low. This situation has aroused much interest in recovering uranium from rock phosphate while it is being processed for fertilizer manufacture. Uranium in the sedimentary phosphate is present principally in the tetravalent state; the remainder is in the hexavalent state. The dissolution characteristics of these two valence states of uranium in acids or in alkalis have been described in full earlier, and so repetition here is unwarranted. It may, however, be pointed out that the phosphate fertilizer industry is well recognized as a producer of a small amounts of fluorine, and increasing amounts of uranium and some lanthanides as byproducts. The present process however, concentrates only on uranium recovery.

In the fertilizer manufacturing scheme, the wet process phosphoric acid most commonly ensues from dissolution of sedimentary phosphate rock in sulfuric acid. Such acid solution contains around 1 g l^{-1} uranium which is recovered as the byproduct. This task is accomplished by three well-proven extraction processes, some salient details of which are presented in Table 5.10.

Table 5.10 Salient features of uranium recovery processes as a byproduct of phosphatic fertilizer industry.

Process	***Technical aspect***
The extractant is octyl pyrophosphoric acid (OPPA process). The stripping is by concentrated hydrofluoric acid. Yields UF_4.	Extracts uranium in tetravalent state. It is, therefore, necessary to use metallic iron as a reducing agent.
The extractant is di(2-ethylhexyl) phosphoric acid (DEHPA) in conjuction with trioctyl phosphine oxide (TOPO). Stripping is by ammonium carbonate, and uranium precipitates as ammonium uranyl tricarbonate.	The mixture shows a synergistic effect. The mixture is stable, and extracts uranium in hexavalent state.
The extractant is a commercial mixture of mono- and dioctyl phenyl phosphoric acid (OPPA). It is used in conjuction with tributyl phosphate (TBP). Stripping is by ammonium carbonate solution.	The mixture shows synergism. Uranium is extracted in the tetravalent state. The process is much less expensive and possesses a higher extracting power than D2EHPA-TOPO combination.

The Uncle Sam uranium production facility in Southern Louisiana illustrates representatively a plant-scale installation on uranium recovery from secondary sources in which rock phosphate has drawn good deal of attention. The flowsheet of the process starting from the phosphate rock that operates in the plant is shown in Figure 5.35. The wet rock received at the Uncle Sam plant is stockpiled, reclaimed, and wet ground in ball mills. The grinding system uses classifying cyclones in closed circuit with the ball mills in order to control the fineness of the grind. The phosphoric acid production involves reaction of phosphate rock with sulfuric acid to produce liquid phosphoric acid (30% P_2O_5) and gypsum crystals. A large amount of high- and low-pressure steam is released during the course of the reaction, and this is used to generate the electric power needed to operate the entire plant facility. This process is indeed a fine example of energy utilization (see Chapter 7) Feed to uranium extraction is 30% phosphoric acid from gypsum filters in the phosphoric acid plant. The uranium plant consists of two circuits – a primary circuit designed to remove the uranium from the large volume of feed acid and concentrate it (by a factor of 50), and a secondary circuit wherein the uranium is recovered from the concentrate. The phosphoric acid is first treated to remove undesirable impurities and then oxidized to convert uranium to the hexavalent state; the form in which it is most easily extractable. Oxidized acid is contacted in the primary circuit, countercurrently, by an organic solvent in a multistage mixer settler system (Figure 5.36). The solvent, a high-flash hydrocarbon containing D2EHPA and TOPO (phosphine compounds), absorbs the uranium selectively. Loaded solvent flows to the stripping circuit where it is contacted in mixer–settlers by treated phosacid to reduce the uranium back to the tetravalent state. Loaded strip acid solution contains 90% of the uranium concentrated into 2% of the original phosphoric acid flow. This loaded strip solution is oxidized back to the hexavalent state for re-extraction in the secondary circuit. Secondary extraction, like primary extraction, occurs in a battery of mixer settlers, but the equipment is much smaller in size. This secondary circuit also uses D2EHPA/TOPO solvent. Uranium is stripped from the solvent by an ammonium carbonate solution in a bank of mixer-settlers. Steam stripping of this solution removes ammonia and carbon dioxide and causes

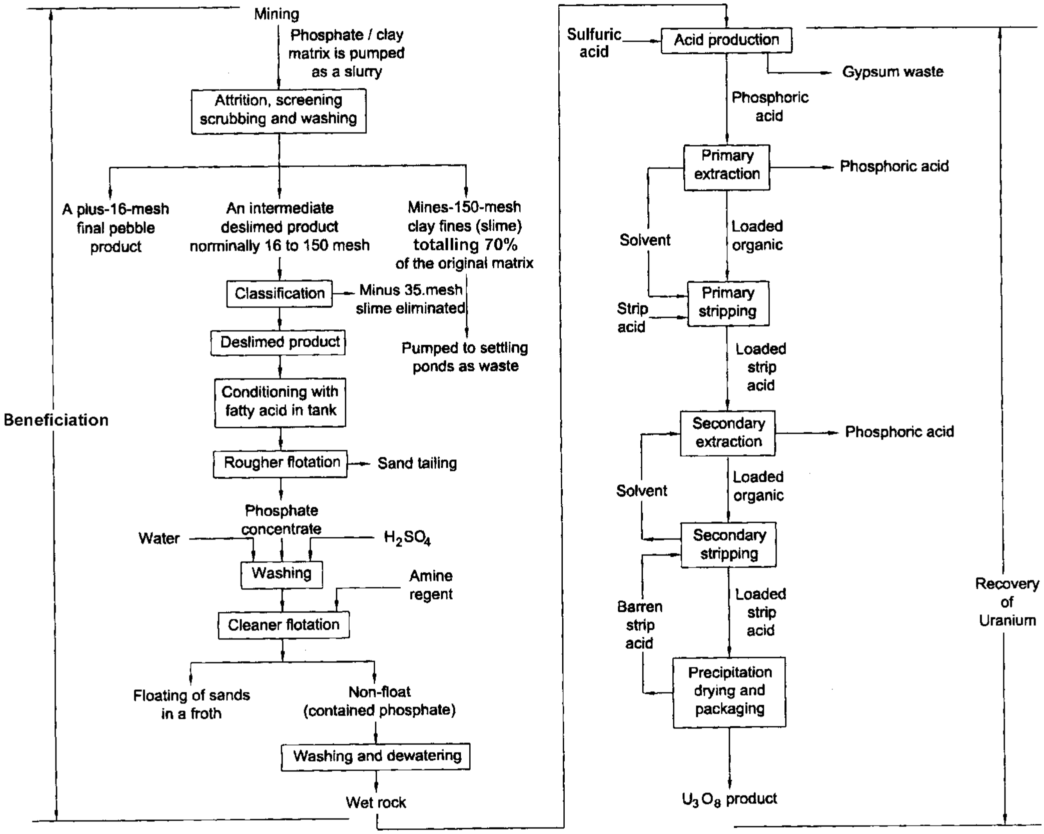


Figure 5.35 Uranium from phosphoric acid International Minerals and Chemical Corporations (IMC's) Uncle Sam plant.

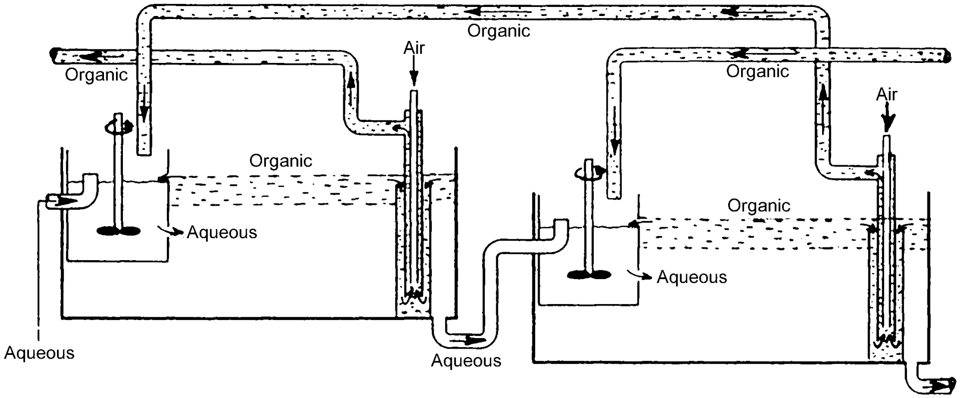


Figure 5.36 Multistage mixer–settler system.

the uranium to precipitate. Thickened precipitate (yellow cake) is centrifuged, pumped to a drier, and calcined at about 400 °C. The dried cake is crushed to size in a hammer mill and packaged in steel drums which contain about 500 kg (1000 lb) of 93–95% U_3O_8.

This account on uranium is completed by the inclusion of another important aspect of uranium extraction. This pertains to In Situ Leach (ISL) uranium mining, and on a global basis, nearly 15% of world uranium production currently originates from ISL operations (Figure 5.37). This figure is expected to increase somewhat in the future, however. Outside the United States, the uranium deposits in the sandstone basins of Kazakhstan, Uzbekistan, and possibly Mongolia and China, are especially well suited for production by ISL, and some of these areas already have an extensive history of ISL uranium production. In addition, ISL production has been (and is still being) used in Eastern Europe, whilst some efforts have also been made to use the method in Australia and elsewhere. At present, the countries of the Commonwealth of Independent States (CIS) realize that although most of their conventional uranium mining is no longer economic to operate, many of their sandstone uranium deposits are amenable to ISL mining. As a result, a pattern similar to that which occurred in the United States is now emerging in the region, albeit with a significant time delay. Uranium production from ISL projects now dominates the uranium industries in Kazakhstan and Uzbekistan. Instead of an alkaline leach process, CIS operators commonly use an acid leach process.

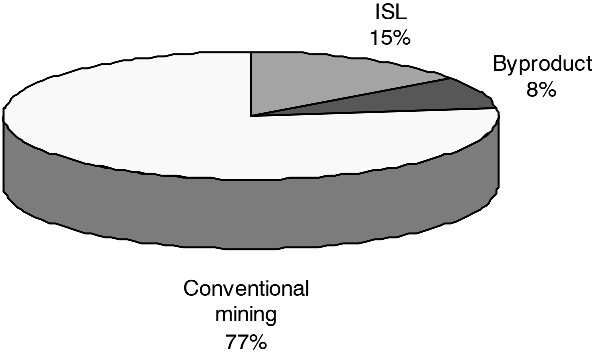


Figure 5.37 World uranium production methods.

Other than by-product uranium and uranium derived from reclamation, ISL mining now provides all of the newly produced US uranium. The United States is the best example of the evolution of the application of ISL mining, as commercial ISL mining has been practised there since 1974. An example is the Crow Butte ISL operation; this is the newest uranium production facility in the United States, with production starting in 1991, and is in fact, one of four commercial ISL mines currently operating in the United States. The Crow Butte deposit is located in Northwestern Nebraska, near the small town of Crawford. The project is owned by three companies: Uranerz, Geomex, and KEPRA. Situated in an area of grassy ranchlands on the High Plains of Nebrasaka, there are few surface indications that an ISL mine is operating. However, underlying the surface, at a depth of approximately 150–200 m, are highly permeable Oligocene sandstones of the Chadron Formation, containing a roll front uranium deposit. The uranium-bearing permeable sandstone is both underlain and capped by impermeable clay and siltstone layers, which confine the sandstone's extensive aquifer. The ore occurs in three mineralized horizons averaging 1.5 to 4.5 m thick. Ore grades average 0.25% U_3O_8 and presently mineable in-situ reserves are estimated at 30 million pounds (11500 tU). The uranium mineralization occurs as coffinite and uraninite in the matrix of the permeable sandstone. An alkaline leach process in used to extract the uranium. This begins with a series of wells being drilled into the deposit using standard rotary drills. The wells are spaced approximately 20 m apart to create a wellfield consisting of a recovery well surrounded by four to six injection wells. The uranium leaching process involves an oxidization step and a dissolution step. The leaching solution consists of formational waters fortified with Na_2CO_3 and CO_2 to form a sodium bicarbonate alkaline leach chemistry. Gaseous oxygen is added to the solution and pumped into each injection well. The oxygen oxidizes the uranium, causing it to dissolve and then to complex with the bicarbonate. The solution containing the dissolved uranium is then pumped up the recovery well. Each recovery well has a submersible downhole pump, and the solutions from the wellfield are transported via buried plastic pipes to the processing plant, where an ion-exchange circuit removes the uranium from the water and produces yellow cake as a saleable product. The plant has the capacity to handle 220 liters sec^{-1} (3500 gallons min^{-1}). The barren water from the processing plant is refortified with sodium carbonate and piped back to the wellfields where the dissolution process is repeated.

The ADU form of uranium is called the "mill concentrate" and because of its bright yellow color this product has come to be more known as "yellow cake". This forms the starting resource that undergoes further refining and chemical processing in order to produce different uranium products for reactor applications. The traditional route involves the dissolution of the uranium mill concentrate in nitric acid, followed by solvent extraction using TBP as the extractant. The refined uranium product obtained after solvent extraction is in the form of uranyl nitrate which is denitrided to uranium trioxide. This is then hydrogen-reduced to the dioxide which is hydrofluorinated with anhydrous hydrogen fluoride to yield uranium tetrafluoride. This compound is either metallothermically reduced to metallic uranium or is fluorinated to uranium hexafluoride; the latter is subjected to enrichment which implies increasing the uranium-235 isotopic content in the final product. The enriched uranium hexafluoride compound is hydrolyzed and then chemically processed to yield what is known as "enriched uranium dioxide". The tetrafluoride compound, without going through enrichment, undergoes similar hydrolysis and chemical processing and yields "natural uranium dioxide".

Another, more modern, route of processing the yellow cake is shown in Figure 5.38, accomplishes the production of enriched uranium oxide entirely by pyroprocessing. Thus, uranium is finally obtained in three forms: metallic uranium, enriched uranium dioxide, and natural uranium dioxide. As the flowsheet shows, and as briefly described herein, these are essentially the products of hydro and pyro-based processing schemes.

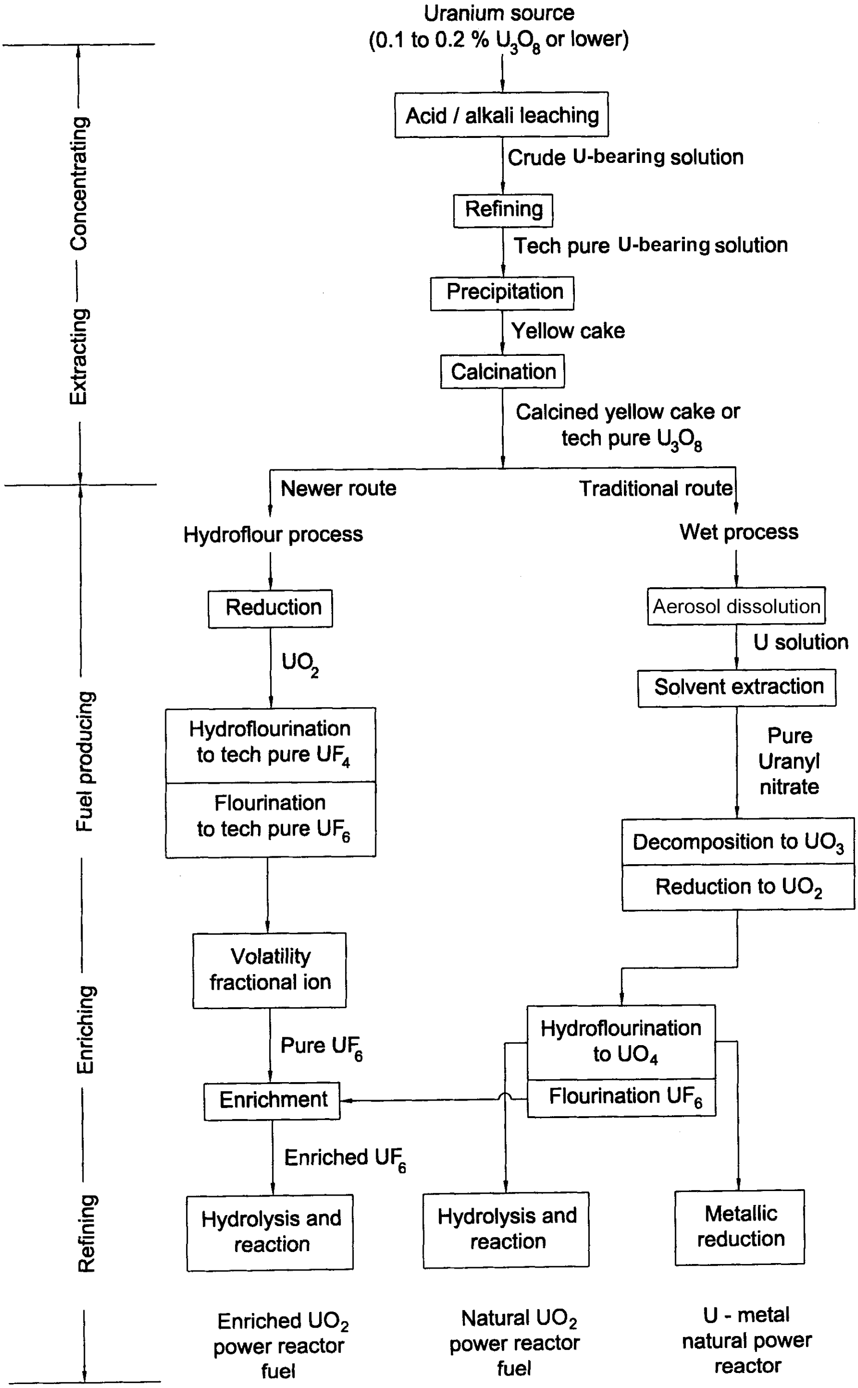


Figure 5.38 Routes to uranium mill concentrate processing to power/research reactor fuel products.

5.4.3
Titanium

Titanium, although not a very abundant constituent in the Earth's crust, is very well distributed world-wide. The resources can be divided into two broad categories: natural resources, and secondary resources. The natural resources are ilmenite, rutile, ananatase, leuxozene, arizonite, brookite, pseudo-brookite, perovskite, laporite, and sphine. The secondary resources are red mud, synthetic rutile, titania slag, and ferrotitanium. Among the natural resources, the most important titanium-bearing minerals are ilmenite, ($FeO \cdot TiO_2$) and rutile, (TiO_2). The former represents about 90% of the world's titanium reserves while the latter accounts for the balance of 10%. About 95% of the titanium minerals processed annually are utilized for the preparation of pure titanium dioxide which is used as a pigment. Natural rutile, because of its high titanium oxide content and its low impurity levels, is the preferred feed on some accounts. Since ilmenite is more abundant than rutile, it is of considerable technical importance. Processes have been established for the beneficiation of ilmenite to produce a rutile substitute. Beneficiated ilmenite yields a product known as "synthetic rutile" – a material that can be treated in the same way as rutile to produce the titanium dioxide pigment.

Although a large number of technologies are known to have been developed for the beneficiation of ilmenite, only a limited number of processes are found to be in use. These may broadly be grouped under three heads: (i) partial reduction of iron oxide followed by acid leaching; (ii) full (metallization of iron oxides) reduction followed by aeration (oxidation), desliming acid leaching; and (iii) full ((metallization of iron oxides) reduction followed by smelting (tappings: pig iron and titania slag) followed by acid washing/leaching of the slag.

Partial reduction and leaching process bear the advantages such as least (direct) energy consumption, utilization of waste acids, and good-quality product. This route is, however, associated with pollution-related problems. The metallization and desliming approach has registered success (particularly in Australia), as the process has the advantages of lower operating costs and fewer pollution-related problems. The reduction smelting (electric arc) process is perhaps the most attractive avenue because pig iron is produced as a coproduct and the slag (acid-washed) has received acceptability and marketability.

The technology for the production of titania slag by direct reduction smelting in electric arc furnaces (particularly for smelting of iron titanates and ilmenites having lower amounts of titania) is very old and the process has been in vogue in Canada, Norway, South Africa, CIS, and Japan. The slag which contains about 80% TiO_2 has been (and is still being) used for the production TiO_2 pigment by the sulfate route. The USA and CIS have used the process involving chlorination of slags with the without ilmenite and in the presence or absence of chloride melts. In current lines, the development of a process involving reduction smelting in plasma arc furnaces for the production of pig iron and titania slag from ilmenites has been reported and according to published literature, this process is becoming more exploited on a commercial basis. Table 5.11 details the different metallurgical process options for the beneficiation of ilmenite to titania.

Table 5.11 Different metallurgical process options for ilmenite beneficiation.

Process	*Short process description*	*Examples of plants*
QIT electromelting	Hard rock ilmenite carbothermically smelted at 1700 °C to pig iron and sulphatable TiO_2 slag (86–87% TiO_2)	SOREL, Quebec, Canada
RTZ iron and titanium electromelting	–	Richard's Bay, South Africa
Submerged arc smelting process	Pre-reduction of ilmenite (50% TiO_2) followed by smelting in arc furnace to yield pig iron and titania slag (87% TiO_2)	TINFOS, Norway
Plasma DC arc smelting technology – South Africa Anglo American Corp.	Carbothermic smelting of ilmenite in DC arc plasma furnace to yield pig iron and titania slag	(A) Namakwa Sands Ltd., South Africa (B) ISCOR, South Africa
Upgraded slag technology	Conditioning of the SOREL slag followed by acid leaching and calcinations to UGS (95% TiO_2)	SORE, Quebec, Canada

5.4.4
Tungsten

The oxidic ores, wolframite ($FeWO_4$) and scheelite ($CaWO_3$), are the two traditionally used principal commercial sources of tungsten. The flowsheet for processing these to produce tungsten is shown in Figure 5.39. The high densities of wolframite (7.1 to 7.9) and scheelite (5.9 to 6.1), make them highly amenable to physical beneficiation methods involving gravity separation. Quite often, wolframite and scheelite need to be separated from other associations such as cassiterite (SiO_2) and pyrite (FeS). Since wolframite is magnetic and cassiterite is not, a magnetic separation operation can effectively separate the two. Magnetic separation is frequently preceded by calcination which converts pyrite into the magnetic oxide (Fe_2O_3) which can be separated from wolframite in a low-intensity magnetic field. The magnetic separation of wolframite and cassiterite is hindered when cassiterite is coated with an iron oxide layer. In such a situation the wolframite concentrate is leached with hot sulfuric acid or hydrochloric acid. Unlike wolframite, scheelite is nonmagnetic, and magnetic separation cannot be used to separate scheelite from cassiterite. Scheelite is separated from cassiterite by flotation or by electrostatic separation. The flotation methods have gained popularity recently in the enrichment of scheelite ores, especially when they are lean and are finely impregnated in others. A combination of methods comprising flotation, gravity separations and chemical treatments is sometimes employed for enriching scheelite ores. In many cases, powellite ($CaMoO_4$) is present in scheelite-type ores, and this can be separated, provided that it is not isomorphically bound to the scheelite. This explains the presence of molybdenum in scheelite concentrates. In order for the two concentrates to be treated for tungsten recovery, they are first decomposed. Whilst wolframite can be decomposed with sodium carbonate, scheelite cannot undergo similar treatment be-

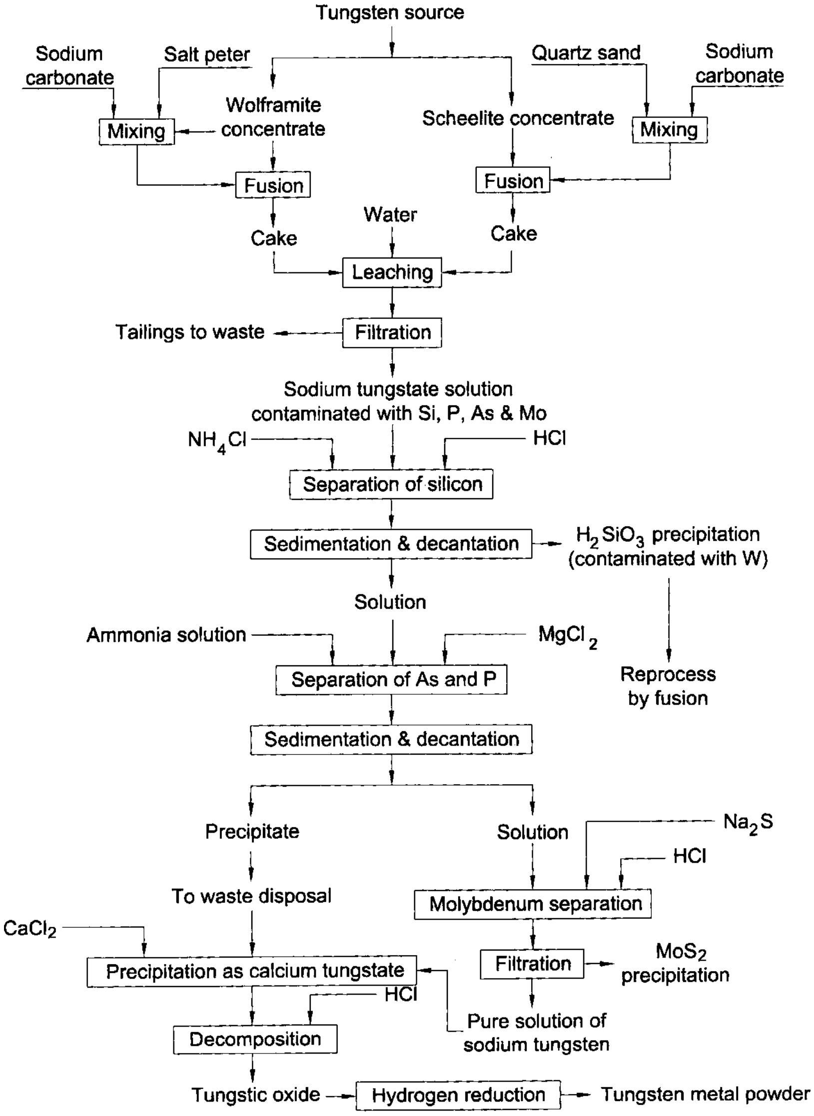


Figure 5.39 Processing of tungsten resources.

cause the fusion reaction between scheelite and sodium carbonate reverses when the fused mass is leached:

$$CaSO_4\ (s) + Na_2CO_3\ (s) \underset{\text{Leaching}}{\overset{\text{Fusion}}{\rightleftarrows}} Na_2WO_4\ (s) + CaCO_3\ (s)$$

In order to make scheelite decomposition irreversible, quartz sand is added to the charge in an amount sufficient to bind calcium as an insoluble silicate. Alternatively, scheelite concentrates are directly decomposed with hydrochloric acid according to the reaction:

$$CaWO_4 + 2\ HCl \rightleftharpoons H_2WO_4 + CaCl_2$$

As a result of the decomposition, calcium chloride and other soluble impurities pass into solution, while tungstic acid, together with silica and undecomposed scheelite, remain in the residue. The technical grade tungstic acid thus obtained is purified using the ammoniacal method.

The sodium tungstate solution obtained by processing either the wolframite or scheelite concentrate usually contains silicon, phosphorus, arsenic, molybdenum, and sulfur as impurities. The solution is heated to boiling, and hydrochloric acid is slowly added; neutralization of the solution is carried out by adding ammonium chloride. This operation eliminates silica by the formation of silicic acid (H_2SiO_3) under the conditions of boiling, hydrochloric acid addition, and finally neutralization by ammonium chloride, as described. The solution is then cooled and ammonia solution and magnesium chloride are added. These procedures result in the formation of magnesium ammonium phosphate ($Mg(NH_4)PO_4 \cdot 6\ H_2O$) and magnesium arsenate ($Mg(NH_4)AsO_4 \cdot 6\ H_2O$) which precipitate out; thus gets rid of the associated arsenic and phosphorus impurities are lost from the solution. The process is not yet complete however, as there is one more impurity, molybdenum, which must be removed. The best way to do this is to treat the solution with sodium sulfide and adjust the pH with hydrochloric acid; this causes the molybdenum to precipitate out as its sulfidic form. The purified solution is finally treated with calcium chloride to precipitate calcium tungstate, which is decomposed by heating with hydrochloric acid. The tungstic acid (H_2WO_4) obtained is calcined to tungstic oxide (WO_3), which is thermally reduced with hydrogen to yield metallic tungsten powder.

5.4.5
Molybdenum

Molybdenite, MoS_2, is the most important and abundant of all the molybdenum minerals. A condensed flowsheet for processing molybdenite to yield the various commercially used forms of molybdenum is shown in Figure 5.40. The run-of-mine source material is subjected to physical beneficiation, in which flotation plays a key role, to produce 90–95% grade molybdenite. The concentrate is the starting point for further processing. Some of the molybdenite, after purification, is used as a lubricant on account of its antiwear properties. Molybdenite is converted to technical grade molybdic oxide by treatment in a fluid bed roasting or a multiple hearth roasting furnace. During roasting, all the rhenium that occurs in association with molybdenite oxidizes to the hepoxide, Re_2O_7, and joins the off-gas stream (the sublimation point of Re_2O_7 is 363 °C), to be retained in the electrostatic precipitator.

Technical grade molybdic oxide is the starting material for almost all the molybdenum products. Molybdic oxide as such is used, to a small extent, by glass and ceramics industries. A major portion of molybdenum is marketed in a number of forms for use as additives to iron and steels. The various forms of molybdenum, and the ways in which they are produced to serve as additives, are indicated in Figure 5.40. Among the various forms, the molybdic oxide–carbon mixture is by far the most economical additive to iron and steels. The carbon in the mixture helps in the quick dissolution of molybdenum in the melt by acting as a reductant at the melt temperature and by promoting turbulent mixing as the

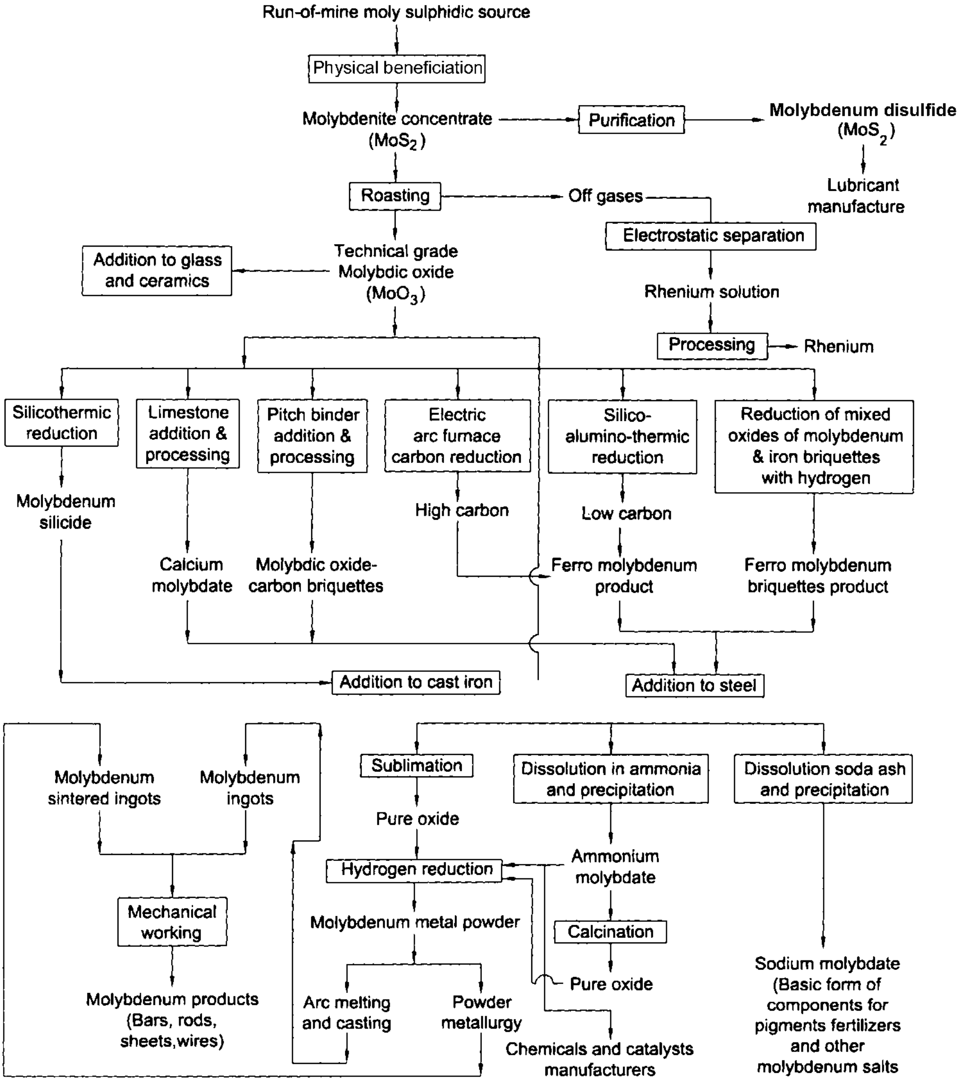


Figure 5.40 Molybdenum processing flowsheet.

product gas comes out of the briquette. The forms in which molybdenum is used in the production of cast and wrought steels depends largely on the steel-making process, on local conditions, on the amount of molybdenum to be added and, of course, on economics. Ferromolybdenum is adaptable to any of the processes, and is preferred over other additives when relatively large additions of molybdenum are needed.

Pure molybdenum trioxide, a higher quality product, is in great demand with regard to chemicals and catalyst manufacturers, superalloy producers, and molybdenum metal producers. This refined quality oxide is produced by the volatilization of the technical grade oxide or by calcining ammonium molybdate, which is probably the purest commercially available molybdenum compound. It is prepared by leaching the technical grade oxide or even the pure oxide in ammonium hydroxide. The solution is filtered and evaporated, thereby crystallizing the pure compound. It is used by chemicals and catalyst manufactures. The calcination of this compound produces pure molybdic oxide. The pure oxide produced by this route or by the volatilization route, or the ammonium molybdate as such, is reduced by hydrogen to yield molybdenum metal powder. The powder is converted to consolidated ingot by either powder metallurgy methods or by the melting and casting route. These ingots, through various mechanical working processes, end up as bars, rods, wires, and sheets.

5.4.6
Precious Metals

The platinum group metals (PGMs) consists of six closely related metals which commonly occur together in nature: platinum, palladium, rhodium, iridium, ruthenium, and osmium. These are among the scarcest of metallic elements, and together with gold and silver, they are known as "precious" or "noble metals". The naturally occurring resources of the precious metals are invariably associated with large amounts of gangue materials which greatly influence their extraction process. As a representative example of precious metals group, the metallurgical processes for gold will be discussed in this chapter.

PGMs are usually found together and are thus produced together. Their ratios depends on the ore location. The two metals, platinum and palladium, together account for about 90% of PGMs. Focusing attention only on platinum as representative of the six major group, it may in the first instance be pointed out that this element is found in about 0.01 ppm in the Earth's crust. The major chemical form are $PtAs_2$, (PtPd)S, (PtPd)NiS, and as native metals in platinum–iridium and palladium–platinum. The ores and metals are found in placers deposit chemical form basic/ultra basic igneous rocks. In sedimentary and igneous rocks the platinum is associated with chromite, magnetite, ilmenite, iridium, and osmanium. The Sudbury area in Canada reports one of the major sources of PGMs. They are produced their as the byproduct of nickel and copper production. The anode slime that results from copper-nickel electrolytic refinery forms the substantial source of PGMs. The method by which they are extracted from concentrates, separated and refined are entirely chemicals – they are in essence chemical methods implemented on the large scale. Prior to 1974 the greatest use of platinum was in jewelry but since then its use in automotive converter has taken the lead.

5.4.6.1 Gold

The processing of gold ores is one of the peer examples of assemblage of a number of important hydrometallurgical unit operations. Historically, the starting point dates back to 1887 and 1888 when two key British patents were awarded to MacArthur and Forrest Brothers. The first patent covered the dissolution of gold from ores using dilute solutions of potassium cyanide, while the second covered the use of finely divided zinc to recover gold from cyanide solutions. These two patents laid the foundation of the cyanide process, and this very quickly became established as the industry standard for the processing of gold ores. Indeed, the cyanide process still dominates as the method of universal choice for the dissolution of elemental gold.

The cyanide process requires that the gold be oxidized in the presence of a complexing agent (a ligand) that can complex with the gold and stabilize it in solution. It is, therefore, necessary that both an oxidant and a ligand must be present otherwise gold will not dissolve. It is also often necessary to add a pH modifier, either acid or alkali, to maintain an optimum pH. For example, gold dissolves in aqua regia, a mixture of nitric acid (which provides the oxidant) and hydrochloric acid (which provides the chloride ligand), but does not dissolve to any appreciable extent in the individual acids. Oxidation is required because the gold usually occurs in ores in the elemental form (oxidation state of zero), while other gold minerals, (e.g., tellurides) require oxidation to make the gold amenable for leaching. Complexing agents are necessary because the simple aqua ions of gold (I) and gold (III) (e.g., $[Au(OH_2)_2]^+$ and $[Au(OH_2)_4]^{3+}$, respectively) are not stable in simple aqueous solutions.

The overall reaction for the dissolution of gold in dilute aerated, aqueous alkaline cyanide solution may be expressed by the classical Elsner equation:

$$4\ Au + 8\ NaCN + O_2 + 2\ H_2O = 4\ NaAu(CN)_2 + 4\ NaOH$$

or

$$4\ Au + 8\ CN^- + O_2 + 2\ H_2O = 4\ Au(CN)_2^- + 4\ OH^-$$

In the above reaction, oxygen is the oxidant and cyanide ion is the complexing agent or ligand. The gold in the aurocyanide ion is present as gold (I). It should be noted that in the equation above, silver may be substituted for gold, and potassium cyanide for sodium cyanide. The dissolution reaction between gold and potassium cyanide is chemically represented as

$$4\ Au + 8\ KCN + O_2 + 2\ H_2O = 4\ KAu(CN)_2 + 4\ KOH$$

However, sodium cyanide is usually selected for leaching because it is the least expensive cyanide. As regards the oxidizing effect, the addition of oxidizing reagents in place of atmospheric oxygen to perform the function has not been very successful because of their tendency to oxidize the cyanide to cyanate. Another important parameter in the leaching process is the pulp pH, as both low pH (< 8) and high pH (> 11) result in a decreased dissolution rate. The use of a pH value less than 9 is taken to be quite advantageous.

The precipitation process for gold from cyanide solution by zinc is chemically a simple metathesis, or cementation reaction:

$$2\ NaAu(CN)_2 + Zn = Na_2Zn(CN)_4 + 2\ Au$$

or

$$2\ Au(CN)_2^- + Zn = 2\ Au + Zn(CN)_4^{2-}$$

$$2\ KAu(CN)_2 + Zn = K_2Zn(CN)_4 + 2\ Au$$

From the thermodynamic behavior of metals pertinent to gold leaching in cyanide solutions it may be observed that Au(CN) shows a large region of stability over the whole pH range, whilst metallic gold, which is usually stable in aqueous solutions under all conditions (except chloride solutions), becomes soluble in cyanide solutions in relatively low oxidation potentials. The region of stability of zinc metal ranges well below that of gold, and hence zinc is a very effective precipitant or reductant for gold in cyanide solutions. Any iron which dissolves forms ferro- or ferricyanide complex ions, and these provide a bluish tint to the gold ore leach solutions. In the case of copper, there is a large region of solubility of copper–cyanide complex ions under conditions where gold is dissolved. Both iron and copper solution tie up cyanide ions and give rise to excess cyanide consumption during gold dissolution.

An outline flowsheet of the cyanide process essentially based on the process chemistry described above is shown in Figure 5.41. Following comminution, the ore is leached at 50% pulp density with sodium cyanide solution containing 0.01 to 0.25 wt-% CN^-. The pH of the leach solution is kept at about 10.5 by lime addition. Leaching is performed in large, aerated tanks, either mechanically or air agitated, with residence times of 24–48 h. The leached ore pulp is then filtered and washed, with barren solids being disposed of, while the leach liquor, which contains only 5–10 ppm gold proceeds to the precipitation stage. The Merrill–Crowe process accomplishes the precipitation. It involves four stages: (i) clarification; (ii) deaeration; (iii) precipitation of gold by addition of zinc dust along with a small amount of lead nitrate to catalyze the reaction; and (iv) filtration of the precipitated gold slime. A cleansing operation for the gold slime then follows with dilute sulfuric acid to solubilize excess zinc particles. It is then subjected to drying, calcination and smelting with fluxes, and finally molten gold bullion is poured into ingot molds.

An elegant method called the carbon-in-pulp (CIP) process is also considered as the industry standard process for gold, and Figure 5.42 shows an outline flowsheet of the technique. The three main components of the circuit are adsorption, elution, and reactivation. It is true that were it not for the development of effective methods to remove gold from the carbon to enable recycling of the latter, the CIP method would not have attained its present status of an industrially economic process. Prior to this significantly important development, the only recourse available to recover the gold was by burning the carbon. It was at the US Bureau of Mines that a method that involved contacting a solution of sodium cyanide and sodium hydroxide at about 90 °C with a fixed bed of gold-loaded carbon for removing gold was developed. This method is used today in the majority of plants. In practice, the carbon column stands in series with a bank of electrolytic cells that remove eluted gold from solution by electrodeposition on stainless-steel cathodes. The solution is continuously recirculated through the elution column and the electrowinning cells. During the adsorption cycle of CIP, various inorganic and organic species are also adsorbed onto the carbon. These species are not removed by elution, and this results in a loss of activity of the carbon for gold adsorption; hence, a reactivation procedure becomes mandatory. This is commonly carried out in two stages – acid washing and thermal treatment. Acid washing eliminates calcium carbonate which is one of the major inorganic adsorbates. Following this, the wet carbon is heated to about 650 °C in the absence of air. This results in elimination of adsorbed organic and a partial burning of the carbon itself. The major advantage of the CIP process compared with the traditionally applied route with zinc is the elimination of the filtration and washing steps involved with the leached pulp. This can bring about savings of up to 50% on the capital cost of a gold plant, and 20–30% savings in operational costs. Carbon absorption is reputed to be productive and is at its best at very low gold

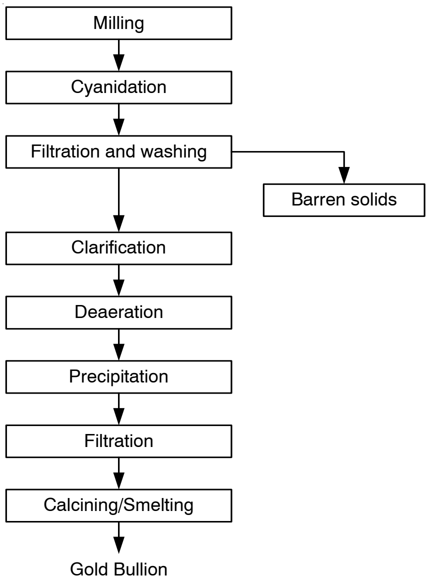


Figure 5.41 Standard cyanide process of gold production.

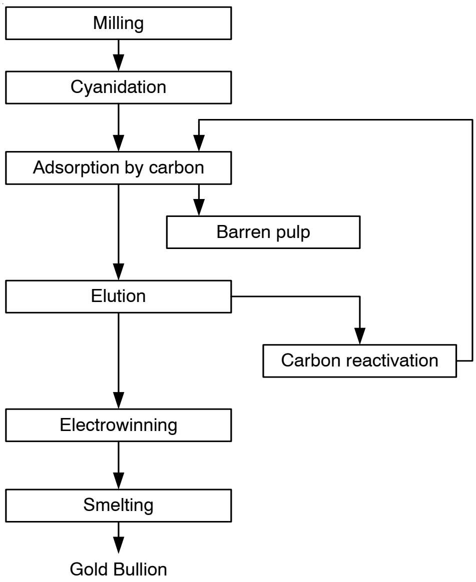


Figure 5.42 Carbon-in-pulp process.

concentrations; hence it can be employed very well to recover gold from very lean sources, as for example, retreated gold ore tailings.

Gold ores grouped as "refractory" are those in which the gold does not lend itself easily to dissolution in cyanide solutions. There are at least three different types of refractory ores that are encountered:

1. Free gold, which is locked in sulfide minerals, usually pyrite and arsenopyrite; this is the most common reason for refractoriness.
2. Ores which are associated with carbonaceous matter which reabsorbs dissolved gold.
3. Ores in which the gold is in chemical combination in the form of an alloy, typically with tellurium, this is less common, but it creates recovery problems where it does occur.

Gold associated with sulfide minerals can be subjected to flotation, to give a gold-bearing sulfide concentrate. The gold can subsequently be made soluble by oxidizing the sulfide minerals, to destroy the mineral lattice and thereby release "free" gold, making it available to leaching by cyanide solutions. It is thus seen that refractory sulfidic gold ores are given some sort of oxidative pretreatment before applying conventional cyanide leaching and subsequent gold recovery by CIP or zinc precipitation. The oxidation of sulfidic gold ores or concentrates is currently implemented by one of three processes – roasting, pressure oxidation, or biooxidation (Figure 5.43).

Roasting of ores or concentrates containing pyrite and arsenopyrite is carried out in two stages. The first stage is carried out in a restricted supply of oxygen in order that arsenic is oxidized to the trivalent state and removed as volatile As_2O_3. The second stage is carried out in a full supply of oxygen in order to remove sulfur as SO_2 and to convert iron to hematite.

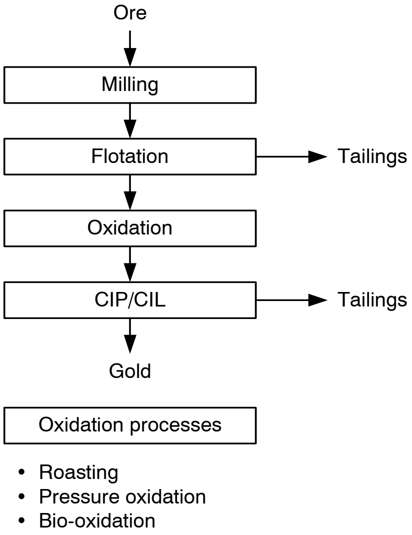


Figure 5.43 Treatment of refractory gold ore.

The roasting process gives rise to the formation of SO_2 and As_2O_3, both of which are environmentally undesirable. For this reason, roasting, although still practised, is less favorably disposed as compared with the newer alternatives of pressure or biological oxidation.

The modern trend is to employ processes based on aqueous oxidation of pyrite and arsenopyrite, and the chemical reactions involved can simplified as:

$$4\ FeS_2 + 15\ O_2 + 10\ H_2O = 4\ (FeOOH) + 8\ SO_4^{2-} + 16\ H^+$$

$$2\ FeAsS + 7\ O_2 + 2\ H_2O = 2\ (FeAsO_4) + 2\ SO_4^{2-} + 4\ H^+$$

As seen in the above equations, the aqueous oxidation processes convert sulfur in the feed to dissolved sulfate, while arsenic is oxidized and precipitated as ferric arsenate compounds. So, problems of the emission of sulfur and arsenic oxides caused by roasting are avoided in the aqueous oxidation processes. The two different industrial methods which achieve the oxidation reactions are pressure oxidation and biological oxidation.

In the *pressure oxidation* process, the sulfidic ore or concentrate is made to react in an autoclave with pure oxygen at 5–10 bar pressure at temperatures of 180–200 °C for nearly an hour.

Biological oxidation essentially involves the same aqueous oxidations, but these are carried out in a less intensive manner by using the catalytic action of naturally occurring bacteria, in particular Thiobacillus ferrooxidans. These bacteria can be employed to produce a culture which is capable of oxidizing the sulfide minerals in gold ores at temperatures of 35–45 °C in about 3–7 days the time of residence. The reactions are implemented in mechanically agitated tanks, and are supplied with substantial amounts of air to provide the oxygen required for the oxidation reactions to occur. The bioreactors must be cooled to keep the contents in the 35–45 °C range, where the bacterial action is optimized. The Sao Bento mine in Brazil represents a good example of the Genmin BIOX biological oxidation process working finally in combination with pressure oxidation process.

Table 5.12 Mines carrying out gold ore processing.

Process	*Names of mines, location*
Roasting	Golden Bear, USA; Cortez, USA; Big Springs, USA; North Kalgusli, USA; Newmont, USA
Biooxidation	Fairview, South Africa; Sao Bento, Brazil; Harbour Lights, Australia; Wiluna, Australia; Ashanli, Ghana
Pressure oxidation	Mclaughlin, USA; Mercur, USA; Sao Bento, Brazil, Campbell River, Canada; Getchell, USA; Goldstrike, USA; Porgera, PNG, Lihir, PNG

A list of the mines where different processing of gold ores is carried out is shown in Table 5.12. Although the pressure oxidation process appears to be the current leading technology, selection of the optimum route depends on several factors.

5.4.7
Dispersed Metals

Reference has been made earlier to scattered rare metals, the five most important members of this particular group being gallium, indium, thallium, rhenium, and germanium. A common feature of these metals is that they do not form commercially significant mineral sources of their own, but are invariably produced from the processing of other mineral sources. The description given here pertains to rhenium, and serves as one example of these dispersed metals.

In molybdenite processing described earlier, it was indicated that rhenium is collected from the gaseous fractions when the outgoing gas stream passes through the electrostatic separator/scrubber during the roasting process. The dust typically contains 0.4 to 1.5% rhenium (Re) in addition to the main molybdenum components, MoO_3 and MoS_2, and a fairly large amount of sulfuric acid (this is because the roasting gases contain sulfur trioxide and water vapor). The flowsheet for the dust processing operation was shown in Figure 5.26. The dust is leached with the addition of finely ground pyrolusite to the solution so as to bring about oxidation of the lower rhenium compounds. In order to separate most of the molybdenum as well as copper and iron, the solution is neutralized to pH 11–12 using milk of lime, and heated to 60–70 °C. The precipitate formed contains calcium sulfate and molybdate, and copper and iron hydroxides. The solution is evaporated to obtain a somewhat concentrated solution of rhenium, which contains about 15–20 g l^{-1} of rhenium. The solution is filtered and potassium perrhenate ($KReO_4$) is precipitated by heating the solution and adding potassium chloride (about 50–60 g of potassium chloride per liter of the solution). The solution is then allowed to cool. The crystalline precipitate of technical grade $KReO_4$ produced in this way is purified by successive recrystallization. The purified material is hydrogen-reduced in two stages. The first operation is carried out at 500–550 °C. The reduced powder is washed to remove the hydroxide, after which it subjected to a second reduction at a higher temperature of 900–1000 °C, washed first with dilute hydrochloric acid and then with water, and dried in a vacuum or in a current of hydrogen. Solid rhenium is made either by powder metallurgy techniques involving compacting and sintering, or by melting (arc or electron beam melting). Highly pure rhenium can be produced by zone melting.

5.4.8
Copper

The basic copper extraction process has traditionally used two main approaches: pyrometallurgical and hydrometallurgical processing. It should be noted, however, that the general trend of modern extractive metallurgy tends to integrate these approaches. This is reflected for instance in the roast-leach-electrowin processes for both copper and zinc. In the case of the two methods, the first part of the flowsheet is the roasting unit operation (this is a typical pyrometallurgical stage), while leaching of the roasted product and further electrowinning of metal values belong respectively to hydrometallurgy and electrometallurgy. As far as the copper industry is concerned, however, a pyrometallurgical process has a distinctive feature in that copper is made in a furnace as liquid metal. In the pyrometallurgical field (see Chapter 4), different approaches can be used. All of these essentially try to integrate the roasting-smelting-converting stages into an autogenous continuous process. The differences among the different pyrometallurgical approaches for copper extraction lie mostly in the engineering techniques adopted and the design of the reactions rather than in process principles. The extractive metallurgy of copper can truly be cited as the leading example where hydrometallurgy has been very extensively applied. It is in this area that bacterial leaching can be said to have worked at its best and has been commercially exploited. (This aspect is further elaborated in Section 0.0 bacterial leaching). By far the greatest tonnage among all nonferrous metals produced by acid leaching is copper.

Several copper minerals, containing copper in the divalent state, are completely soluble in sulfuric acid according to the following reactions:

$$Cu_3(OH)_2(CO_3)_2 + 3\ H_2SO_4 \rightarrow 3\ CuSO_4 + 2\ CO_2 + 4\ H_2O \qquad \text{(azurite mineral)}$$

$$Cu_2(OH)_2(CO_3) + 2\ H_2SO_4 \rightarrow 2\ CuSO_4 + CO_2 + 3\ H_2O \qquad \text{(malachite mineral)}$$

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O \qquad \text{(tenorite mineral)}$$

$$CuSiO_3 \cdot 2\ H_2O + H_2SO_4 \rightarrow CuSO_4 + SiO_2 + 3\ H_2O \qquad \text{(chrysocolla mineral)}$$

$$Cu_4(OH)_6SO_4 + 3\ H_2SO_4 \rightarrow 4\ CuSO_4 + 6\ H_2O \qquad \text{(brochantite mineral)}$$

Most of the leaching techniques mentioned earlier, such as in-situ leaching, dump leaching, heap leaching, vat leaching and agitation leaching, have been practiced for the dissolution of oxide ores, mixed oxide/sulfide ores and certain sulfide ores of copper in sulfuric acid. Table 5.13 summarizes the range of solutions produced by the various leaching techniques. The contents of these solutions determine the metallurgical parameters under which the copper extractant must be able to extract copper efficiently and selectively. These solutions exhibit wide ranges of copper concentrations and pH values.

With regard to the sulfidic sources of copper, the main emphasis, as far as hydro-based process applications are concerned, has been on the chalcopyrite concentrates. Of the copper-bearing minerals, chalcopyrite ($CuFeS_2$) is by far the most abundant but its reactivity in

Table 5.13 Typical sulfuric acid leach solutions.

Leaching technique	*Copper (g l^{-1})*	*pH*
In-situ	< 1–3	1.8–2.1
Dump	< 1–3	1.2–2.2
Heap	3–6	1.5–2.2
Vat	5–50	1.6–2.0
Agitation	1–6	1.8–2.0

many of the leaching media is at best modest. The chemistry of processing chalcopyrite looks attractive. The main leach reaction with sulfuric acid is generally represented by:

$$CuSO_4 + H_2SO_4 + 1.25\ O_2 \rightarrow CuSO_4 + 0.5\ Fe_2O_3 + 2\ S + H_2O$$

The reaction is apparently straightforward, and if it proceeds to completion should yield iron oxide and elemental sulfur as easily recoverable solid product leaving behind a cupric sulfate solution suitable for electrowinning or hydrogen reduction for copper production. The sulfuric acid would be regenerated and be in balance with reaction shown above for recycling to the leach system. However, under the optimum conditions not more than 65% of the copper present in the mineral is extracted into the solution. This has naturally led to development of many improved and alternative leaching processes for processing of chalcopyrite and other copper concentrates. The list of hydrobased copper process includes: (i) Sherritt–Cominco process; (ii) Cymet process; (iii) Cyprus process; (iv) Clear process; (v) Minimet Recherche process; (vi) processes using nitric acid in sulfate systems; (vii) Arbiter process; and (viii) acetonitrile process. A number of standard references exist on the details of these processes and they may be examined for the process pros and cons and features associated.

5.4.9
Manganese Nodules

Deep-sea manganese nodules constitute a unique type of mineral resource that is characterized by extensive and extremely diverse polymerization. There are perhaps, if at all, only extremely limited known sources which can surpass this particular feature. It is by far a highly complex resource, and only rarely are other materials found of similar composition. Truly, this mineral resource is among the most severe challenges to current to chemical metallurgists to devise cost-effective ways and means of processing. In general, there are two major constituents of mineralogical importance, namely, manganese dioxides and iron oxides. Economically important minor elements such as nickel, copper, cobalt and molybdenum, are distributed within these major constituent minerals, having been incorporated either by an adsorption mechanism or by a lattice substitution mechanism. As some of the special characteristics of this source, mention may be made of the following:

1. They are highly porous conglomerates and, because of their large porosity, the nodules are very light, with an apparent density of only about 1.4 g ml^{-1}.

2. They have a tenaciously held, high water content. The fact that raw nodules contain typically more than 30% moisture, which must be removed during high-temperature processing is a major disadvantage for both smelting and reduction roasting routes.

The combination of physical and chemical characteristics of nodules make impossible the application of methods of physical beneficiation such as flotation and magnetic separation to produce concentrates of valuable metals, and so chemical processing must be used. Their processing also tends to be much more energy-intensive, vis-à-vis that of conventional land-based ores. Deep-sea manganese nodules are quite unlike any terrestrial ores, both with respect to their physical characteristics and to their mineralogical and chemical compositions; new processes are, therefore, required.

Nevertheless, manganese nodules can, at best, be considered to be similar to land-based nickel laterites, and consequently most of the processing techniques that have been tried are similar to those used on lateritic ores. Reduction roasting followed by ammonia leaching, as in the Nicaro process, and high-temperature sulfuric acid leaching, as in the Moa Bay operation, have been extensively tried to process nodules.

Literature surveys record the accomplishment of processing of modules basically in two ways: pyrometallurgical and hydrometallurgical, by which manganese nodules are processed to extract the contained valuable metals such as manganese, nickel, cobalt, and copper. Figure 5.44 presents a summary of all the processes examined to treat ocean-floor manganese nodules. Initially, the nodules are subjected to comminution to break down the size of the particles amenable for various treatments. The ground products can led directly to leaching or pyro-processing following drying or pretreatment such as reduction, sulfation, chlorination, etc. prior to taking on to leaching.

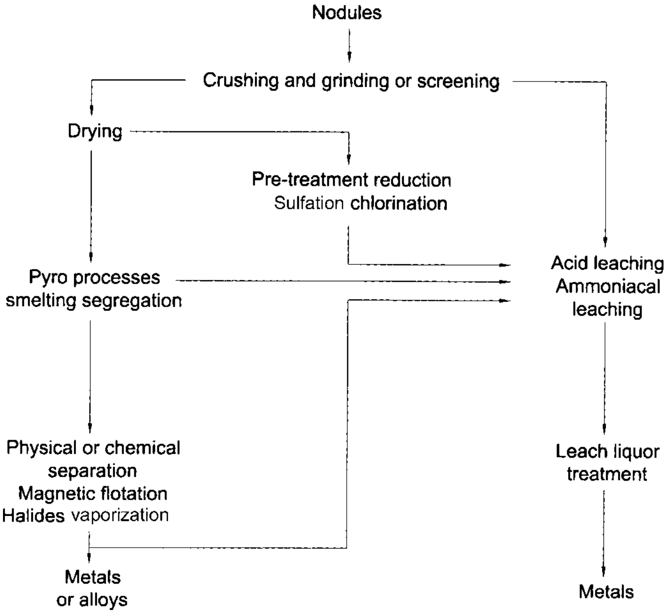


Figure 5.44 Summary flowsheets of hydro- and pyro-processes of manganese nodules.

Acid leaching is very effective in the selective extraction of nickel, cobalt, and copper. It should, however, be noted that several major species (e.g., calcium, magnesium, and silicate) that are also acid-soluble are present in nodules. As a consequence, the acid consumption is relatively high. Acid leaching permits good recoveries of not only nickel, cobalt and copper but also rare elements. The occurrence of rare metals and rare earth elements in nodules makes their processing unique. The economic consideration of these minor elements might be critical in the final decision-making process regarding the selection of process options of nodules. Process options to treat manganese nodules should be considered in view of the trend of such metals as nickel, cobalt and copper present, as well as other metals to be included in nodules. For example, the process selection would be quite different if manganese is to be extracted compared with the situation when manganese is not required. The selection of manganese extraction is, of course, based on the need and demand of manganese at the rate that this metal will be produced. In some cases, iron would be considered for production, particularly when steels containing iron, manganese and others such as nickel and cobalt are to be extracted via the nodules process.

Ammoniacal leaching bears the reputation of being selective for nickel, cobalt and copper against manganese and iron. In this case, however, nodules need to go through high-temperature reduction to realize the oxidic form of these metals into their metallic forms prior to passing them for effective leaching. Ammoniacal leaching suffers from a disadvantage in that it complexes with very selected elements, usually with those belonging to the transition metals category. The ammonia leaching technology is applicable to nodules without pretreatment but with the assistance of number of reductants, amongst which the most widely used is sulfur dioxide or sulfurous acid.

The pyro method of processing the nodules involves a number of tested roasting processes, and these include sulfation, chlorination, and direct smelting. The sulfation roasting has been tested with appropriate mixture of SO_2 and O_2, and sometimes in the presence of chlorides. The usual process for sulfation roasting involves heating of the nodules mixed with sulfuric acid to about 650 °C. The product obtained after roasting is then leached. The sulfation roasting process can also be implemented in an atmosphere of SO_2 and air. The chlorination roasting process can be carried out by a number of agents such as HCl, Cl atmosphere, and gaseous hydrogen chloride; water leaching is then performed to solubilize the chlorinated species. In the process called “segregation”, nodules are mixed with chloride solids, NaCl, calcium chloride and magnesium chloride, and carbon, and then heated at a temperature of 500–700 °C in an inert atmosphere. Metals such as copper, nickel and cobalt deposit on carbon particles; this occurs as they are transported from their original location in the nodules to a new location carbon, or they become segregated on carbon. Subsequent adoption of flotation, magnetic separation or screening can then accomplish separation between the carbon and the metals that have deposited on it. The smelting process involves direct smelting of the nodules with coke or carbon, and yields a mixture of the carbothermically reducible metals contained in the nodules. Separation of the metals is then carried out by leaching followed by applying electrowinning, solvent extraction or gaseous reduction technique.

Whether the pyro or the hydro-route of processing of nodules is used, it is found that – depending upon the treatment given – three types of solutions are produced, these being chloride solution, sulfate solution, and ammonia solution. Each of these solutions is entirely processible to recover the metals values held by them.

5.4.10
Zinc Solution Purification

The zinc extraction industry represents a prominent application of ionic precipitation on a large scale for the removal of impurities such as iron. As far as zinc extraction goes, hydrometallurgists and electrometallurgists can justifiably take pride in establishing the zinc roast-leach-electrowin process which has caused pyrometallurgical methods of extraction of zinc to pale into insignificance. Currently, the elegantly simple roast-leach-electrowin route accounts for a sizeable quantum of the production of primary zinc worldwide.

The starting resource is most commonly the lead–zinc sulfides, together with a miscellany of unwanted associations. The resource is usually processed at concentration plants incorporated at the mine sites, with the production of essentially two concentrates, one zinc-rich and the other lead-rich. The zinc-rich concentrate contains well over 50% zinc and iron at concentrations typically assaying in the range of 5–12%. This concentrate forms the input material for hydrometallurgical extraction of zinc. The first step, however, is roasting which is, of course, totally a pyrometallurgical operation. Roasting is autogenous and is carried out in fluid bed roasters. These are efficient, highly automated units and so there is no requirement for external fuel. The sulfur in the feed is oxidized to sulfur dioxide, which possess in to the roaster off-gases that are consequently rich in SO_2, and this results in a high degree of conversion to sulfuric acid and low SO_2 emissions in the outlet gases. Heat in the form of process steam is also recovered from the furnace off-gases in waste heat boilers. During roasting, particularly under the conditions employed in modern fluidized bed roaster units, most of the iron present (5–12%) in the sulfide concentrate becomes bound to zinc in the form of ferrites, which may be represented as $ZnFe_2O_4$. With the roasting step concluded, the two subsequent steps in the extraction of zinc are: (i) leaching of zinc calcine in sulfuric acid, and (ii) electrowinning of zinc from the acid-leached, zinc-bearing solution.

The conditions of temperature and acidity normally employed to dissolve the major portion of the zinc oxide in roasted product are not suitable for the dissolution of zinc ferrites. This implies zinc loss in the leach residues, and thus the overall zinc recoveries amount to only 85–93%. The reduced zinc extraction has been the most serious shortcoming of the electrowinning process, particularly in those instances where high iron feeds were meant to be treated. A strong sulfuric acid solution, maintained close to boiling, is a suitable medium conducive for the dissolution of zinc ferrites. The use of this solution, however, results in the dissolution of most of the iron in the residues in addition to that of the zinc present. Removal of this iron was mandatory before the zinc solution could be returned to the main leach circuit. The removal of rather huge amounts of iron from the solution has not been an easy task in the past, and the only known royal method of iron removal was precipitation as ferric hydroxide. However, this was not without problems as the precipitate is gelatinous; it occludes a great deal of solution; and it presents difficulties in respect of filtering and washing. However, with the introduction of several methods such as the jarosite process, the conversion process, the goethite process, and the hematite process, the scenario with regard to zinc extraction has changed dramatically and zinc metallurgy today stands on a strong foundation and is practically free of the problems of yesteryears. Many existing electrolytic zinc plants and all new plants have embodied one or more of these processes into their leaching circuits. The result has been rewarding in that the typical overall recoveries of zinc in the electrolytic process have enhanced to the 95–97% level.

In the jarosite process, the precipitation of iron occurs from acidic sulfate solutions as one of a group of basic ferric sulfates known as jarosites. The conditions for the precipitation of iron in the specific form of jarosite require a solution pH of about 1.5 and a temperature of about 95 °C. The reaction may simplifiedly be represented as:

$$3\ Fe^{3+} + 2\ SO_4^{2-} + M^+ + 6\ H_2O \rightarrow MFe_3(SO_4)_2(OH)_6 + 6\ H^+$$

where M stands for the added monovalent cation, $NH_4{}^+$ or Na^+. The most common cations used industrially are NH_4^+ or Na^+. A feature of the jarosite precipitation reaction, that is common with other hydrolysis reactions, is that hydrogen ions are produced and these have to be neutralized to maintain the pH at the required level during precipitation. A simplified flowsheet of the process is shown in Figure 5.45.

The principal advantages of the jarosite process compared with the other iron precipitation processes described subsequently, ensue mainly from the nature of jarosite itself. Being a basic sulfate, it is divorced from relatively acidic solutions, thus permitting an efficient consumption of the zinc roast added as a neutralizing agent. It also authorizes excess sulfate to be removed from the closed leaching cycle. This is a pronounced advantage in many works where extra sulfate hailing from the zinc roast produces sulfate balance problems. When formed, jarosite is immune to acid attack, and therefore undissolved zinc roast combined with jarosite can be readily recovered by washing with acid. These features bestow a considerable amount of flexibility on the operation of the process and concede for optimization to fetch particular process requirements. The process, however, suffers from two disadvantages. The first is the need to incorporate a precipitating reagent, usually ammonia, to implement jarosite formation. The second is that the low iron content of jarosite (theoretically 35%) implies that rather huge amounts are produced for disposal.

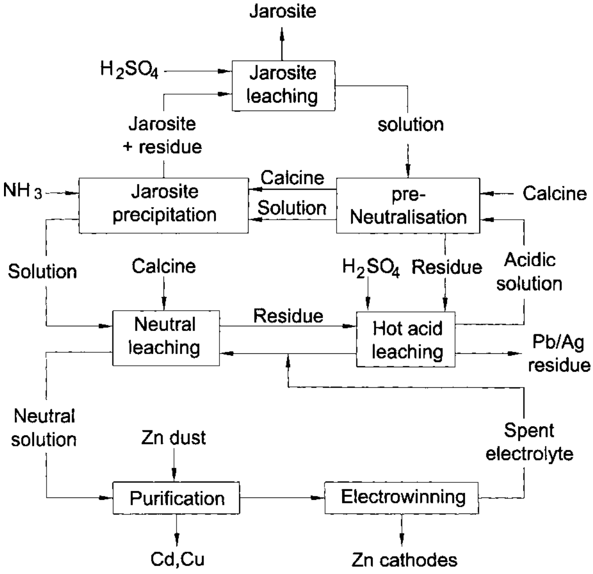


Figure 5.45 The integrated jarosite process flowsheet.

The conversion process (developed by Outokumpu) is a modification of the jarosite process and involves simultaneously zinc ferrite dissolution and jarosite precipitation in the same reaction vessel. The overall reaction may be represented in simplified form as:

$$3\ ZnFe_2O_4 + 6\ H_2SO_4 + (NH_4)_2SO_4 \rightarrow 2\ NH_4Fe_3(SO_4)_2(OH)_6 + 3\ ZnSO_4$$

The process relies fundamentally on the fact that zinc ferrites are more soluble in sulfuric acid than are jarosites. It is thus possible to control the acidity optimally and develop conditions under which ferrites will dissolve while, jarosites will precipitate. As is apparent from the chemical equation shown above, the reaction is a consumer of sulfuric acid and so may be controlled by the rate at which the acid is fed to the conversion reactor. This is essentially the difference between the conversion process and the jarosite process. In the latter, the starting solution holds excess acid, which is neutralized by adding zinc roast, and there is the associated danger that incorrect control can give rise to excess neutralization which in turn can give rise to precipitates with difficult solid-liquid separation features. In contrast, it is declared that because the conversion reaction is controlled by acid addition, the problems of extra neutralization are removed. The conversion process is characterized by its operational stability, yielding very consistent precipitates. In the absence of availability of operational details of the process it is only a fairly good guess that requirement of a long residence time in the conversion reactor is a major drawback of the process.

In the goethite process, the precipitation of iron from solution occurs in the form of hydrated ferric oxide, FeOOH. The commercial development of the process was due to Societe de La Vielle Montagne. The process basically involves the reduction of iron to the ferrous state, and this is followed by oxidation by air at a temperature of around 90 °C and at a pH controlled at around 3.0. The reaction can chemically be shown as:

$$4\ Fe^{2+} + O_2 + 6\ H_2O = 4\ FeOOH + 8\ H^+$$

The principal differences between the goethite and the jarosite processes take place following the hot acid leaching of the zinc ferrite residues. In the goethite process, the liquor from hot acid leaching, holding (in g l^{-1}) 100 Zn, 25–30 Fe^{3+} and 50–60 H_2SO_4, is initially subjected to a reduction step, where the ferric iron is reduced to the ferrous form by reaction with unroasted zinc sulfide concentrate at 90 °C:

$$2\ Fe^{3+} + ZnS \rightarrow 2\ Fe^{2+} + Zn^{2+} + S^0$$

The goethite process flowsheet is shown in Figure 5.46.

The goethite process does not appear to possess the inherent flexibility of the jarosite process. The process succeeds when conditions are extremely carefully controlled during precipitation, especially the pH. The relative solubility of goethite in sulfuric acid medium is a major shortcoming, because the iron residue cannot be subjected to working with acid to recover undissolved zinc arising from the zinc roast added for the purpose of pH control. In the Van Den Neste E. Metallurgie Hoboken – Overpelt's zinc electrowinning plant, this problem is triumphed by employing meticulously selected zinc roast having a low ferrite content at the time of neutralisation during goethite precipitation. This type of solution is, however, not likely to be pertinent to plants fastened to single major sources of raw material, where gross variations in the compositions of the zinc roasts will not develop. In such plants, the application of the goethite process would nearly unavoidably lead to reduced

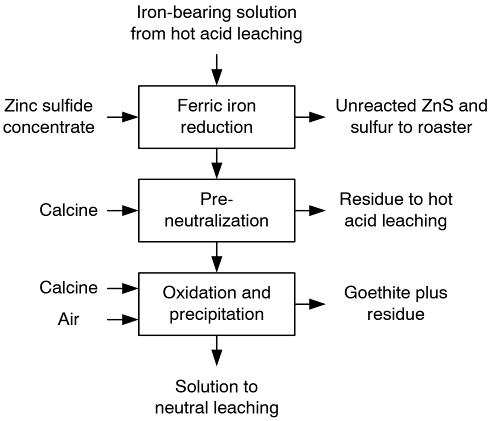


Figure 5.46 The Vielle Montagne goethite process.

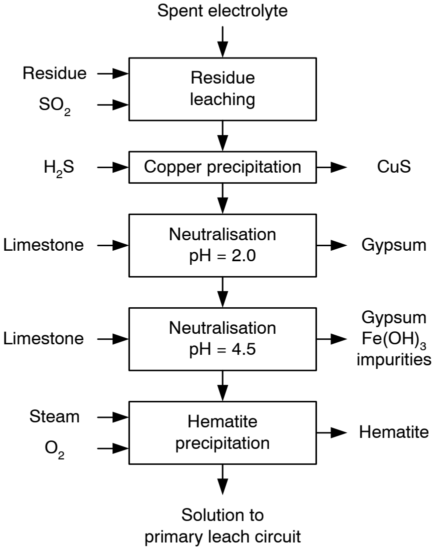


Figure 5.47 The hematite process.

overall zinc recoveries than could be obtained with the jarosite process. This is presumably the main reason for the jarosite process to be applied much more widely as compared with the goethite process.

The hematite process is practised by Akita Zinc Company in Japan. A flowsheet of the process is shown in Figure 5.47.

There are two advantages associated with the process. The high temperatures used for iron precipitation in the process cause hematite to continue to form, even in relatively acidic conditions. Thus, a requirement for the addition of zinc roast to destroy the acidity produced by the hydrolysis reaction is eliminated. This means that, in theory, no zinc should be lost with the zinc residue. The second advantage pertains to the high iron content of the hematite residues, theoretically 70% Fe, but in practice closer to 60% Fe, which leads to much smaller amounts of iron residues for disposal. A given quantity of iron, when precipitated in the form of hematite, will weigh less than half that of the same quantity of iron when precipitated in the form of jarosite. The major disadvantage of the process, as could clearly be seen, is that high-cost pressure reactors are needed.

In the ultimate analysis it may be pointed that the aforesaid hydrolysis processes are no doubt technically very satisfactory and tolerable, but environmentally this is not the case. The different processes yield jarosite, goethite and hematite, all of which retain considerable amounts of other elements, especially, zinc and sulfur. The zinc originates mainly from undissolved zinc roast in the iron residues, and sulfur from sulfate, which is either embodied into the crystal lattice or adsorbed in the precipitate. As a consequence of the association of the impurities, none of these materials is suitable for iron making and therefore they must be disposed of by dumping. The extent of soluble impurities present in the iron residues means that environmentally safe disposal not an easy task, and increasing concern is being voiced about these problems. An alternative way of removing iron from zinc leach liquors, and which produces an iron product suitable for the production of iron, would be an ideal solution to these problems. One method (which is conceptual, to say the least) is to remove iron by solvent extraction, and this and contain other innovations may appear as future developments in the metallurgy of zinc.

5.5
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6
Electrometallurgy

6.1
Introduction

Chemical reactions which have the capacity to occur spontaneously are in a position to generate electrical energy under appropriate conditions. Chemical reactions or processes which do not have the capacity to take place spontaneously can be induced to do so if an appropriate quantity of electrical energy is supplied under appropriate conditions. Both types of chemical changes are regarded as being *electrochemical* in nature. For implementing changes of either type it is necessary to have an electrolyte in which at least two electrodes are dipped. Such a set-up is generally called a *cell*, and cells from which electrical energy is derived are known as electrochemical cells (or Galvanic cells or Voltaic cells). Those to which electrical energy has to be fed to drive chemical reactions are known as electrolytic cells. In a nutshell, therefore, in an electrolytic cell, electrical energy supplied from an outside source causes a spontaneous reaction to occur. A galvanic cell, on the other hand, harnesses a spontaneous reaction to generate electric current. In either, the electrode at which oxidation occurs is called the anode, and the electrode at which reduction occurs is called the cathode. Electrolytic cells have numerous commercial applications. Many galvanic cells are of commercial importance. The content of this chapter basically deals with the two different areas of electrical energy as described above. It should also be pointed out in passing that there is one other area which is equally important and represents bulk utility of electrical energy; examples include arc furnaces and heating appliances. This involved area is familiarly called *electrothermics*; however, the present text does not enter into the realm of these significantly important technological areas.

6.2
Electrical Conductance

Electrical conductance is fundamental to the functioning of electrolytic and electrochemical cells. The following presentation incorporates a review of the conduction of electricity by a variety of substances in the solid state, as well as in the liquid state.

Electrical conductors may be divided into two distinct classes: (i) electronic conductors and (ii) electrolytic conductors or electrolytes.

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The passage of electricity through electronic conductors involves the flow of electrons from a point of higher negative or lower positive potential to a point of lower negative or higher positive potential, without the transfer of any matter. A metal, which is a typical electronic conductor, is regarded as a three-dimensional assembly of positively charged metal ions and the corresponding free electrons. An important observable change in a conductor during such conduction is a rise in its temperature. However, no chemical changes occur in it; neither does it undergo any permanent physical change. Besides this, the conductor exhibits certain magnetic and electrical effects during such conduction. Whilst the extent of electronic conduction generally diminishes with rising temperature, there exists a class of materials – known as semiconducting materials – in which the conductivity increases with rising temperature.

Electrolytic conductors are distinguished from electronic conductors in that the passage of an electric current in the former is accompanied by a chemical reaction (or reactions) and a transfer of matter. An electrolyte, although containing positive ions like a metal, also contains negative ions instead of free electrons as present in a metal. The positive ions present in a metallic salt are often metal atoms but may be radicals which have lost one or more electrons, the number of electrons lost corresponds to the valency of the metal or the radical. The negative ions are either nonmetal atoms or acid radicals which have gained one or more electrons, according to their valencies, from the metal atoms or the positive radicals.

6.2.1
Ionics

In the solid or crystalline state most salts are composed entirely of an assembly of ions, and as such may be regarded as insulators from an electrical point of view. However, when such a salt is melted, or when it is dissolved in water or some other solvent, the rigid lattice structure breaks up: the ions acquire freedom of movement so that under the influence of a potential difference the positive ions migrate in one direction, and the negative ions in the opposite direction. On account of the absence of free electrons in metallic salts, the passage of an electric current either through a fused salt, or through a solution of a salt, is brought about entirely by the migration of positive and negative ions. Unlike in electronic conduction, transfer of matter occurs simultaneously with the passage of an electric current by electrolytic conduction. The extent of electrolytic conduction increases with increasing temperature, this being a consequence of the increased ionization brought about by an increase in temperature.

Ions are derived from electrically neutral atoms (or groups of atoms) but differ from them in that they possess an electrical charge. This charge is positive for the hydrogen ion and for ions derived from metals (or nonmetallic groups such as NH_4^+) and negative for ions derived from nonmetals or acidic radicals.

The number of electric charges possessed by an ion (corresponding to its valency) is indicated by writing as a superscript one or more positive or negative signs after the chemical symbol for the element or the radical concerned according as to whether the ion is positive or negative in character. Thus, Na^+ depicts the univalent sodium ion, Cl^- the univalent chloride ion, SO_4^{2-} the divalent sulfate ion, and Cu^{2+} the divalent cupric ion.

Some examples of compounds, along with their constituent ions shown in parentheses, are: sulfuric acid (2 H^+, SO_4^{2-}); sodium chloride (Na^+, Cl^-); sodium hydroxide (Na^+, OH^-); copper(II) sulfate (Cu^{2+}, SO_4^{2-}); lead(II) nitrate (Pb^{2+}, 2 NO_3^-); and hydrochloric acid (H^+, Cl^-).

It is very important to recognize that an ion is very different from the corresponding neutral atom. A metal ion is formed form the atom by the loss of *n* electrons, where *n* is equal to the valency of the metal (e.g., $K - e^- \rightarrow K^+$, univalent metal; $Ca - 2\ e^- \rightarrow Ca^{2+}$, divalent metal). Similarly, a nonmetallic ion is formed from the corresponding atom by the gain of electrons equal in number to the valency of the nonmetal (e.g., $0.5\ Cl_2 + e^- \rightarrow Cl^-$, univalent nonmetal; $S + 2\ e^- \rightarrow S^{2-}$, divalent nonmetal). Their electrical charges impart to the ions properties quite different from those of the corresponding (electrically neutral) atoms. Ions do not behave in the same way as atoms. For example, by dissolving electrically neutral, molecular chlorine in water, a solution is produced which is yellow in color and is a vigorous bleaching agent; however, a solution containing chloride ions (Cl^-) has neither of these properties. Similarly, a sodium atom will act immediately upon water, whereas a sodium ion (Na^+) can exist in water without acting upon water in any way. Since most salts are ionized in solution, the reactions involving them occur between ions. For example, when sodium chloride is added to silver nitrate solution, the free silver ions and the free chloride ions react and form insoluble silver chloride, which is precipitated. The free sodium ions and the free nitrate ions do not take part in the reaction. Instead of the chemical equation:

$$AgNO_3 + NaCl = AgCl + NaNO_3,$$

a better representative expression is:

$$Ag^+ + NO_3^- + Na^+ + Cl^- = AgCl + Na^+ + NO_3^-$$

or, since the sodium and nitrate ions are not involved, the ionic equation: $Ag^+ + Cl^- = AgCl$. In an ionic equation, the sum of the positive and the negative charges must be the same on both sides:

$$(2\ NO_2^- + 2\ I^- + 4\ H^+ = I_2 + 2\ NO + 2\ H_2O; \quad 2\ Fe(CN)_6^{4-} + Cl_2 = 2\ Fe(CN)_6^{3-} + 2\ Cl^-)$$

In the case of ions, it is seen that oxidation is associated with an increase in the positive charge of a cation, e.g., Fe^{2+} becomes Fe^{3+}, and reduction involves a decrease in the positive cation charge. In the case of anions, a decrease in the negative charge corresponds to oxidation, and an increase in the negative charge to reduction: the ferrocyanide ion, $Fe(CN)_6^{4-}$, is oxidized to the ferricyanide ion, $Fe(CN)_6^{3-}$, and the manganate ion, MnO_4^{2-}, is oxidized to the permanganate ion MnO_4^-. Changes in the principal valency of the metal atom in the ion take place here: bivalent iron in $Fe(CN)_6^{4-}$ becomes trivalent in $Fe(CN)_6^{3-}$, and hexavalent manganese in MnO_4^{2-} becomes heptavalent manganese in MnO_4^-. If the main valency of the metals is treated as positive, and that of oxygen, the halogens, and negative radicals as negative, the ionic charges may be found. Since the net charge must remain constant in an ionic reaction, oxidation and reduction must take place simultaneously, with some members undergoing oxidation and others reduction.

The tests for metallic and acid radicals in chemical analysis are essentially tests for ions. For example, all soluble silver salts release silver ions in solution in water; likewise, all soluble chloride salts release chloride ions in solution. When a solution of a silver salt is treated with a solution of a chloride salt, the positively charged silver ions and the negatively charged chloride ions are mutually attracted, combine, and form a precipitate of insoluble silver chloride (AgCl). The precipitate dissolves in $NH_4(OH)$ and is insoluble in HNO_3. It is, therefore, possible to identify any soluble silver salt by using dilute HCl, and any soluble chloride by using a solution of $AgNO_3$.

6.3
Electrolytes

It may be recalled from Chapter 1 that one of the several ways in which classification of materials is accomplished is on the basis of their electrical conductivities. Randomly chosen examples of substances, together with the types of conductivity associated with them are presented in Table 6.1. The metals and many nonmetallic substances such as graphite, manganese dioxide, lead sulfide, etc. exhibit electronic conductivity; the passage of electricity through these materials produces heating and magnetic effects but no chemical changes occur. One of the major types of electrical conductivity relevant to this classification is electrolytic conductivity, which pertains to electrolytes. When a current is passed between electrodes through an electrolyte, not only are heating and magnetic effects produced but definite chemical also changes occur at or in the neighborhood of the electrodes, the cathode and the anode.

The difference between a metallic conductor and an electrolyte can be brought out in an interesting mode of expression. A metallic conductor acts as a bridge, over which electricity

Table 6.1 Materials classified on the basis of electrical conductivity.

State	*Example*	*Type of conductivity*
Solid	Metals	Electronic conductor
	Nonmetalic graphite	Electronic conductor
	Compounds:	
	Manganese oxide	Electronic conductor
	Sulfides (copper, molybdenum, lead)	Electronic conductor
	Carbides	Electronic conductor
	Oxides:	
	Doped zirconia, yttria and thoria	Electrolytic conductor
	Other oxides (magnesia, alumina, etc.)	Nonconductors
Liquid	Water	Electrolytic conductor*
	Aqueous solutions	Electrolytic conductor
	Mercury	Electronic conductor
	Organic acids	Weak electrolytic conductor
	Molten salts	Electrolytic conductor
	Organic compounds (alcohols, carbon tetrachloride, etc.)	Nonconductor

* Not a nonconductor but a poor conductor.

can pass freely under the action of electric force. In a solution of an electrolyte in water, the ions act like ferry boats, and transport electricity through the extremely poor conducting water. It is a characteristic property of all electrolytes that, either in the molten state or in solution, they give rise to ions.

6.3.1
Chemical Behavior

The behavior of electrolytes in solutions constitutes one of the important areas fundamental to the study of electrochemistry. There will be much to gain by going through a presentation essentially to refreshen an elementary chemical text on the three most popular, extensively studied, and thoroughly understood electrolytes: the acids, the bases, and the salts.

6.3.1.1 **Acids**

An acid is classically known as a substance whose aqueous solution: (i) turns blue litmus red; (ii) neutralizes bases; (iii) reacts with active metals with the evolution of hydrogen; and (iv) possesses a sour taste. A base is again classically known as a substance which in aqueous solution: (i) turns red litmus blue; (ii) neutralizes acids; (iii) tastes offensive; and (iv) gives a “soapy” feel. These given descriptions of acids and bases may also be regarded as being operational or or experimental definitions.

According to the Arrhenius concept (some aspects of which have been dealt with later in this chapter), an acid is a substance that produces hydrogen ions, H^+ (aq), as the only positive ion by itself or when dissolved in water. The qualities of acids depend upon the qualities of the H^+ ions, and this explains why acids generally have common properties. The situation is not as simple as it may appear, however. Pure water-free HCl shows no acidity because it contains no ions; it is a covalent compound. The aqueous solution contains ions. The ion responsible for acidity, however, is not the simple H^+ ion, but a hydrated form of it, the hydroxonium ion (H_3O^+) produced by a reaction between HCl and water ($HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$). For ordinary purposes the hydration of the hydrogen ions is often ignored and reference uses H^+ ions exclusively. Again, taking the thread of Arrhenius theory, the basicity of an acid is expressed in terms of the number of hydrogen ions, H^+ (aq), which can be produced by one molecule of the acid on dissociation. The basicity of an acid is not necessarily the number of hydrogen atoms present in one molecule of it. Acetic acid (CH_3COOH), though containing four hydrogen atoms in its single molecule, is only monobasic, as three of the four hydrogen atoms are so combined as to be incapable of ionization. Similarly, phosphoric acid (H_3PO_3), having three hydrogen atoms per molecule, is dibasic. An acid is generally termed as a polybasic acid when a molecule of it has more than one replaceable hydrogen atom.

The acidic character of acids depends on the availability of hydrogen ions in their solution. An acid X_1 is said to be stronger than another acid X_2 if, in equimolar solutions, X_1 provides more hydrogen ions than does X_2. This will be possible provided that the degree of dissociation of X_1 is greater than that of X_2. Based on the Arrhenius theory of electrolytic dissociation, solutions may be classified in the manner shown in Figure 6.1. If the ionization of an acid is almost complete in water, the acid is said to be a strong acid, but if the

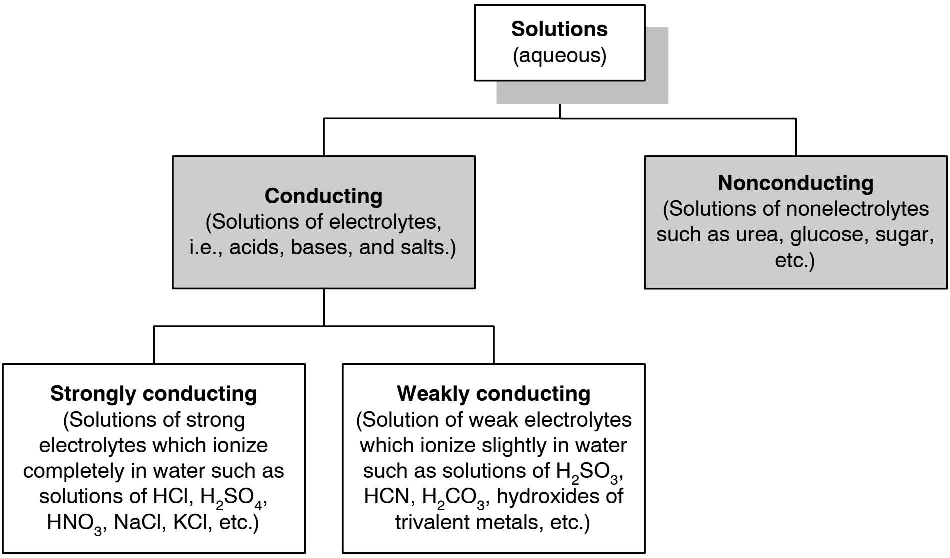

Figure 6.1 Classification of solutions based on Arrhenius' theory.

ionization is only slight, the acid is said to be weak. For example, bench acetic (ethanoic) acid is only 0.4% ionized; that is, only four out of every thousand molecules of the acid pass into the ionized state.

There are a number of ways by which acids have been classified. On the basis of their molecular constitutions, acids are generally divided into two classes: (i) hydracids and (ii) oxy-acids. Acids which contain hydrogen and a nonmetallic element (other than oxygen) or a radical are known as hydracids. It should be noted that the names of the hydracids usually begin with the prefix hydro and end with the suffix ic; for example, HCl (hydrochloric acid), HI (hydroiodic acid), HCN (hydrocyanic acid), and H_2SO_4 (hydrosulfuric acid). The acids which contain oxygen besides hydrogen and a nonmetallic element or a radical are called oxy-acids. The oxy-acids are named according to the nonmetallic elements present in them and their oxygen content. It is customary that the names of the acids having larger proportions of oxygen terminate in "ic", and the names of the acids containing smaller proportions of oxygen end in "ous". If an element forms a series of oxy-acids, the prefixes "hypo" or "per" are added to the names of the acids, respectively. All these points have been conveyed in Table 6.2. Besides these, acids are also classified according to the sources, to the basicity or number of replaceable hydrogen atoms and to their strength. According to their sources, acids may be classified into:

- Mineral acids: these are acids derived from mineral substances, such as, for example, hydrochloric acid which is obtained from common salt, nitric acid from sodium or potassium nitrate, sulfuric acid from sulfur, phosphoric acid from calcium phosphate, etc.
- Organic acids: these are acids which contain carbon as an essential element and are obtained from either plants or animals, such as, for example, formic acid (HCOOH), acetic acid (CH_3COOH), etc.

Table 6.2 Different nomenclatures of oxy-acids.

Acid-yielding element	*Oxy-acids*			
	"ic" acid	*"ous" acid*	*"hypo" acid*	*"per" acid*
Sulfur	H_2SO_4 sulfuric	H_2SO_3 sulfurous	$H_2S_2O_3$ hyposulfurous	$H_2S_2O_8$ persulfuric
Nitrogen	HNO_3 nitric	HNO_2 nitrous	$H_2N_2O_2$ hyponitrous	
Chlorine	$HClO_3$ chloric	$HClO_2$ chlorous	HOCl hypochlorous	$HClO_4$ perchloric
Phosphorous	H_3PO_4 phosphoric	H_3PO_3 phosphorous	H_3PO_2 hypophosphorous	

According to the second criterion, acids are classified into:

- Monobasic acids: these are acids whose molecules contain only one replaceable hydrogen atom, such as, for example, HCl, HNO_3, $HClO_3$, etc.; acetic acid (CH_3COOH), although containing four hydrogen atoms per molecule, is only monobasic since only one hydrogen atom belonging to it can be replaced by a metal or a group of elements equivalent to a metal.
- Dibasic acids: these are acids that have two replaceable hydrogen atoms in each molecule, such as, for example, H_2SO_4, H_2SO_3, H_2CO_3, etc.
- Tribasic acids: these are acids which have three replaceable hydrogen atoms in each molecule, such as, for example, H_3PO_4.

According to the criterion of the strength of acids they are grouped into two classes: strong acids and weak acids. Some examples of strong acids include HCl, H_2SO_4, HNO_3, $HClO_4$, etc., and those of weak acids include H_2CO_3, CH_3COOH, etc.

6.3.1.2 **Bases**

A base, in terms of the ionic theory, is a substance which yields hydroxy ions as the only negative ion, when dissolved in an ionizing solvent (usually water). The general and characteristic properties of bases are predominantly due to the properties of hydroxy ions.

The acidity of a base is the number of hydroxy ions formed per molecule of the base in aqueous solution. It may also be considered as the number of H^+ ions that can be accepted by one molecule of the base. Thus, NaOH and KOH are monoacid bases, $Ca(OH)_2$ and $Mg(OH)_2$ are diacid bases, and $Al(OH)_3$ and $Fe(OH)_3$ are triacid bases.

It is often customary to describe acids and bases together instead of considering them separately as individuals.

There are certain limitations of the Arrhenius concept of acids and bases. Acids and bases have been described in terms of their aqueous solutions and not in terms of the entities themselves. The theory is thus applicable exclusively to aqueous solutions. An entity such as HCl is accounted as an acid only when it is dissolved in water; if dissolved in some other solvent, such as benzene or other organic solvent, or in the gaseous state (can also be liquified), it is not judged as an acid. There is no evidence of hydrogen ions, yet it reacts with gaseous ammonia to form ammonium chloride. The theory restricts bases merely to water-soluble hydroxides and does not recognize metal oxides as bases. According to the theory, a mere proton, H^+, occurs in solutions. In spite of these grievous limitations of the theory of acids and bases, it is quite useful because of its simplicity and its elementary approach, and much of the terminology that Arrehenius bore out is still in use in chemistry. The theory, on the whole, represents a marvelous beginning for describing acids and bases.

Any text on acids and bases would not be deemed complete if mention were not made of the extended definition of acids and bases that is embodied in the Lowry–Bronsted theory. The theory basically proposed a more general definition of acids and bases to overpower the limitations of the theory arising from the Arrhenius concept.

One difficulty of the simple ionic theory of acids is that in order for a substance to ionize, it must be an ionic or electrovalent compound; however, one finds that many acids when pure, do not conduct electricity and, on this basis, must be presumed to be covalent compounds. The explanation of this anomaly is given in terms of the concept that the ion formed is not H^+, but H_3O^+. Here is evidence in support of the contention that the bare hydrogen ion, i.e., the hydrogen atom from which the orbital electron has been knocked out, does not exist in aqueous solutions. It has been shown that the free energy change in the reaction $H^+ + H_2O = H_3O^+$ (hydronium, or hydroxonium or oxonium ion) is large and negative, and this fact clearly indicates that the hydrogen ion H^+ would be practically nonexistent in aqueous solutions. The phenomenon of hydronium ion formation is a manifestation of the general tendency that ions are usually hydrated, as depicted in Figure 6.2 (A). Water is capable of coordination and can act as a donor by virtue of the lone pair of electrons on the oxygen atom. Considering the case of hydrogen chloride, which is a covalent compound (when pure, it is a nonconductor), the oxygen atom of a water molecule can coordinate on to the hydrogen chloride molecule, giving rise to a "molecule" which can now ionize, with one of the ions being H_3O^+. This has been illustrated by the schemes shown in Figure 6.2 (B), (C) or (D). The reaction involving sulfuric acid and water, as shown in Figure 6.2 (E), is an additional illustration of the manner in which acid ionization occurs through hydronium ion formation instead of hydrogen ion formation as implied in the theory of Arrhenius. In general, therefore, the solution and the ionization of a strong acid in water is to be represented by the equilibrium $HA + H_2O \leftrightarrow H_3O^+ + A^-$ and the term "hydrogen ion concentration" should be taken to refer to the H_3O^+ or the hydroxonium ion.

Lowry and Bronsted used the reaction shown above ($HA + H_2O \leftrightarrow H_3O^+ + A^-$) as a basis for different definitions of an acid and a base. They pointed out that the formation of the H_3O^+ ion involves, in essence, the transfer of a proton from the molecule of the acid to the molecule of water, and they, therefore, described or defined an acid as any molecule, radical, or ion, which bears a tendency to give up protons to a base; a base, similarly was described or defined as any molecule, radical, or ion which bears a tendency to accept protons from an acid. According to Lowry and Bronsted's description or definition, the molecule of anhydrous ammonia (NH_3) is a base (which it is not in terms of the ionic theory) for it can react with hydrogen chloride ($HCl + NH_3 = NH_4^+ + Cl^-$). Similarly, the anion of a weak acid (such as the acetate ion) is, according to this theory, a strong base since it readily combines with protons and readily forms the undissociated acid.

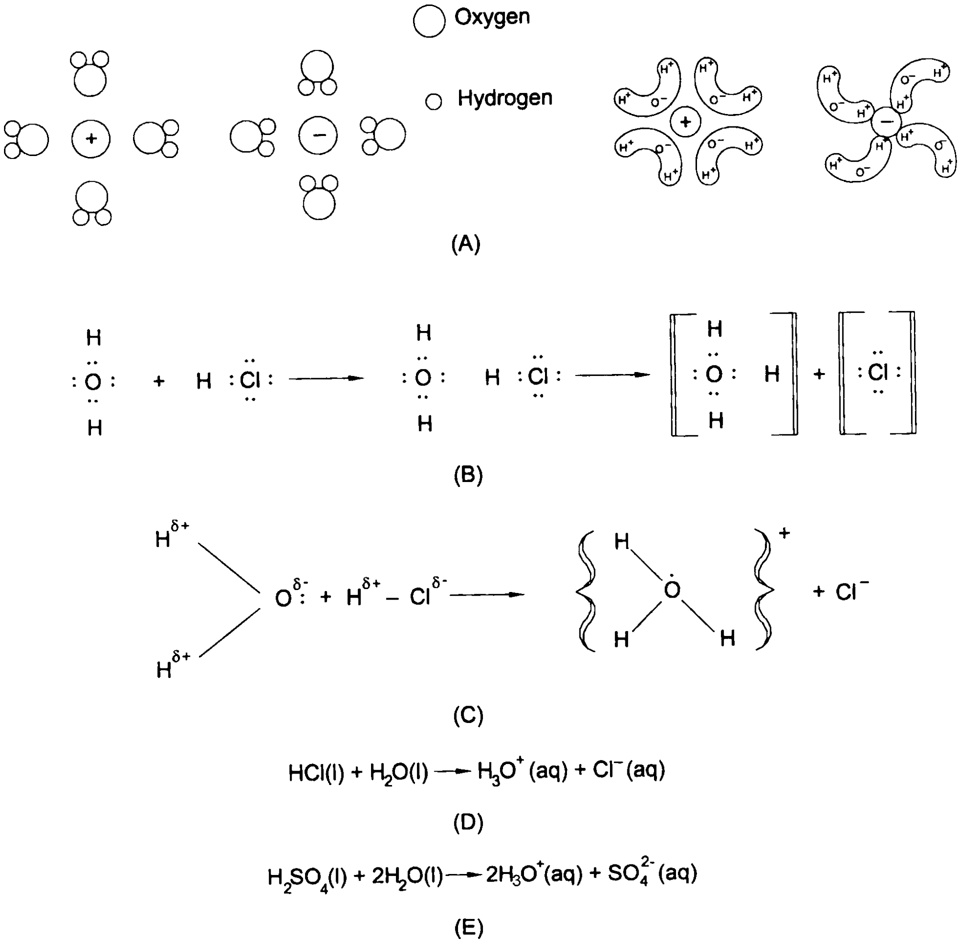

Figure 6.2 (A) Hydration of ions; (B)–(D) ionization phenomenon for HCl acid depicted in different ways; (E) reaction between sulfuric acid and water.

It may, in summary, be recorded that an acid is a proton donor whilst a base is a proton acceptor. An advantage of this definition of an acid or a base is that it is not restricted to neutral molecules. This can be illustrated from the example shown below:

$HCl\ (aq) + H_2O \rightarrow Cl^-\ (aq) + H_3O^+\ (aq)$

In this example, the HCl molecule donates one proton to become the Cl^- ion and the H_2O molecule accepts one proton to become the H_3O^+ ion. Thus, HCl is an acid and H_2O is a base. Now, H_3O^+ has a proton which it can donate; therefore, according to the theory, H_3O^+ is an acid. Similarly, HCl, having lost a proton, has became Cl^- and this Cl^- ion can take the proton back; therefore, it is a base. Thus, donating protons is a reversible process. Every acid must form a base on donating a proton, and every base must form an acid on accepting a proton. The above reaction can be rewritten as:

$HCl\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + Cl^-\ (aq)$
acid 1 base 2 acid 2 base 1

The base that results when an acid donates a proton is called the conjugate base of the acid. Correspondingly, the acid that results when a base accepts a proton is called the conjugate acid of the base. In the reaction cited above, Cl^- is the conjugate base of the acid HCl and H_2O is the conjugate base of the acid H_3O^+. Thus, the conjugate acid differs from its conjugate base by one proton.

Certain acids can give up two or three protons; these are called diprotic (for example, H_2SO_4) or triprotic (for example, H_3PO_4) acids, respectively. According to the Lowry–Bronsted concept, each acid is regarded as giving up only one proton. Diprotic or triprotic acids are perceived as giving out protons in different steps.

There are certain substances which can act acids as well as bases, and these are called amphoteric. A number of metallic hydroxides are amphoteric; examples include aluminum hydroxide, zinc hydroxide, and tin hydroxide. Thus, zinc hydroxide, $Zn(OH)_2$, is capable of reacting with hydrochloric acid to form zinc chloride:

$$2\ HCl + Zn(OH)_2 = ZnCl_2 + 2\ H_2O$$

whilst with a caustic alkali, such as caustic soda, zinc hydroxide forms sodium zincate:

$$Zn\ (OH)_2 + 2\ NaOH = Na_2ZnO_2 + 2\ H_2O$$

In zinc chloride, zinc is present as the positive cation, Zn^{2+}, whereas in sodium zincate, zinc is present as part of the negative zincate anion, $(ZnO_2)^{2-}$. In the present context, reference must be drawn to water. It can accept a proton and can act as a base; similarly, it can part with a proton and can act as an acid. Thus, it has an amphoteric (dual) nature. Water can function as a base in the presence of acids stronger than itself and as an acid in the presence of bases stronger than itself. As an example in the former category reference may be drawn to the reaction,

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

and as one in the latter category to the reaction,

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$$

The strength of an acid or a base is determined by its tendency to lose or gain protons. A strong acid is a substance which loses protons easily to a base. The conjugate base of a strong acid is a weak base:

$HCl\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + Cl^-\ (aq)$
strong acid weak base

In the above example, the chloride ions, Cl^-, the conjugate base of hydrogen chloride, show little tendency to react with protons in water solution to form hydrogen chloride molecules; hence it is a weak base. Conversely, the conjugate base of a weak acid is a strong base:

$$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CH_3COO^-\ (aq)$$

The conjugate base CH_3COO^- (aq) of the weak acid CH_3COOH shows a very strong attraction for protons and is, therefore, a strong base.

A strong base has a pronounced tendency to accept protons. Therefore, the conjugate acid of a strong base is a weak acid and conversely, the conjugate acid of a weak base is a strong acid:

CH_3COO^- (aq) + H_3O^+ (aq) ↔ CH_3COOH (aq) + H_2O (l)
strong base weak acid

The Lowry–Bronsted theory suffers from the following drawbacks: (i) it explains the acidic or the basic nature of a substance only if a solvent such as water is present. In other words, molecules such as HCl, H_2SO_4, etc. are not acids in the absence of water; (ii) this concept fails to explain how acidic oxides (such as CO_2, SO_2, etc.) are neutralized by basic oxides (such as CaO, BaO) since there is no involvement of protons in these reactions, e.g.:

$CaO + CO_2 \rightarrow CaCO_3$; $BaO + SO_2 \rightarrow BaSO_3$

The ability of an acid to lose a proton (acid strength) is experimentally measured by its acid ionization constant; the higher the value of this constant the higher is the concentration of H_3O^+ ions, and the stronger the acid.

To sum up, it may be pointed out that a base exists corresponding to each acid. The corresponding pairs can be called conjugates and, if the acid is weak, the conjugate base is strong. For the purpose of the elementary treatment presented in the present portion of the chapter, the most important of all the bases is the hydroxy ion, OH^-. It is a very strong base indeed and when it combines with a hydrogen ion, the water formed is almost un-ionized, i.e., from this point of view, water acts as a very weak acid. Metallic oxides and hydroxides are usually electrovalent compounds, containing the O^{2-} (oxide), or the OH^- (hydroxide) ions, in addition to the metallic ion. The ion O^{2-} can enter the equilibrium $O^{2-} + H_2O \rightleftharpoons 2\ OH^-$ with water. Consequently, metallic oxides and hydroxides of this kind can produce the base, OH^-, and are known as basic oxides or hydroxides. By reacting with an acid, i.e., with H^+ ions, they produce molecules of water:

H^+ (aq) + OH^- (aq) $\rightleftharpoons$ H_2O (l)

At the same time, the metallic ion from the oxide and the negative ion from the acid remain together to constitute a salt. Some examples are:

Na^+OH^- (aq) + H^+Cl^- (aq) $\rightarrow$ Na^+Cl^- (aq) + H_2O (l)

$Ca^{2+}(OH)_2^-$ (aq) + 2 $H^+NO_3^-$ $\rightarrow$ $Ca^{2+}(NO_3^-)_2$ (aq) + 2 H_2O (l)

Those ions which take no part in the reaction are known as "spectator ions", and from these considerations, the following definitions can be derived. A basic oxide (or hydroxide) is a metallic oxide (or hydroxide) which contains the O^{2-} (or OH^-) ion; it will react with an acid to form a salt and water only. It is necessary to realize the importance of the word "only" in this definition, as were it to be omitted, then certain compounds which are quite different from basic metallic oxides and hydroxides would be covered by this definition. Thus, Pb(IV) oxide reacts with hydrochloric acid to produce Pb(II) chloride (a salt) and water, but does not belong to the class of bases because chlorine gas is also produced:

PbO_2 (s) + 4 HCl (aq) → $PbCl_2$ (aq) + 2 H_2O (l) + Cl_2 (g)

A comparison of this equation with the equations provided above points out that lead (IV) oxide is clearly not a base. The nature of metallic hydroxides varies according to the position of the metal in the reactivity series, as given in Table 6.3. Metallic hydroxides are electrovalent compounds, composed of metal ions, which are positively charged, and hydroxy ions, OH^-. The number of OH^- ions associated with one metallic ion is equal to the valency of the metal, e.g., Na^+OH^-: sodium is monovalent; $Ca^{2+}(OH^-)_2$: calcium is divalent. The metallic hydroxides form a very important series of compounds, and are known to have many uses both in the laboratory and in industry.

It was G. N. Lewis who extended the definitions of acids and bases still further, the underlying concept being derived from the electronic theory of valence. It provided a much broader definition of acids and bases than that provided by the Lowry–Bronsted concept, as it furnished explanations not in terms of ionic reactions but in terms of bond formation. According to this theory, an acid is any species that is capable of accepting a pair of electrons to establish a coordinate bond, whilst a base is any species capable of donating a pair of electrons to form such a coordinate bond. A Lewis acid is an electron pair acceptor, while a Lewis base is an electron pair donor. These definitions of acids and bases fit the Lowry–Bronsted and Arrhenius theories, and cover many other substances which could not be classified as acids or bases in terms of proton transfer.

For a Lewis acid, there must be at least one available unfilled or vacant orbital in the valence shell of an atom of the species. This is the only requirement for a substance to qualify as being called as an acid. Any species is potentially a Lewis acid if it has at least one available unfilled or vacant orbital in the valence shell of one of its atoms. Lewis acids are, therefore, of various types.

The various types of Lewis acids are protons, simple cations, electron-deficient molecules, compounds in which the central atom can expand its octet, and elements with an electron sextet.

Table 6.3 Variation in the nature of hydroxides of metals according to their positions in the electrochemical series.

Metals (listed in accordance with their positions in the electrochemical series)	*General properties*
K Ca Na	The hydroxides of these metals are soluble in water and are alkalis. The hydroxides of sodium and potassium are not decomposed by heat.
Mg Al Zn Fe Pb	The hydroxides of these metals are insoluble in water. The hydroxides of magnesium and iron react with acids only, but the hydroxides of aluminum, zinc, and lead react with both acids and alkalis. When heated, these hydroxides decompose into oxides of the metals and water.
Hg Ag Au	Hydroxides of these metals are nonexistent.

Lewis' view can be extended even further to define an acid as a substance which can accept a negative ion, and a base as a substance which can provide a negative ion. In the reactions

$$Ca^{2+}O^{2-} + SO_3 \rightarrow Ca^{2+}SO_4^{2-}$$

$$Na^+ + Cl^- \rightarrow Na^+Cl^-$$

SO_3 and Na^+ are acids and CaO and Cl^- ions are bases. According to this extended view forwarded by Lewis, all cations are potentially acids and all anions are potentially bases.

6.3.1.3 **Alkalis**

A basic hydroxide has been defined earlier. If such a hydroxide is soluble to a considerable extent in water, it is known as an alkali.

Very few alkalis are known, the most common being sodium hydroxide (caustic soda), NaOH, potassium hydroxide (caustic potash) KOH, calcium hydroxide (slaked lime), $Ca(OH)_2$, and ammonia solution, which, strictly speaking, is not a hydroxide. The ammonia molecules form dative bonds with protons form the equilibrium $H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$, causing more water to ionize and more hydroxy ions to be present in the solution. This property of solubility in water is the only difference between the small select group of alkalis and the other basic hydroxides, but it is a very important difference. It is because of this that the alkalis can be used in a very large number of reactions in solution and for a great many purposes for which the insoluble basic hydroxides are of no use. It must be realized that in general the alkalis possess all the properties of basic metallic hydroxides, but also have the property of dissolving to a great extent in water. Slaked lime is the least soluble of the common alkalis. It is necessary to avoid any confusion between the terms alkali and base for they are not synonymous. All alkalis are bases, but not every base is an alkali. Based on the consideration of its limited solubility in water, slaked lime may be looked upon as a borderline case between an alkali and a base. Some prefer this substance to be called a base and not an alkali.

6.3.1.4 **Salts**

The word salt is a descriptive term applied to a distinct family of substances, and not to any particular species. A salt is an ionic compound containing a positive ion other than the hydrogen ion, and a negative ion other than the hydroxy ion. Salts constitute a class of compounds obtained by a partial or total replacement of the replaceable hydrogen atoms or the atoms present in the molecule of an acid by a metal or a group of elements behaving like a metal. Salts are generally grouped into three classes: normal salts, acid salts or bisalts, and basic salts. A summary of information on these is provided in Table 6.4. Table 6.5 provides certain general rules regarding the nomenclature of salts.

It may be pointed out that salt solutions owe their color to the ions which they yield when dissolved in water. Thus, Cu^{2+}, CrO_4^{2-}, MnO_4^{2-} and Co^{2+} ions in the bulk are blue, yellow, purple, and pink, respectively, and any solution of a salt containing one of these ions will have the same absorption spectrum. If the colored ion is removed from solution by the formation of a colorless complex ion, the solution will lose its color, e.g., by addition of KCN to $CuSO_4$.

Table 6.4 Classification of salts*.

Classification	***Description***	***Examples***	
		Acid/Base	***Salt***
Normal salts	The salts produced by the partial displacement of the replaceable hydrogen atoms present in the molecule of an acid by a metal or a group equivalent to a metal.	HCl H_2SO_4 H_3PO_4	KCl, NH_4Cl K_2SO_4, $(NH_4)_2SO_4$ K_3PO_4, $(NH_4)_3PO_4$
Acid-salts or bi-salts	• The salts produced by the partial displacement of the replaceable hydrogen atoms present in the molecule of an acid by a metal or a radical acting like a metal.	H_2SO_4 H_2CO_3 H_3PO_4	$NaHSO_4$ $NaHCO_3$ NaH_2PO_4
	• Acid salts react with alkalis to give normal salts.	$NaHSO_4 + NaOH = Na_2SO_4 + H_2O$ $KHCO_3 + KOH = K_2CO_3 + H_2O$	
Basic salts	• The salts which are produced as a consequence of reaction of an acid with a greater proportion of the base required to form a normal salt.	$2\ Cu(OH)_2 \rightarrow$ $3\ Pb(OH)_2 \rightarrow$	$CuCO_3 \cdot Cu(OH)_2$ $2\ PbCO_3 \cdot Pb(OH)_2$
	• A basic salt in many cases may be considered as the double compound of a normal salt and a base.	$2\ Pb\begin{matrix} OH \\ \\ NO_3 \end{matrix} \rightarrow$	$Pb(OH)_2 \cdot Pb(NO_3)_2$

* The table describes essentially the simple salts. There are, in addition, two special types of salts. They are known as the double salts and the complex salts (see text).

The salts so far described are said to be simple salts. In addition to these, there are two special types of salts known as the double salts and the complex salts. The two distinct classes of such compounds are distinguished according to their behavior in solution. Sometimes it so happens that when a solution of a normal salt is mixed with that of another normal salt in molecular proportions and the mixed solution is subjected to crystallization, the crystals of a new, single salt separate out. The salt thus obtained has a definite amount of water of crystallization per molecule, a definite crystal structure, and specific properties which are altogether different from those of the component salts. The new salt contains both the normal salts in molecular proportions and exists as a stable compound only in the solid crystalline state. In aqueous solutions, however, it breaks up into its constituent salts which, on dissociation, give all the ions contained in the simple salts. Such a salt is called a double salt. A familiar example of a double salt is potash alum which has the molecular formula, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O$. This is formed by the crystallization of the solution containing K_2SO_4 and $Al_2(SO_4)_3$ in molecular proportions. It gives all the ions of its constituent salts when dissolved in water: $K_2SO_4 \cdot Al_2(SO_4)_3 \rightleftharpoons 2\ K^+ + 2\ Al^{3+} + 4\ SO_4^{2-}$. Another example of a double salt is ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$. This is formed by the crystallization of a solution containing the simple salts, ferrous sulfate and ammonium sulfate, in correct proportions. It may finally be reiterated that a characteristic feature of double salts is their complete dissociation and loss of individuality of the two constituents in solution; they retain their distinct entity only in the solid crystalline state.

Table 6.5 Nomenclature of salts – certain general rules.

Description	**Examples**	
	Acid	**Salt**
A salt derived from a hydracid is named according to the nonmetal present in the parent acid, and the salt will end in -"ide". The metallic part of the salt is named first. The prefix "hydro" is dropped and suffix -"ic" (of the acid) is changed to -"ide".	HCl HBr HCN H_2S	Sodium chloride ($NaCl$) Magnesium chloride ($MgCl_2$) Potassium bromide (KBr) Zinc bromide ($ZnBr_2$) Sodium cyanide ($NaCN$) Potassium sulfide (K_2S)
A salt obtained from an oxy-acid is named according to the nonmetal other than oxygen present in it, and the suffix -"ic" of the acid is changed to -"ate" while -"ous" is changed to -"ite". In other words, the ic acids will yield -"ate" salts and the ous acids the -"ite" salts.	H_2SO_4 H_2SO_3 HNO_3 HNO_2	Sodium sulfate (Na_2SO_4), Calcium sulfate ($CaSO_4$) Potassium sulfite (K_2SO_3) Ammonium nitrate (NH_4NO_3) Ammonium nitrite (NH_4NO_2)
To name an acid salt, the word bi- or hydrogen is placed between the metallic and the acid parts, while a basic salt is indicated by adding the word basic before the name of the salt. If the parent oxy-acid has any prefix such as per, metal, hypo, etc. in its name, it will remain as such in the salt.	H_2SO_4 H_2CO_3 $HOCl$	Sodium hydrogen sulfate or Sodium hydrogen bisulfate ($NaHSO_4$) Basic copper carbonate ($CuCO_3 \cdot Cu(OH)_2$) Potassium hypochlorite ($KOCl$)
Salts may contain metals which can show variable valency. If the metal exhibits lower valency, the metallic part of the name ends in -"ous", and if the metal shows higher valency, the name ends in -"ic".		Ferrous chloride ($FeCl_2$) Ferric chloride ($FeCl_3$)

Sometimes it so happens that crystals of a new salt are formed when solutions of two simple salts are mixed and the mixed solution is evaporated. The salt thus obtained is a distinct chemical substance in the solid state as well as in solution. In aqueous solution, it does not dissociate into all the simple ions of the salts it is obtained from, but yields complex ions along with the simple ions. Such a salt is known as a complex salt. A characteristic feature of complex salts is that in these the constituents retain their separate entities both in the solid state and in solution. Potassium ferrocynide, $K_4Fe(CN)_6$, is a complex salt and is obtained on mixing the solution of a ferrous salt with an excess of potassium cyanide solution. From its composition $[Fe(CN)_2, 4\ KCN]$, it appears to be a mixture of ferrous cyanide and potassium cyanide in the ratio of 1 : 4, and is thus taken to be an ordinary double salt. This representation of the compound is, however, not satisfactory since it responds neither to tests for Fe^{2+} ions nor to those for CN^- ions but does respond to tests for K^+ ions and tetravalent $Fe(CN)_6^{4-}$ ions. The ionization reaction of the complex salt cited in the present example can be represented as:

$$K_4Fe(CN)_6 \rightleftharpoons 4\ K^+ + Fe(CN)_6^{4-}$$

6.3.1.5 **Neutralization and Hydrolysis**

When solutions of an acid and an alkali are mixed in the correct proportions the resulting solution has no acidic or alkaline character, and on evaporation it gives a solid salt. This reaction is called neutralization because the product has neither acidic nor alkaline properties (Latin, neuter, neither). Neutralization is an example of the quantitative aspects of chemistry; acid and alkali react to form a salt in fixed ratios which are not the same for different acids and bases.

Solutions of salts prepared by the combination of equivalent quantities of acid and base may be expected to show a neutral character. In many cases, however, this is not true. Thus, for example, although solutions of sodium chloride are neutral, as would be expected, solutions of potassium cyanide are alkaline, while those of ferric chloride are acidic. The nature of this effect depends upon the relative strengths of the acid and the base from which the salt results. Thus, sodium chloride is the salt of a strong acid and a strong base and is, therefore, neutral. On the other hand, hydrocyanic acid is a very weak acid and hence its potassium salt (potassium hydroxide being a strong base) is alkaline in solution. In a similar fashion, as ferric hydroxide is a weak base, its salt with strong hydrochloric acid is acidic in aqueous solution. This behavior of salts is known as salt hydrolysis. It follows from the fact water itself is very slightly dissociated into hydrogen and hydroxy ions:

$$H_2O \rightleftharpoons H^+ + OH^-$$

A salt AB that results from the combination of the acid HA and the base BOH is considered to be in solution:

$$HA + BOH = AB + H_2O$$

The salt in solution will be largely ionized:

$$AB \rightleftharpoons A^+ + B^-$$

so that the solution will contain high concentrations of A^+ ions and B^- ions. It will contain low concentrations of H^+ and OH^- ions from the ionization of water. If HA and BOH are both strong, nothing particular will occur. This is because the equilibria,

$$HA \rightleftharpoons H^+ + A^-$$

$$BOH \rightleftharpoons B^+ + OH^-$$

are such that large concentrations of ions are in equilibrium with very small concentrations of acid or base. There may be a conjecture that HA is a weak acid, which implies that it breaks down or dissociates only to a very slight extent in solution. The circumstances resulting from the solution of a salt of such an acid will then momentarily involve the coexistence in the solution of H^+ ions along with a high concentration of A^- ions, so that the product of the two concentrations will largely exceed that required by the equilibrium relations of the acid, as defined by its dissociation constant, i.e., $[H^+][A^-]/[HA]$ = dissociation constant (small for a weak acid). Accordingly, H^+ ions and A^- ions will combine to yield undissociated HA; the equilibrium between the H^+ and the OH^- ions from water will thereby be disturbed, and more OH^- ions will be formed from the water for restoration of the equilibrium between water and its constituent ions. Hydroxy ions will thus build up in the solution, which will, therefore, be alkaline. A similar reasoning will explain why the salt of a weak base with a strong acid will give an acid solution.

A formal definition of salt hydrolysis can follow from the description outlined above. Salt hydrolysis may be defined as a reaction in which the anion or the cation of a salt reacts with the solvent water to produce acidity or alkalinity. Evidently, it is the nature of the anion or the cation constituting the salt which will determine whether the solution produced as a result of hydrolysis will be acidic or alkaline. If the matter is examined from these points of view, the following three different cases can arise.

The first case corresponds to the hydrolysis of salts of strong acids and weak bases. This can generally be shown as:

$$B^+ + A^- + H_2O \rightleftharpoons \underset{\text{weak}}{BOH} + H^+ + A^-$$

The common ion A^- is disregarded. In this case only the cation B^+ reacts with water, and the mass law equation for the above reaction is

$$[BOH]\,[H^+] \,/\, [B^+][H_2O] = K \text{ (} K \text{ is the familiar equilibrium constant)}$$

Since H_2O is in large excess as the solution is dilute, its concentration is taken as constant. It is amalgamated with the equilibrium constant K to give a new constant K_h, called the hydrolysis constant, which is given by

$$K_h = \frac{[BOH][H^+]}{B^+}$$

In the same solution, there are two more equilibria. For the equilibrium

$$H_2O \rightleftharpoons H^+ + OH^-$$

the following relationship is known

$$K_w = [H^+]\,[OH^-]$$

where K_w is the ionic product of water; and for the equilibrium,

$$BOH \rightleftharpoons B^+ + OH^-$$

the following relationship can be written:

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

where K_b is called the dissociation or ionization constant of the weak base. Taking all these relationships into account, the following relationship can finally be arrived at:

$$K_h = \frac{K_w}{K_b}$$

If h is the degree of hydrolysis of the salt, c moles per liter is its concentration, and v liters per mole is its dilution, then one has the following:

	B^+	+	H_2O	$\rightleftharpoons$	BOH	+	H^+
Initial mole:	1		excess		0		0
Mole at equilibrium:	$1 - h$		excess		h		h
Conc. at equilibrium: (mole/liter)	$1 - h/v$		excess		h/v		h/v

when h is so small that $(1 - h)$ may be taken as 1,

$$\text{then,}\quad K_h = \frac{\frac{h}{v} \cdot \frac{h}{v}}{\frac{1-h}{v}} = \frac{h^2}{(1-h)\,v}$$

can be written as

$$K_h = \frac{h^2}{v} \quad \text{so that} \quad h = (K_v\ v)^{0.5}$$

or $h = [(K_w/K_b) \cdot v]^{0.5}$

Substituting $v = 1/c$, the following relationship for h can be obtained.

$$h = \left(\frac{K_w}{K_b \cdot c}\right)^{0.5}$$

The second case pertains to the hydrolysis of salts of strong bases and weak acids. This can be generally be shown as:

$$BA + H_2O \rightleftharpoons BOH + HA$$

or

$$B^+ + A^- + H_2O \rightleftharpoons B^+ + OH^- + \underset{\text{(weak)}}{HA}$$

Disregarding the common B^+ ion, then only an anion A^- reacts with water:

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

Proceeding further using the arguments given in the first case, the following relationship can be derived for the hydrolysis constant (K_h):

$$K_h = \frac{K_w}{K_a}$$

where K_a is the dissociation or ionization constant of the weak acid. Thus, the hydrolysis constant, K_h of a salt of a strong base and a weak acid is a ratio of the ionic product of water to the dissociation constant of the weak acid. It follows that the weaker the acid, the greater is the hydrolysis constant of the salt.

Table 6.6 Hydrolysis constant and degree of hydrolysis for hydrolysis of salts.

Description of hydrolysis of salt	*Hydrolysis constant (K_h)*	*Degree of hydrolysis (h)*
Salt of strong acid and weak base	$\frac{K_w}{K_b}$	$\left(\frac{K_w}{K_b \cdot c}\right)^{0.5}$
Salt of strong base and weak acid	$\frac{K_w}{K_a}$	$\left(\frac{K_w}{K_a \cdot c}\right)^{0.5}$
Salt of weak acid and weak base	$\frac{K_w}{K_a \cdot K_b}$	$(h)^{0.5}$ (Independent of dilution or concentration of the salt solution)

K_w = ionic product of water; K_a = dissolution constant of weak acid;
K_b = dissociation constant of weak base; and c = concentration of salt solution.

The third case is of the hydrolysis of salts of weak acids and weak bases. This can generally be shown as

$$BA + H_2O \rightleftharpoons BOH + HA$$

$$\text{or} \quad B^+ + A^- + H_2O \rightleftharpoons BOH + HA$$

In this case, both cation B^+ and anion A^- react with water:

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA$$

Proceeding further by using the arguments given in the two previous cases and also taking into account the three equilibria in the solution (involvement of ionization of weak base BOH; weak acid HA and H_2O) the following relationships for K_h and h can be derived:

$$K_h = \frac{K_w}{K_a \cdot K_b}; \quad h = (K_h)^{0.5} = \left(\frac{K_w}{K_a \cdot K_b}\right)^{0.5}$$

where K_a and K_b are the dissociation constants for the weak acid and the weak base respectively. Thus, the hydrolysis constant (K_h) of a salt of a weak acid and a weak base is the ratio of the ionic product of water to the product of the dissociation constants of the weak acid and the weak base. To sum up, reference is drawn to Table 6.6 which presents the results of the three cases of the hydrolysis of salts as described above.

Neutralization, which may be represented by the equation,

$$\text{HA (acid)} + \text{BOH (base)} = \text{BA (salt)} + H_2O \text{ (water)}$$

is in one sense, the formation of a salt and water from an acid and a base. Hydrolysis is thus, in one sense, the formation of an acid and a base by the action of water on a salt:

$$\text{BA (salt)} + H_2O \text{ (water)} = \text{HA (acid)} + \text{BOH (base)}$$

and is therefore, the reverse of neutralization. These facts may be conveniently shown by combining the two expressions into one:

Table 6.7 Distinction between neutralization and hydrolysis.

Neutralization	***Hydrolysis***
1. Neutralization is a reaction involving the union of H^+ ions of an acid and OH^- ions of an alkali to form undissociated molecules of water when both the acid and the alkali are in equivalent amounts.	1. Hydrolysis is a special type of double decomposition in water which in addition to its function as a solvent splits up a normal salt partially to form the acid and the base from which the salt is derived. In short, hydrolysis is a partial reversal of neutralization.
2. In neutralization, the acid and the base are the reactants, while the salt and water are the products.	2. In hydrolysis, the salt and water are the reactants and the acid and the base are the products.
3. Neutralization is an irreversible process.	3. Hydrolysis is a reversible process.
4. Any acid and base can be participants in neutralization.	4. All salts do not give rise to hydrolysis. For example, salts of strong acids and bases (NaCl, K_2SO_4, etc.) do not suffer hydrolysis.

$$\mathrm{HA} + \mathrm{BOH} \underset{\text{hydrolysis}}{\overset{\text{neutralization}}{\rightleftarrows}} \mathrm{BA} + \mathrm{H_2O}$$

The distinction between the two processes, neutralization and hydrolysis, is illustrated in Table 6.7.

6.3.1.6 Ionization of Water

Present treatment does not take into account the phenomenon of hydration involved with the ionization of water. This permits the ionization of water to be expressed in its most commonly used convenient form as:

$$H_2O \rightleftharpoons H^+ + OH^-$$

It is important to note that each hydrogen ion is accompanied by a hydroxy ion, so that in neutral solution the concentrations of these two ions are equal to each other, and therefore from the equation, $[H^+][OH^-] = K_w$, each of these concentrations is equal to $(K_w)^{0.5}$. It is worthwhile adding additional fundamentals pertaining to the ionization of water. The equilibrium constant (K') of the ionization reaction of water as shown above is:

$$K' = \frac{[H^+][OH^-]}{[H_2O]}$$

Water is considered like any other pure liquid; its concentration does not alter significantly in dilute solutions, so it does not figure in the equilibrium expression:

$$K_w = [H^+]\,[OH^-]$$

The ionization of water is so important in the study of aqueous equilibria that the equilibrium constant is given the special symbol, K_w. It can be seen that, K_w, like all equilibrium constants, depends on temperature. Since K_w is larger (the forward reaction is encouraged) at higher temperatures, the forward reaction must consume heat, so the ionization of water must be endothermic.

Conductivity experiments show that at 25 °C, water contains 1.008 g of hydrogen ions in 10,000,000 liters; therefore, the concentration is 1.008 ÷ 10,000,000 or $1.008 \cdot 10^{-7}$ g l^{-1}. Since ion concentrations are expressed in g equivalent liter^{-1}, the concentration of H^+ ions becomes 10^{-7} g equiv. liter^{-1}, or, $[H^+] = 10^{-7}$. Since for each H^+ ion one OH^- ion is set free, the concentration of OH^- ions in water is 17.008 ÷ 10,000,000 g l^{-1}. But 17.008 is the equivalent weight of the OH^- group; therefore, the concentration of OH^- ions is 10^{-7} g equiv. liter^{-1}, or, $[OH^-] = 10^{-7}$. These values imply that the ionic product of water, K_w is equal to 10^{-14} moles^2 liter^{-2} at a temperature of 25 °C.

As pointed out in the paragraph above, pure water has equal concentrations of H^+ and OH^- ions, each being 10^{-7} mole liter^{-1}, and is regarded as neutral between acids and bases. Other aqueous solutions which have equal concentrations of H^+ and OH^- ions, as is the case with some salts and nonelectrolytes, are also said to be neutral. Solutions having concentrations of hydrogen ions in excess of 10^{-7} mole liter^{-1} (and, through the ionic product of water, having lower values for the OH^- ion concentration than 10^{-7} mole liter^{-1}) are said to be acidic, while those having hydrogen ion concentrations of less than 10^{-7} mole liter^{-1} are termed basic or alkaline. However, the ionic product, namely, $[H^+]\,[OH^-]$ is the same in all these solutions. In this product, when one factor is large, the other factor must be small; however it can never be zero. For example, even a solution of potassium hydroxide has a certain hydrogen ion concentration. For any aqueous solution, the hydrogen ion concentration can be specified. The concept of the ionic product of water has provided a facility for classifying solutions as acidic, neutral, or basic, using either the H^+ ion concentration or the OH^- ion concentration in them. However, it is a convention to refer to the hydrogen ion concentrations of solutions rather than to their OH^- ion concentrations.

Since hydrogen ion concentrations have been found to be of very low orders, exponential expressions such as $2 \cdot 10^{-5}$, $0.5 \cdot 10^{-5}$, $3.5 \cdot 10^{-12}$, etc. have to be employed for stating them. It was S. P. Sorensen who used a French expression, “puissance à hydrogen”, meaning “hydrogen power”, to indicate the hydrogen ion concentration in a solution and proposed the symbol pH for it, and is defined as the “negative of the logarithm of the hydrogen ion concentration”. Another way of saying the same thing is the “logarithm of the reciprocal of the hydrogen-ion concentration”. Symbolically, these are represented as follows:

$$\mathrm{pH} = -\log_{10} C_{H^+} = -\log_{10}[H^+] \quad \text{or} \quad \mathrm{pH} = -\log_{10}\frac{1}{C_{H^+}} = \log_{10}\frac{1}{[H^+]}$$

where both CH^+ and $[H^+]$ are ways of representing concentration of hydrogen ion. It is usual to denote common (base-10) as “log” instead of $\log_{10}$, simply for convenience. Natural logarithms are denoted “ln” in order that they will not be confused with logarithms. The usual units for CH^+ are moles l^{-1}, or molarity, but this may lead to problems. Logarithms of CH^+ do not have units, and, in fact, pH does not have units. There is no way at the present elementary level that one can completely resolve this difficulty, except to refer to the discussion on “activity” given in Chapter 3. In the strict definition, pH is the negative logarithm of the hydrogen ion activity. Activity is a unitless quantity which one can regard as the actual concentration divided by unit concentration of a reference state. If it is straining the mind to comprehend, the advice at this stage is not to worry too much about this elegance. Simply defining $\mathrm{pH} = -\log[H^+]$ and not worrying about the units, is what most chemists do in practice.

The negative sign was introduced in the definition to avoid repetitive use of the sign which would have otherwise been inevitable, as most solutions handled have fractional values for the hydrogen ion concentration.

Expressing the hydrogen ion concentration of a solution by a logarithmic function, such as the pH, is helpful in another way too; many physicochemical properties of these solutions are linearly proportional to the logarithm of the hydrogen ion concentration.

The mathematical expression given for pH permits the computation of pH if $[H^+]$ is known, and vice versa. In a neutral solution $[H^+] = [OH^-] = 10^{-7}$ g · ion/liter, and this gives a pH of 7. In an acid solution $[H^+]$ is $> 10^{-7}$ g · ion · liter^{-1}, and this gives a pH < 7. In an alkaline solution, $[H^+]$ is $< 10^{-7}$ moles liter^{-1} and this gives a pH > 7. Different acids contain different numbers of H^+ ions, and the strength of an acid depends on the concentration of these H^+ ions. Among the acids, the strongest one is that which gives the largest number of H^+ ions in equivalent solutions. Similarly, among the alkalis, the strongest is that which gives the largest number of (OH^-) ions in equivalent solutions. It may be recounted here that the strengths of acids and alkalis are determined by electrical conductivity measurements. On the basis of such measurements, HCl may be taken to be the strongest acid, followed sequentially by HNO_3 and H_2SO_4. The usual pH range for most purposes of interest is from 0 (corresponding to a 1 M solution of H^+ ions) to 14 (corresponding to a 1 M solution of OH^- ions). Just as the parameter pH refers to the concentration of H^+ ions, a parameter pOH, pertaining to the concentration of hydroxy (OH^-) ions, is also used: $pOH = -\log [OH^-]$. Thus, in a neutral solution, where $[H^+] \cdot [OH^-] = 10^{-14}$, by taking logarithms one obtains $\log [H^+] + \log [OH^-] = \log 10^{-14}$. This leads to the relationship $-\log[H^+] - \log[OH^-] = 14$ or $pH + pOH = 14$.

While the pH scale has made it convenient to describe the order of hydrogen ion concentrations and to give a measure of the acid strength or alkalinity of a solution, it suffers from a defect which is less obvious. A $4 \cdot 10^{-5}$ N HCl solution is clearly twice as acidic as a $2 \cdot 10^{-5}$ N solution, but the pH values of these solutions, 4.40 and 4.70, provide no idea of the relative strengths of these solutions.

When solutions of acids and bases are sufficiently dilute or when other electrolytes are present, the activity, rather the concentration of hydrogen ions, should be substituted in the pH equation.

In the calculation of the pH of an aqueous solution, the H^+ ions contributed by the dissociation of water should be ignored since their concentration is negligible when compared with that of H^+ ions contributed by the acid. The same is true for pOH value.

Only at high voltages does water conduct electricity appreciably, decomposing to give hydrogen gas at the cathode and oxygen at the anode. It is surprising that water conducts electricity at all when it is supposed to be composed of neutral H_2O molecules. In this context, it may be recalled, that water molecules can split into hydrogen ions, H^+, and OH^- ions, in a reversible reaction:

$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$$

However, the resulting equilibrium is heavily biased towards H_2O molecules. Experiments suggest that, on an average, out of every ten million water molecules there is just one that has split into ions. Nevertheless, a beaker of water, holding billions of water molecules, will contain a large number of hydrogen and hydroxy ions, and the presence of these ions has a profound influence on the products of electrolysis.

6.3.1.7 **Buffer Solutions**

Solutions which resist changes in their pH values on the addition of small amounts of acids or bases are called buffer solutions or simply buffers. The resistance to a change in the H^+ ion concentration on the addition of an acid or an alkali is known as buffer action. Just as the “buffer” of railway carriages resists shocks, similarly buffer solutions resist the action of various substances which can affect the pH value. There are two types of buffers: (i) acidic buffer and (ii) basic buffer.

An acidic buffer has a pH value less than 7 and is prepared by dissolving in water a weak acid and its salt of a strong base. Thus, the following pairs can be used to prepare acidic buffers: (a) CH_3COOH and CH_3COONa; (b) HCOOH and HCOONa; (c) C_6H_5COOH and C_6H_5COONa. A solution of acetic acid and sodium acetate may be considered for explaining the mechanism of acidic buffer. In the solution, there would be only a few H^+ ions as acetic acid is weak and a large concentration of Na^+ ions and CH_3COO^- ions as the salt would be almost completely ionized. When an acid (even a strong acid like HCl) is added, the H^+ ions would combine with the CH_3COO^- ions to produce slightly dissociated CH_3COOH:

$$H^+ + CH_3COO^- \rightleftharpoons CH_3COOH$$

Hence the pH does not change to an appreciable extent. When an alkali (even a strong alkali such as NaOH) is added, the OH^- ions would combine with the H^+ ions of CH_3COOH, dissociating more and more of the undissociated molecules of CH_3COOH, and H_2O would be formed:

$$OH^- + CH_3COOH \rightleftharpoons H_2O + CH_3COO^-$$

Thus, the OH^- ions are consumed and hence the pH of the solution is not altered by the addition of an alkali.

A basic buffer has a pH value in excess of 7. The solution of NH_4OH and NH_4Cl in water is considered as an example. This contains only a few OH^- ions as NH_4OH is weakly ionized, and a large excess of $NH_4{}^+$ ions as the salt is highly ionized. When a base (even a strong one such as NaOH) is added, the OH^- ions combine with the $NH^+{}_4$ ions, producing weakly ionized NH_4OH:

$$OH^- + NH_4^+ \rightleftharpoons NH_4OH$$

Thus, the pH is not altered to an appreciable extent. When an acid (even a strong one such as HCl) is added, the H^+ ions combine with the OH^- ions, leading to the dissociation of more and more of the undissociated molecules of NH_4OH, and H_2O is formed.

$$H^+ + NH_4OH \rightleftharpoons H_2O + NH_4^+$$

Thus, the H^+ ions are consumed and hence the pH of the solution is not altered to any great degree.

6.3.1.8 **Solubility Product**

The quantitative application of the law of mass action to electrolytes in solution is somewhat limited in scope. However, the law proves to be useful in the elucidation of many of the phenomena connected with precipitation, and the behavior of mixed electrolytes.

All salts are ordinarily considered to be strong electrolytes. Some of these such as NaCl, K_2SO_4, etc. are highly soluble in water. Some others such as AgCl, $PbSO_4$, etc., on the other hand, are sparingly soluble or apparently insoluble in the same solvent. It is important to recognize that these salts, although apparently insoluble, do have a measurable solubility in water. When a sparingly soluble electrolyte is agitated with a limited amount of water until the solution becomes saturated, a special type of heterogeneous equilibrium is established between the salt state and the ions resulting from the complete ionization of the electrolyte in the saturated solution. In the equilibrium condition, the rate at which the ions pass from the solid electrolyte into the solution is equal to the rate at which the ions return to the solid. The following two equilibria exist when a sparingly soluble electrolyte (solid), say BA, is in contact with its saturated solution:

$$\text{BA (solid)} \rightleftharpoons \text{BA (dissolved)} \rightleftharpoons \text{B}^+ + \text{A}^-$$

According to the law of mass action, the equilibrium constant (K) is given by

$$\frac{[\text{B}^+][\text{A}^-]}{[\text{BA (solid)}]} = K$$

or, $K\,[\text{BA (solid)}] = [\text{B}^+]\,[\text{A}^-]$. Here dissolved BA is taken to be completely ionized and the concentrations of B^+ and A^- ions are $[\text{B}^+]$ and $[\text{A}^-]$, respectively. The concentration of undissolved solid BA is taken to be constant at a fixed temperature. So the above equation reduces to $K_{sp} = [\text{B}^+]\,[\text{A}^-]$. The constant, K_{sp}, representing the product of the ionic concentrations of B^+A^- is known as the solubility product constant, or simply the solubility product of BA. In general, the solubility product of a sparingly soluble electrolyte is the maximum value of the product of the concentrations of the ions in its saturated solution at a given temperature and is usually denoted by K_{sp}. It turns out that just as the ionic product of water has been defined, the ionic product of a salt can also be specified and this is in the form of the solubility product. Let the example of AgCl which is sparingly soluble in water be considered. When a small amount of it is agitated with water, most remains undissolved and the supernatant solution is saturated with the dissolved AgCl, which in turn is ionized. It is thus clear that there are two equilibria:

$$\text{AgCl (solid)} \rightleftharpoons \text{AgCl (dissolved)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$$

This is the condition of finding out the solubility product of a substance at a given temperature, and under this condition the solubility product of AgCl = $[\text{Ag}^+][\text{Cl}^-]$. Hence,

$$[\text{Ag}^+][\text{Cl}^-] = K_{sp}$$

In a solution, when the ionic product becomes equal to the solubility product, the solution is said to be saturated. If the ionic product is less than the solubility product, the solution is said to be unsaturated. When the ionic product is greater than the solubility product, precipitation of the electrolyte occurs.

In general, if S is the solubility (in g-moles liter^{-1}) of a sparingly soluble salt having the formulae B_xA_y in pure water, one has $[\text{B}^+] = x\,\text{S}$ and $[\text{A}^-] = y\,\text{S}$, assuming complete dissociation. Therefore, $K_{sp} = [\text{B}^+]^x \cdot [\text{A}^-]^y = (x\,\text{S})^x \cdot (y\,\text{S})^y = x^x\,y^y \cdot \text{S}^{x+y}$. This is the general expression showing the relationship between solubility and the solubility product. It is known that solubility varies with temperature, and so does the solubility product.

6.3.2
Electrical Behavior

Having covered the chemical behavior of electrolytes, the text is now directed to their electrical behavior. The importance of the chemical and the electrical behaviors of electrolytes in galvanics and electrolytics hardly needs any elaboration. The term galvanics, used here, implies the generation of electrical energy directly from a spontaneous chemical reaction. The term electrolytics, on the other hand, implies the other aspect that involves the use of electrical energy to bring about a desired chemical reaction which, otherwise, does not occur spontaneously.

6.3.2.1 Arrhenius' Concept

The elucidation of the electrical behavior of electrolytes owes much to Arrhenius, who was the originator of the theory of electrolytic dissociation, generally, known as the ionic theory. The main postulates of the theory are enumerated in the following:

1. Nearly all the molecules of an electrolyte are spontaneously dissociated into charged ions. The ions carrying positive charge are called cations, while those carrying negative charge are called anions. The number of electrical charges carried by an ion is equal to the valence of the atom or the radical from which the ion originates. The process of the spontaneous splitting up of an electrolyte into ions, when dissolved in a solvent, is called electrolytic dissociation or ionization.
2. Cations are generally metallic radicals obtained by loss of electrons from metal atoms (M (metal) $\rightarrow$ M^{n+} (cation) + n e^- (electrons)), while anions are nonmetallic ions or radicals (a group of atoms of two or more elements) obtained by the acquisition of electrons by nonmetallic atoms (A (nonmetal) + m $e^- \rightarrow A^{m-}$ (anion).
3. The sum of the charges on the cations in a solution must always equal the sum of the charges on the anions, since the whole solution is uncharged (e.g., Cu^{2+} and SO_4^{2-} and 2 Na^+ and SO_4^{2-}).
4. A state of dynamic equilibrium exists between the ionized and the non-ionized molecules (XY (non-ionized molecule) $\rightleftharpoons$ X^+ (cation) + Y^- (anion)). The process of electrolytic dissociation is reversible.
5. The ions are free to move and under influence of an electric field they are directed towards oppositely charged electrodes.
6. The properties of electrolytes in solution are the properties of the ions produced.
7. The electrolyte at a given dilution may not be completely ionized, and the fraction of the total molecules ionized is termed the degree of ionization or dissociation. It may be added here that some of these postulates embodied in the Arrehenius concept have appeared in some form or another in the two preceding sections.

The degree of ionization of an electrolyte in solution depends upon a number of factors, of which the nature of the solute is perhaps the most important. The nature of the solvent also affects ionization to a marked degree. The solvent weakens the force binding two ions and thus separates them; this effect of the solvent is measured by its dielectric constant. The dielectric constant of a solvent may be defined as its capacity to weaken the force of attraction between the electrical charges immersed in that solvent. The third important factor is the concentration of the electrolyte in the solution. The extent of ionization of an electrolyte is inversely proportional to the concentration of its solution. The less concentrated the solution, the greater will be the ionization of the electrolyte; this ensues from the fact that in a dilute solution the ratio of the number of solvent molecules to the number of solute molecules is large, and the greater the number of solvent molecules, the greater will be the number of solute molecules which will be separated into ions. The fourth factor to influence ionization is temperature; the higher the temperature, the greater is the ionization.

A molecule HA of a weak electrolyte is now considered. It is assumed to dissociate in its aqueous solution according to the equation $HA \rightleftharpoons H^+ + A^-$. The application of the law of mass action to the above equation gives

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

where K_a is called the dissociation constant or the ionization constant of the electrolyte. If α is the degree of dissociation of the electrolyte in a solution containing 1 gram-molecule of it in V liters, then at equilibrium the gram-molecular concentration of the non-ionized electrolyte, and the gram-ionic concentrations of the ions, are respectively, $(1 - \alpha)/V$, α/V, and α/V. Substituting these values in the expression for K_a, one obtains

$$K_a = \frac{\alpha^2}{(1-\alpha)\,V} \quad \text{or} \quad K_a = \frac{\alpha^2\, C}{(1-\alpha)}$$

where C is the concentration in moles per liter (C is equal to $1/V$). For a weak electrolyte, α is small compared with 1 ($\alpha \ll 1$), so that the term $(1 - \alpha)$ may be taken to be approximately equal to 1. In this situation,

$$\frac{\alpha^2}{V} = K_a \quad \text{or} \quad \alpha = (K_a\, V)^{0.5} = (K_a/C)^{0.5}$$

i.e., the degree of ionization of a weak electrolyte is proportional to the square-root of dilution (the volume of the solution containing 1 mole of the solute) or inversely proportional to the square-root of concentration.

Any one of these expressions for K_a represents what is known as Ostwald's dilution law, which has essentially been obtained by applying the law of mass action to solutions of weak electrolytes. It deals with the variation in the degree of dissociation with concentration or dilution of solutions of weak electrolytes. It is not applicable to solutions of strong electrolytes. The failure of strong electrolytes to obey Ostwald's dilution law is known as the anomaly of strong electrolytes.

6.3.2.2 **Conductance**

Electrolytes, like electronic conductors, obey Ohm's Law, except under such extreme conditions as those involving very high voltages and/or very high-frequency alternating currents. The conductance of an electrolyte is calculated from measurements of its resistance.

Ohm's law states that a direct current carried between two points of a conductor varies in direct proportion to the voltage difference between the two points and is inversely proportional to the resistance offered to the conduction of the current by the conductor between the two points taken as a reference. Using the symbols I, V, and R to represent the quantities in the order given, Ohm's law can be written as:

$$I = \frac{V}{R} \quad \text{or} \quad V = I \cdot R$$

The quantity $1/R$ is a measure of conducting power; this quantity is called the conductance. Whilst resistances are usually expressed in ohms, conductances are quoted in reciprocal ohms or mhos. The resistance, R, of any conductor of length L and area of cross-section A is given by

$$R = \rho\ L/A$$

In the above relationship ρ is an intrinsic property called the specific resistance (or resistivity) of the conductor. The definition of the specific resistance of any given conductor follows from this relationship. It is the resistance in ohms of a specimen of the material, 1 cm long and 1 cm^2 in cross-sectional area (units: ohm cm^{-1}), the length being in the direction of the current and the cross-section normal to it. In other words, the specific resistance ρ of a conductor is the resistance of a cube of 1 centimeter edge. If the conductance is denoted by $C = 1/R$, then the specific conductance (or conductivity) K, is given by $K = 1/\alpha$ (units: ohm^{-1} cm^{-1}, mho cm^{-1}, reciprocal ohm cm^{-1}). Therefore, the relationship $R = \alpha\ L/A$ may be written as $R = L/K\,A$ (units: ohms) and the conductance can be expressed as $C = 1/R = K\,A/l$ (units: reciprocal ohms).

The resistance of a conductor at any temperature can be defined as follows:

$$R_t = R_0\ (1 + \alpha\ t)$$

where R_t = resistance at temperature t °C; R_0 = resistance at temperature 0 °C. The coefficient, α, is called the temperature coefficient and it can be described as the ratio of the increase in resistance per degree C elevation in temperature compared with the actual resistance at 0 °C.

While on the topic on electrical conduction and resistance offered by an electrically conducting medium it is usual to extend to a phenomenon called superconductivity; this has now been recognized as having a profound impact on the electrical field. Exciting possibilities exist. The phenomenon is exhibited by certain types of matter and is characterized by two fundamental properties:

- The abrupt disappearance of resistance at temperatures close to absolute zero; in comparison to these specific materials copper, a very good electrically conducting material, appears to be an insulator.
- The tendency to expel any magnetic field from its interior.

The application of superconductivity in electrical engineering offers revolutionary possibilities: huge current densities with no resistive loss; very high magnetic fields with no power supply required; the possible elimination of iron in electrical machines; and the reduction in size and cost of plant. The first wide-scale application of superconductivity has been in making magnets for solid-state physics research. Large-scale magnets have been produced for research in nuclear physics and nuclear fusion research. A number of d.c. machines (mainly experimental and prototype units) have also been built. Superconducting cables are only relevant to transport of large powers of 2 GVA and higher and for long cable runs, say in excess of 10 km. Many more items may be added to this list, but this brief list serves mainly to introduce the electrical phenomenon of super conductivity.

It is not usual to talk about the resistance of electrolytes, but rather about their conductance. The specific conductance (K) of an electrolyte is defined as the reciprocal of the resistance of a part of the electrolyte, 1 cm in length and 1 cm^2 in cross-sectional area. It depends only on the ions present and, therefore it varies with their concentration. To take the effect of concentration into account, a function called the equivalent conductance, Λ, is defined. This is more commonly (and conveniently) used than the specific conductance to compare quantitatively the conductivities of electrolytes. The equivalent conductance Λ is the conductance of that volume of the electrolyte which contains one gram equivalent of the ions taking part in the electrolysis and which is held between parallel electrodes 1 cm apart (units: $\mathrm{ohm}^{-1}\ \mathrm{cm}^{-2}$). If V cubic centimeters is the volume of the solution containing one gram equivalent, then the value of L will be 1 cm and the value of A will be V square centimeters, so that

$$\Lambda = K \frac{A}{L} = K\,V$$

In aqueous solutions, concentrations are sometimes expressed in terms of “normality” (gram equivalents per liter), so that if C is concentration, then $V = 10^3/C$ and $\alpha = 10^3\ K/C$. To calculate C, it is necessary to know the formula of the solute in solution. For example, a one molar solution of $Fe_2(SO_4)_3$ would contain $6 \cdot 10^{-3}$ equivalents cm^{-3}. It is now clear as to why Λ is preferred. The derivation provided herein clearly brings out the fact that Λ is the measure of the electrolytic conductance of the ions which make up 1 g-equiv. of electrolyte of a particular concentration – thereby setting conductance measurements on a common basis. Sometimes the molar conductance α_m is preferred to the equivalent conductance; this is the conductance of that volume of the electrolyte which contains one gram molecule (mole) of the ions taking part in the electrolysis and which is held between parallel electrodes 1 cm apart.

It may be pointed out that for uni-univalent electrolytes the values of α and α_m are identical since the gram equivalent weight and the gram molecular weight are the same. In the case of uni-bivalent and bi-univalent electrolytes the α value is half the α_m value since the equivalent weight of such compounds is half the molecular weight.

As in the case of solutions, the specific conductance, K, the equivalent conductance, α, and the molar conductance, α_m, are also distinguished for molten electrolytes. These are defined in the same manner as done for the case of solutions of electrolytes. It may, however, be pointed out that molten salts generally have much higher conductivities than equivalent aqueous systems.

6.3.2.3 Conductance Measurement

A modification of the method of determining the resistance of a solid conductor by the Wheatstone bridge is used for determining the conductance of the solution of an electrolyte. The solution whose conductance is to be determined is placed in a special type of cell known as a conductivity cell. In preparing the solutions to be subjected to conductance measurements, it is necessary to use specially pure water known as conductance water. Water obtained by redistilling distilled water, to which a little potassium permanganate has been added, is satisfactory for most determinations. Alternatively, it may be prepared by using a de-ionizing resin. The main difficulty in determining the conductance of the solution of an electrolyte is that electrolysis of the solution takes place simultaneously with the conduction of the current, and this results in two complications: (i) polarization soon sets in and causes the resistance to vary; (ii) the concentration of the solution changes. In order to avoid these complications, an alternating current is used. Such a current is supplied by an induction coil. Since under these conditions a galvanometer cannot be used (as in the Wheatstone bridge), it is replaced by the current detector *D* which may either be an a.c. galvanometer, or a telephone receiver; or alternatively the output from the points *x* and *y* (Figure 6.3) may be connected through a triode valve to a "magic eye" tuning indicator (a miniature cathode-ray oscilloscope). This latter course of current detection is probably the most sensitive one. The conductivity cell itself is made either of chemically resistant glass or of fused silica. The electrodes used in the cell consist of platinum discs coated with finely divided platinum black and welded to platinum wires fused in two glass tubes.

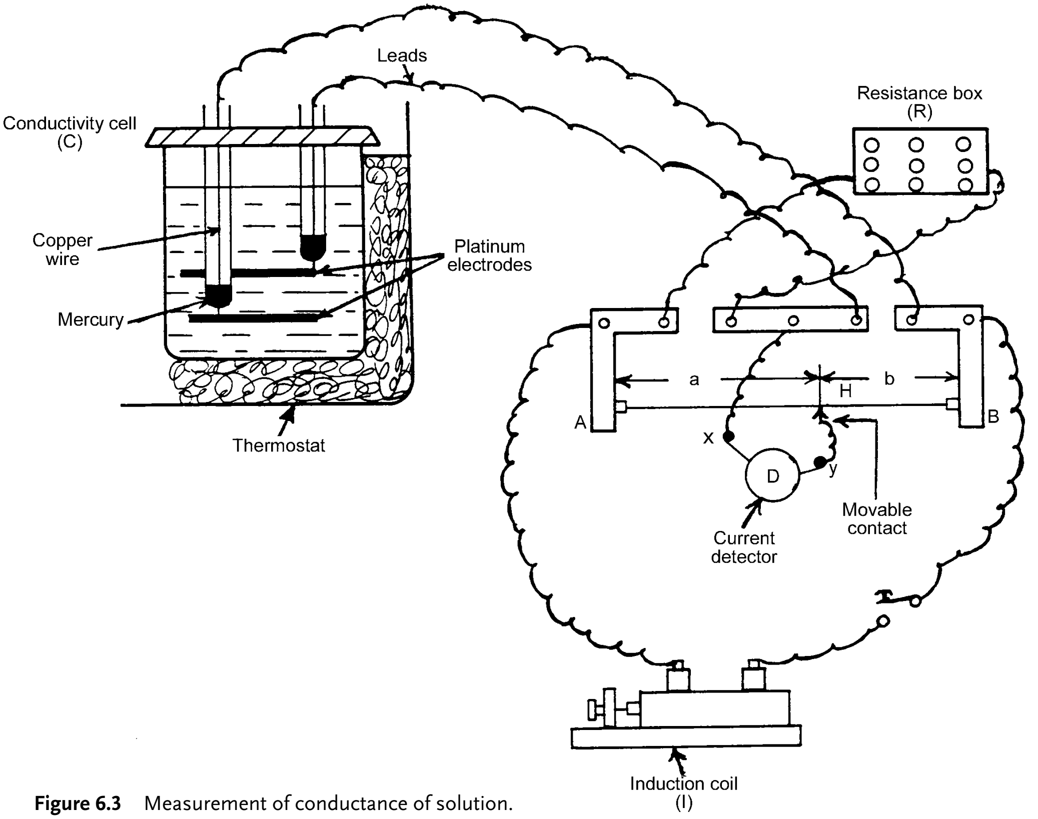

Figure 6.3 Measurement of conductance of solution.

The glass tubes contain mercury and are firmly fixed in the ebonite cover of the cell so that the distance between the electrodes may not change during the experiment. Contact with the platinum electrodes is made by dipping the copper wires of the circuit in the mercury contained in the tubes. The coating of the electrodes with platinum black is carried out in order to inhibit polarization. When examining certain electrolytes, platinized electrodes cannot be used since platinum black may catalyze the decomposition or the oxidation of the electrolyte. The cell is maintained at constant temperature thermostatically, as conductivity increases rather significantly with temperature.

The Wheatstone bridge arrangement, modified as described above and commonly used in class experiments, is shown in Figure 6.3. *AB* is a wire having a uniform thickness (since the wire is of uniform material and thickness, the ratio of lengths on the scale gives the ratio of resistances) and tightly stretched. A movable contact *H* (shown by the arrow head) moves along this wire. *R* is a resistance box and *C* is the thermostated conductivity cell containing the solution. The alternating current source, i.e., the induction coil *I* is connected to the bridge network at the points shown in the diagram and the resistance of *R* varied in conjunction with appropriate adjustment of the contact *H* on the slide wire *AB* until the position of minimum current is secured as indicated by the indicator *D*; this will be the minimum deflection in an a.c. galvanometer, or the minimum sound in a telephone receiver, or minimum area of fluorescence in a “magic eye” tuning indicator. This condition represents the null-point (or balance point). When this adjustment has been made, one has the following relationship:

$$\frac{\text{Resistance of cell }(X)}{\text{Resistance of resistance box }(R)} = \frac{\text{Resistance }BH}{\text{Resistance }AH} = \frac{\text{Length }BH}{\text{Length }AH} = \frac{b}{a}$$

where *R* is the known resistance, corresponding to the plugs which have been removed from the resistance box while *a* and *b* are the lengths of the wire between the movable contact and the ends of the bridge wire.

From the measurements made on the bridge wire, the resistance *X* of the electrolyte in solution is determined by the relationship given above. Therefore, the conductance of the solution ($1/X$) will also be known. The specific conductance, *K*, of the solution is related to the conductance of the solution thus determined by the equation:

$$\frac{1}{X} = K \cdot \frac{A}{L}$$

where *A* is the area of the solution between the electrodes and *L* is the distance between the electrodes. Rearranging the above relationship, one obtains

$$K = \frac{1}{X} \cdot \frac{L}{A} = \frac{1}{X} \cdot L^1$$

where L^1 is a constant. It is called the cell constant because its value remains constant as long as *A* and *L* are kept constant. Stated in words, the above relationship implies that the specific conductance is equal to the product of the cell constant and the measured conductance. The value of L^1 is determined by measuring the resistance of a solution of potassium chloride of known specific conductance K_1 with the help of the cell at a particular temperature. If R_1 is the resistance of this solution measured with this cell, the specific conductance K_1 is given by

$$K_1 = L^1 \cdot \frac{1}{R_1}$$

i.e., $L^1 = K_1 R_1$

If the resistance of any other electrolyte is found by measurement to be R_x when using the same conductance cell, then the specific conductance of this electrolyte is L^1/R_x. Thus, on multiplying the value of specific conductance so obtained by V, the volume of solution in milliliters containing one gram equivalent weight of the electrolyte under investigation, the equivalent conductance Λ is calculated.

6.3.2.4 **Classification of Electrolytes**

Electrolytes, in the first instance, may be classified into two groups: true electrolytes and potential electrolytes. *Potential electrolytes* are essentially those chemical substances which become electrically conducting only after reacting with an ionizing solvent such as water, and a large proportion of the electrolytic processes relevant to technological applications involve the use of solutions of potential electrolytes. A very common example of a potential electrolyte that can be cited is that of hydrogen chloride. Although hydrochloric acid is undoubtedly an electrolyte, liquid hydrogen chloride is an insulator and cannot be electrolyzed. Potential electrolytes include common acids (HCl, H_2SO_4, HNO_3, etc.) and some bases (NH_4OH). *True electrolytes* are essentially those chemical substances, which are ionized in the crystalline and molten states as well as in solution in an ionizing solvent. True electrolytes include most salts (e.g., NaCl, KCl, Na_2SO_4), highly basic hydroxides (e.g., KOH, NaOH), and solid electrolytes. A wide range of technical electrolytic processes involve aqueous solutions containing true electrolytes, and most electroplating solutions belong to this category. However, there are also important production processes which use the electrolysis of the molten salt or compound itself, sometimes dissolved in another molten salt.

Electrolytes may also be grouped into strong and weak electrolytes, this classification being based on the conductivities of the chemical substances. The former classification described above, however, is based on the term of reference of the chemical substances concerned as materials involved with the process of electolysis. In a strong electrolyte dissociation of the compound into ions occurs to a large extent, whilst in a weak electrolyte such dissociation occurs only to a very limited extent. Strong electrolytes have high equivalent conductivities which increase only moderately with increasing dilution. Weak electrolytes have much lower equivalent conductivities at high concentrations, but the values increase very significantly with increasing dilution. All salts, mineral acids, and hydroxides of alkali and alkaline earth metals are examples of strong electrolytes. Most of the organic acids and bases such as ammonium hydroxide and hydroxides of metals are examples of weak electrolytes. As a specific example of an weak electrolyte, mention may be made of ordinary bench (2 M) acetic acid. In this, out of every 1000 molecules present, only 4 are ionized while the remaining 996 are not. In addition, there are electrolytes which behave both as acids and as bases. It may be added that it is impossible to draw a sharp dividing line between the two types of electrolytes, the weak and the strong, as many substances show intermediate behavior.

The description of strong and weak electrolytes provided in the paragraph above can be presented in an alternative manner by invoking ionics which, as may be recalled, implies the study of ions. Ions in solution can arise in two ways: (i) the solution may be of a truly ionic compound or salt so that the ions which already occur in the solid state separate more freely in the solution or (ii) the solute may be a polar covalent compound that reacts with the solvent (e.g., water) to form ions. The breaking of compounds in solution into ions is ionization and, as has been stated earlier, the extent to which it occurs is called the degree of dissociation or ionization. Ionic substances are strong electrolytes. It has been mentioned that some typical examples of strong electrolytes are NaCl, KCl, and NH_4Cl. The ions from these compounds are not free particles but are solvated ions. However, in the case of polar covalent compounds a solute may be either a strong or weak electrolyte depending on the degree of ionization. Aqueous solutions of hydrochloric, sulfuric, and nitric acids are almost fully ionized; therefore, equations for the ionization reactions in these are written (for example) as

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

The single arrow directed to the right represents the condition of full ionization as mentioned. On the other hand, acetic acid and ammonia are examples of weak electrolytes, and are weakly ionized. In such cases, the molecules of the electrolyte are in equilibrium with its ions, and ionization of such electrolytes (e.g., ammonia) is represented as

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The double arrow represents the condition of equilibrium that exists between the non-ionized and the ionized species of the electrolyte. Since ionization of strong electrolytes is practically complete there will not be much gain in studying this type of reaction from the point of view of equilibrium. Equilibria involving weak electrolytes, where there is only partial ionization, are of considerable importance.

Apart from the two classifications described above, electrolytes may also be classified according to the number and valence of the ions produced. Thus, sodium chloride and copper sulfate may both be termed binary electrolytes since one molecule of each of these chemical substances is capable of producing two ions. In the case of sodium chloride, both the ions produced are univalent so that this substance may also be called a uni-univalent electrolyte. Copper sulfate, however, yields two bivalent ions and so may be called a bi-bivalent electrolyte. The valences of the ions are quoted in the positive-negative sequence. Calcium chloride and potassium sulfate are both ternary electrolytes since one molecule of each yields three ions; the former is bi-univalent, whilst the latter is uni-bivalent.

6.3.2.5 **Some Properties of Electrolytes**

It is interesting to compare the conductance of the chlorides of the main groups of the periodic table at temperatures just above their melting points. The chlorides may be divided into two groups: good conductors and insulators. In general, conductance values decrease across each horizontal line with increasing valence of the cation. This phenomenon is paralleled by variations in the conductance of the chlorides of metals with variable valence. The chloride with the greatest conductance is always that which corresponds to the lowest valence.

It is interesting to note that those chlorides which are good conductors resist volatilization and have high melting points. The insulators are volatile at low temperatures and have low melting points; some are, in fact, liquids at room temperature. This is due to the fact that the conductors have ionic crystal lattices whilst the insulators consist mainly of undissociated molecules. An ionic crystal is held together by the electrostatic forces between each ion and the surrounding ions of opposite charge, and it is difficult to disrupt the equilibrium of forces in such a system and make it melt or sublime. In the molten state, however, the electrolyte mainly remains in a dissociated condition due to the fact that ions already existed in the solid state. The conductance is consequently very high in the molten state. Materials which exhibit a molecular crystal lattice and are liquid at room temperature, have a lattice held together by forces which are much weaker than those maintaining an ionic crystal lattice. It is for this reason that even a relatively small increase in energy can overcome the cohesive forces and destroy the crystalline form. In going to the liquid state the molecules remain, at least initially, largely undissociated as they were in the crystal; as a consequence the conductance of the melt is low.

Some chlorides exist, however, whose conductances are intermediate between those of good conductors and of insulators. This implies that even molten electrolytes can be categorized as strong, medium, and weak electrolytes.

Molten electrolytes which are good conductors are generally associated, in the solid state, with an ionic crystal lattice in which the ions are not bound into molecules as such. On increasing the thermal energy content of the crystal by raising the temperature, the kinetic energy of each ion can be made to reach a level corresponding to the melting temperature that is sufficiently high to overcome the electrostatic forces holding the structure together, and thus the crystal melts. There is no reason to envisage that the ions would recombine at the melting temperature, prior to melting, to form undissociated molecules. Instead, their ionic state remains unaffected during the transition to the liquid state. Molten weak electrolytes come in another category; in the solid state they exhibit layer lattice or molecular lattice structures in which the molecules are undissociated. It is highly probable that at the point of fusion the substance still contains undissociated molecules in equilibrium with the ions.

When a small amount of a strong molten electrolyte is dissolved in another strong molten electrolyte, the laws of ideal dilute solutions are obeyed until relatively high concentrations are attained, assuming occurrence of a virtually complete dissociation.

6.3.2.6 Conductance Variation

From results of conductance measurements it has been found that although the conductance of an electrolyte becomes progressively smaller with decreasing concentration, the values of equivalent conductance increase as the concentration decreases or the solution dilution increases until a maximum limiting value is finally obtained. The limiting value of the equivalent conductance which is attained with decreasing concentration or increasing solution dilution is termed the equivalent conductance at infinite dilution, and is denoted Λ_0.

A comparison of the equivalent conductance at some finite concentration (Λ_c) with that at infinite dilution (Λ_0) gives a measure of the fraction of electrolyte dissociation at the higher concentration. One introduces α, the degree of dissociation or ionization, and writes

$$\alpha = \frac{\Lambda_c}{\Lambda_o}$$

The above relationship is easy to grasp since Λ_o represents the contribution of the fully dissociated electrolyte and Λ_c the contribution of a partially dissociated one. The ratio, therefore, gives the extent of dissociation or ionization. Measurement of Λ_c permits the evaluation of α if Λ_o is known.

It has been shown that ionic velocities are not constant because of the mutual attraction of ions at appreciable concentration; and the ratio Λ_c/Λ_o is no longer regarded as indicating the degree of dissociation in such a situation. Instead, this ratio is known as the conductance ratio. In fact, as far as strong electrolytes are concerned, the conductance ratio is probably a better index of the change in the speeds of the ions rather than of their number. In the case of weak electrolytes, however, the number of ions is relatively small, and so also is the interionic attraction leading to a reduction of ionic speeds. For such electrolytes, therefore, the ionic velocities are little influenced by variations in concentration with the result that, provided the solution is neither too dilute nor too concentrated, the conductance ratio is a reasonably good index of the degree of dissociation.

The variation of equivalent conductance with concentration occurs according to the modified form of the Onsager equation as given below:

$$\Lambda_c = \alpha\,[\Lambda_o - (A + BA_0)\,(\alpha\,C)^{0.5}]$$

In the relationship shown above, A and B are constants depending on temperature, viscosity of the solvent, and dielectric constant of the solvent, C is the concentration expressed in gram equivalents per liter, and Λ_c represents the equivalent conductance of the solution. Λ_o is the equivalent conductance at infinite dilution – that is, at C = 0, when the ions are infinitely apart from one another and there exists no interionic attraction. α represents the degree of dissociation of the electrolyte. For example, with the compound MN

$$MN = M^+ + N^-$$

and a fraction α of the molecules MN may be dissociated into ions M^+ and M^-. With strong electrolytes such as, salts and strong acids in water, the substances are known to be fully ionized, so that $\alpha = 1$. The Onsager equation in these cases takes the following (original) form:

$$\Lambda_c = \Lambda_o - (A + BA_0)\,(C)^{0.5}$$

With weak electrolytes, such as acetic acid and ammoniacal water, α is less than 1, and a modified form of the Onsager equation is complied. It must be emphasized that modified and original forms of the Onsager equation are only complied in fairly dilute solutions. Several interesting observations and deductions follow from the features corresponding to different electrolytes.

First, it is observed that variation between Λ_c and $C^{0.5}$ is not linear at high concentrations for the strong electrolytes. At relatively low concentrations (dilute solutions), however, the plot of Λ_c against $C^{0.5}$ approaches linearity. The straight line is extrapolated until it intersects the conductance axis, and the intercept on the conductance axis is equal to Λ_o. At comparable concentrations the initial values of Λ_c for weak electrolytes are much smaller than those for the strong electrolytes. This is a consequence of the weak electrolyte dissociating to a much smaller extent as compared to the strong electrolytes. It may so happen that, as the concentration of the electrolyte becomes very low, the degree of ionization rises sharply, causing Λ_c to rise steeply at very low concentrations.

It has been seen above that the value of Λ_c extrapolated to zero concentration provides Λ_o, the equivalent conductance at infinite dilution, for strong electrolytes, HCl and KCl. A similar operation for the determination of Λ_o for the weak electrolytes will just not hold simply because, as it has been seen, weak electrolytes feature the fact their Λ_c rise steeply at high dilutions. The experimental determinations become very uncertain in these situations.

An additional feature of strong electrolytes other than their having high Λ_c is that their Λ_c is found to increase only moderately with increasing dilution. It may well be said that Λ_c shows a somewhat reducing trend with increasing concentration for strong electrolytes. This tendency is not on account of a change in the number of ions with rising concentration, but on account of a change in the interionic attraction. Attention may be focused on KCl, which typically represents a strong electrolyte. At high concentration the attraction between K^+ and Cl^- ions increases due to the occurrence of a greater number of ions per unit volume. Since this increased attraction lowers the conducting ability of the ions, Λ_c falls with increasing concentration. When the concentration decreases, Λ_c increases because of a decrease in interionic attraction. Attention is drawn to Table 6.8 which lists the equivalent conductance values of some electrolytes at 25 °C at infinite dilution. From the table it can be readily observed that the difference in conductivity of any pair of two electrolytes is nearly the same when one replaces anions but keeps the same cations, or alternately with the same anions but with different cations. For example, the difference in conductivity between two pairs of electrolytes with the same cations but different anions LiBr and LiCl is 2.06 and between NaBr and NaCl is 2.06. Similarly, the difference in the conductivity between two pairs of electrolytes with the same anions but different cations NaCl and KCl is 23.41 and between KNO_3 and $NaNO_3$ is 23.41. This indicates that every ion at infinite dilution contributes a definite amount towards the conductance, irrespective of the nature of the other ion with which it is associated in the electrolyte. This feature was first noticed by Kohlrausch and is described as Kohlrausch's law of independent migration of ions. The law is stated as: the equivalent conductance at infinite dilution for different electrolytes is the

Table 6.8 Equivalent conductance (Λ_o) of some of the electrolytes at 25 °C at infinite dilution.

Electrolyte	Λ_o	*Electrolyte*	Λ_o
LiBr	117.09	KCl	149.86
NaBr	128.51	$NaNO_3$	121.55
KBr	151.92	KNO_3	144.96
LiCl	115.03	NaOH	248.11
NaCl	126.45	KOH	271.52

sum of two values, one depending on the anion and the other depending on the cation. Mathematically, the law may be expressed as follows:

$$\Lambda_o = n_+ \Lambda_+ + n_- \Lambda_-$$

when n_+ and n_- are the number of cations and anions per formula unit of electrolyte (e.g., $n_+ = n_- = 1$ for HCl but $n_+ = 1$ and $n_- = 2$ for $MgCl_2$), and Λ_+ and Λ_- are the equivalent ionic conductances, at infinite dilution, of the cation and the anion, respectively. These equivalent ionic conductances are the amounts contributed by each ion, independently of the other, to the total equivalent conductance.

It may finally be recounted that Kohlrausch found that, at infinite dilution, each ion in the electrolyte contributes a characteristic amount to the equivalent conductance of the electrolyte, so that for the electrolyte containing the salt MN:

$$\Lambda_o = \Lambda_{M^+} + \Lambda_{N^-}$$

where Λ_{M^+} and Λ_{N^-} are the equivalent conductance (at infinite dilution). Each ion has its own ionic conductance which it displays whenever it appears in the same solvent. It must be borne in mind that by ion, it is implied ionic complex so that if, for instance, the ligands forming a complex ion with a metal ion in aqueous solution alters, the ionic conductance will alter because its mobility in the solution will have changed. Hydrogen and hydroxy ions in aqueous solutions are characterized by high ionic conductances. The ionic conductance of metal ions, however, decreases as the tendency to form complexes (these are more bulky ions) increases. Attention is drawn to some known values (expressed in $ohm^{-1}\ cm^{-2}$) of conductances for aqueous solutions at 25 °C: $\Lambda_{H^+} = 349.82$; $\Lambda_{OH^-} = 198.5$; $\Lambda_{K^+} = 73.52$; $\Lambda_{Na^+} = 50.11$; $\Lambda_{Cl^-} = 76.34$; $\Lambda_{Li^+} = 36.69$. Although the Li^+ ion is small, it shows a greater tendency to solvation, so that its ionic conductance in water is less than that of larger ions such as Na^+.

It may be added that Kohlrausch's law does not lead to any method of deducing the contributions of the individual ions. The immediate practical application of Kohlrausch's law of independent contributions of the ions at infinite dilution is a method for deducing the limiting equivalent conductance, Λ_o, of weak electrolytes. This will be illustrated by taking a specific example of a weak electrolyte.

In a weak electrolyte such as CH_3COOH, the Λ values rise steeply with decreasing concentration because more of the electrolyte ionizes according to the principle of equilibrium, and ionization is complete at infinite dilution. The sharp rise in the Λ value at lower concentration occurs because of a sharp increase in the number of ions in solution. Kohlrausch's law may be used in the determination of Λ_o for acetic acid or any weak electrolyte. According to this law, Λ_o for acetic acid is the sum of the ionic conductivities of H^+ and CH_3COO^- at infinite dilution

$$\Lambda_o(CH_3COOH) = \Lambda_{H^+} + \Lambda_{CH_3COO^-}$$

In order to calculate of Λ_o for acetic acid it is necessary to determine Λ_o values experimentally for sodium acetate and for hydrochloric acid. These two are strong electrolytes and the method of extrapolation is used to determine their respective values of Λ_o. The procedure involved can be represented as:

$$\Lambda_o(\mathrm{CH_3COONa}) = \Lambda_{\mathrm{CH_3COO^-}} + \Lambda_{\mathrm{Na^-}}$$
$$\Lambda_o(\mathrm{HCl}) = \Lambda_{\mathrm{H^+}} + \Lambda_{\mathrm{Cl^-}}$$
$$\Lambda_o(\mathrm{NaCl}) = \Lambda_{\mathrm{Na^+}} + \Lambda_{\mathrm{Cl^-}}$$

Therefore, $\Lambda_o(\mathrm{CH_3COOH}) = (A) + (B) - (C)$

Apart from the above, Kohlrausch's law may also be applied to a number of other instances, and these are detailed in the following section.

6.3.2.6.1 **Ionic Mobilities**

The electrical conduction in a solution, which is expressed in terms of the electric charge passing across a certain section of the solution per second, depends on: (i) the number of ions in the solution; (ii) the charge on each ion (which is a multiple of the electronic charge); and (iii) the velocity of the ions under the applied field. When equivalent conductances are considered at infinite dilution, the effects of the first and second factors become equal for all solutions. However, the velocities of the ions, which depend on their size and the viscosity of the solution, may be different. For each ion, the ionic conductance has a constant value at a fixed temperature and is the same no matter of which electrolytes it constitutes a part. It is expressed in $\mathrm{ohm^{-1}\ cm^{-2}}$ and is directly proportional to the mobilities or speeds of the ions. If for a uni-univalent electrolyte the ionic mobilities of the cations and anions are denoted, respectively, by U_+ and U_-, the following relationships hold:

$$\Lambda_+ = KU_+ \quad \text{and} \quad \Lambda_- = KU_- \quad \text{and}$$

$$\Lambda_o = \Lambda_+ + \Lambda_- = K\,(U_+ + U_-)$$

From the relationship provided above, the following relationships are obtained

$$\frac{\Lambda_+}{\Lambda_o} = \frac{U_+}{U_+ + U_-} = N\,; \quad \frac{\Lambda_-}{\Lambda_o} = \frac{U_+}{U_+ + U_-} 1 - N$$

$$\frac{\Lambda_+}{\Lambda_-} = \frac{N}{1 - N}$$

The term N is called the transport or transference number.

It is well known that the flow of either the positive or the negative ions, or of both, is responsible for the electric conduction process through the body of the solution of an electrolyte. Let the fraction of the current carried by each ion in a given electrolyte be considered. For this purpose, the transference numbers mentioned in the previous section are introduced according to the definitions

N_+ = fraction of current carried by the cations
N_- = fraction of current carried by the anions

so that $N_+ + N_- = 1$

In electronic conductors, e.g., a metallic material such as a copper wire, all the current is carried by the electrons, and for such conductors $N_- = 1$ and $N_+ = 0$. For solutions of electrolytes it is not at all easy to ascertain what fraction of the current is carried past a certain position in the electrolyte by the cations and what fraction is carried by the anions.

It will be useful to draw some inferences as regards the transport numbers. As pointed out earlier, the transport number N of an anion is given by

$$N = \frac{U_+}{U_+ + U_-}$$

and for a cation it is given by

$$1 - N = \frac{U_-}{U_+ + U_-}$$

It is clear from these relationships that the transport number of an ion is different in different electrolytes. Thus when solutions of, say, potassium chloride and lithium chloride are electrolyzed, the fraction of current carried by the chloride ions is not the same in the two cases.

The transference or transport number of an ion can be determined by: (i) the analytical method; (ii) the moving boundary method; and (iii) the emf method. The first two methods will be dealt with here, but the third will figure in a later section.

In order to introduce an analytical method to determine the transference or transport number of an ion it may, at the very outset, be appreciated that the speeds of the ions and the type of electrodes used for electrolysis bring about changes in the concentration of ions around each electrode used. As regards the speeds of the ions, there are three possibilities which may arise during electrolysis: (i) cations migrating faster than anions ($U_+ > U_-$); (ii) anions migrating faster than cations ($U_- > U_+$); and (iii) cations and anions migrating with equal speeds ($U_+ = U_-$). By analyzing the three possibilities with inert electrodes the following conclusions can be drawn: (i) an equal number of equivalent ions are discharged at each electrode; (ii) there is always a decrease in the concentration of ions around each electrode; and (iii) the fall in the concentration around any electrode is proportional to the speed of the ions moving away from that electrode (the ratio of the fall around the anode to the fall around the cathode is equal to the ratio of the speed of the cations to the speed of the anions). Analyzing again the three possibilities with the inert electrodes replaced by an inert cathode and a soluble or attackable anode, the conclusions that can be drawn are: (i) the number of univalent ions that are discharged during electrolysis is the same at both electrodes; (ii) there is always a decrease in concentration around the cathode and an increase in the concentration around the anode; and (iii) the decrease in concentration around the cathode is equal to the increase in concentration around the anode.

Based on the general scenario provided above, the analytical method to determine transference or transport numbers has been devised and is carried out in an apparatus which can essentially be regarded as an improvement over the Hittorf apparatus. This consists of two vertical tubes connected together with a U-tube in the middle; all three tubes are provided with stop-cocks at the bottom. The U-tube is also provided with stop-cocks at the top; by closing these, the solutions in the cathode and anode limbs can be isolated. The silver anode is sealed in a glass tube as shown, and the cathode is a piece of freshly silvered silver foil. The apparatus is filled up with a standard solution of silver nitrate and a steady current of about 0.01 ampere is passed for 2–3 hours. In order to avoid the occurrence of too large a change in concentration it is necessary to pass the current only for a short duration. The transport apparatus is connected with a copper or silver voltameter in series. When the current has been passed for about three hours, the stop-cocks at the top of the U-tube are closed and the whole of the liquid in the anode limb is carefully drained into a weighed flask and its weight is determined. Its silver content is determined by titration against a standard solution of potassium thiocyanate. The weight of silver deposited in the silver voltameter is also noted, or if a copper voltameter is used the weight of silver equivalent to the copper deposited there is calculated by multiplication by 108/31.5. There should be no alteration in the concentration of the solution in the U-tube if the experiment has been successfully carried out. In an actual experiment, let W_{Ag} be the weight of silver deposited in the silver voltameter, and let W_1 g of the anode solution contain W_2 g of silver nitrate. Therefore, the weight of water = $(W_1 - W_2)$ g. Let the weight of silver nitrate associated with $(W_1 - W_2)$ g of water at the start of the experiment be W_3. Then the increase in weight = $(W_2 - W_3)$ g of $AgNO_3$ = $(W_2 - W_3) \cdot 108/170$ g Ag = W_4 g silver. If no silver had migrated from the anode, the increase would have been W_{Ag}. Therefore, the fall in concentration due to the migration of silver ions = $(W_{\mathrm{Ag}} - W_4)$ g. Hence, the transport number of Ag^+ ions = $(W_{\mathrm{Ag}} - W_4)/W_{\mathrm{Ag}}$ and that of NO_3^- ions = $1 - (W_{\mathrm{Ag}} - W_4)/W_{\mathrm{Ag}}$.

The second method, namely the moving boundary method, is based on the direct observation of migration of ions under the influence of an applied potential – unlike Hittorf's method in which the changes in concentration at the electrodes are measured.

The apparatus used to determine the transport number by the moving boundary method is shown in Figure 6.4. It consists of a long vertical tube of uniform cross-section which is fitted with two electrodes at the two ends. Let the electrolyte, the transport number of whose

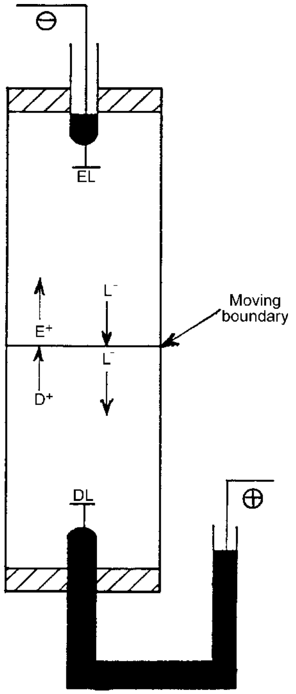

Figure 6.4 Moving boundary experimental set-up for determining the transport number of E^+ ions.

cations, E^+, is to be determined, be represented by EL. A layer of a solution of this electrolyte is gently introduced above the solution of another suitable electrolyte DL having the common anion L^-. The electrolyte DL is so selected that the velocity of the D^+ ions is less than that of the E^+ ions. There will be a clear-cut boundary between the two electrolytes (due to the difference in their refractive indices), even if the two solutions are colorless. On passing current between the two electrodes, both E^+ and D^+ ions move upward towards the negative electrode while the L^- ions move downward towards the positive electrode. Since D^+ ions have a lower velocity than E^+ ions, they never overtake the latter and a sharp boundary is always maintained between the two solutions. However, the D^+ ions are never very far behind, for if that happens the solution beneath the boundary would become diluted and its increasing resistance would cause an increased potential drop, thereby increasing the velocity of the D^+ ions. The boundary thus travels slowly in the upward direction. On passing X Faraday of current a charge of $X \cdot U_{E^+}$ would be carried by the E^+ ions, and a corresponding amount $(X \cdot U_{E^+})$ g-equiv. of it moves up. If C represents the original concentration of E^+ ions in g-equiv. ml^{-1} and the boundary travels through a distance D cm in the tube of cross-section A cm^2, the number of g-equiv. of E^+ travelling upwards is given by $A \cdot D \cdot C$. Thus,

$$X \cdot U_{E^+} = A \cdot D \cdot C$$

or

$$U_{E^+} = \frac{A \cdot D \cdot C}{X}$$

Based on the experimental values of A, D, C, and the value of U_{E^+}, the transport number of E^+ ions can be calculated from the relationship shown above.

The transport numbers of ions are influenced by concentration and also by temperature. It is known that a dissolved solute undergoes solvation in water (hydration). The hydrates are not true compounds in the chemical sense, but arise essentially from the dipole nature of the water molecule. Owing to the hydration effect, the transport numbers of ions may be expected to vary with concentration. Although small changes in the transport numbers may be attributed to the hydration effect, large variations cannot be ascribed to this factor. Such large variations may probably be due to the presence, at higher concentrations, of complex or intermediate ions possessing speeds quite different from those of the simple ions of the electrolyte. With decreasing concentration, these composite ions dissociate into their individual constituents and probably disappear entirely when the solution becomes very dilute. For example, a change is observed in the transport number of the iodide ions in cadmium iodide with dilution due to the disappearance of the complex ion, $(CdI_4)^{2-}$, which is present at higher concentrations. The transport numbers of ions also change with temperature. At sufficiently high temperatures it is observed that transport number tends to attain a limiting value of 0.5.

6.3.2.6.2 Equivalent Conductivity for Weak Electrolytes

It has already been pointed out that weak electrolytes do not ionize to a sufficient extent in solution, and are far from being completely ionized even at very great dilution. The practical determination of Λ_0 in such cases is, therefore, not possible but it can be calculated with the help of Kohlrausch's law. From the relationship, $\Lambda_+/\Lambda_0 = N$, one can straightaway write

$\Lambda_+ = N\ \Lambda_o$. Thus, the ionic conductance of an ion is obtained by multiplying the equivalent conductivity at infinite dilution of any strong electrolyte containing that ion by its transport number. In this manner the ionic mobilities of the two ions present in the weak electrolyte can be calculated, and finally its equivalent conductivity at infinite dilution can be calculated by summing these two values.

6.3.2.6.3 **Absolute Ionic Mobility**

The absolute ionic mobility or the absolute velocity of an ion represents its velocity in centimeters per second under a potential gradient of one volt per centimeter (potential gradient = applied emf/distance between the electrodes). For example, if the velocity of the ion at infinite dilution is U cm per second when the distance between the electrodes is 25 cm and voltage is 125, the potential gradient is 125/25, i.e., 5 volts per cm and the absolute mobility is U/5 cm s^{-1}.

It has been shown that under a potential gradient of 1 volt cm^{-1} the value of the constant K referred to previously, viz. in $\Lambda_+ = KU_+$ and $\Lambda_- = KU_-$ is the charge on one g-equiv. of the ion, i.e., 96,500 coulombs (= 1 Faraday). The absolute ionic mobility is therefore, obtained by dividing the ionic conductance by 96,500.

$$U_+ = \frac{\Lambda_+}{96{,}500}; \quad U_- = \frac{\Lambda_-}{96{,}500}$$

6.3.2.6.4 **Solubility of Salts**

Salts such as silver chloride or lead sulfate which are ordinarily called insoluble do have a definite value of solubility in water. This value can be determined from conductance measurements of their saturated solutions. Since a very small amount of solute is present it must be completely dissociated into ions even in a saturated solution so that the equivalent conductivity, KV, is equal to the equivalent conductivity at infinite dilution which according to Kohlrausch's law is the sum of ionic conductances or ionic mobilities (ionic conductances are often referred to as ionic mobilities on account of the dependence of ionic conductances on the velocities at which ions migrate under the influence of an applied emf):

$$KV = \Lambda_o = \Lambda_+ + \Lambda_-$$

Knowing K and Λ_o, V can be determined as the volume (in ml) which contains 1 g-equiv. of the electrolyte.

6.3.2.6.5 **Conductance Ratio**

It may be recalled that the conductance ratio, Λ, is given by Λ/Λ_0 where Λ is the equivalent conductivity of the electrolyte at dilution V, and Λ_0 is its equivalent conductivity at infinite dilution; according to Kohlrausch's law, this is the sum of Λ_+ and Λ_-.

It will be instructive to explain the matter stated above by an example. The conductance of silver in solution at 18 °C is given as 55.7 and of nitrate ion as 60.8. The specific conductivity (K) of $AgNO_3$ in $N/10$ solution at 18 °C is 0.00947 mhos. From all these given data it is the aim of the present example to calculate the percentage of dissociation of the salt at its given concentration. It may be noted that in this illustration the specific conductivity (K) in $N/10$ solution is 0.00947 mhos. The volume containing 1 g-equiv. is 10,000 ml. Therefore, equivalent conductivity at this dilution = 0.0094 · 10,000 = 94.7 mhos. The equivalent conductivity at infinite dilution $(\Lambda_o) = \Lambda_{Ag} + A_{NO_3^-} = 55.7 + 60.8 = 116.5$. Therefore, the conductance ratio $\alpha = 94.7/116.5 = 0.8128$. The salt can thus be said to be 81.28% dissociated.

6.3.2.6.6 Conductometric Titrations

In accordance to Kohlrausch's law the electrical conductivity of a solution depends upon the number of ions present and their mobility. For this reason, conductivity measurements can be used to determine the end-points of acid–alkali and other titrations. Present attention is focused on the conductometric titration curves shown in Figures 6.5 (A)–(D).

Attention at first is focused on Figure 6.5 (A) which depicts the titration curve for a strong acid (e.g., hydrochloric acid) and a strong base (e.g., sodium hydroxide). The conductivity cell contains, for instance, 25 ml of the acid solution. The conductivity is measured, and this is followed by the addition of 1 ml of solution of strong base. Each such addition is followed by conductance determination, and a plot is obtained between conductance of the solution and the volume of alkali added. The point of intersection of the intrapolated lines is the end-point, and the volume corresponding to this point is the volume of alkali required to neutralize 25 ml of the strong acid. The reason for this is that prior to the addition of alkali, the conductance of the solution is due to the presence of H^+ and Cl^- ions. The greater part of the conductivity is due to hydrogen ions because they possess the greatest mobility of any ion. With the addition of alkali solution, the hydrogen ions are removed by combination with the hydroxy ions forming feebly ionized water molecules, and their place is taken up by comparatively slow-moving Na^+ ions,

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O \text{ (feebly ionized)}$$

As a result of this, the conductivity of the solution falls and continues to fall with each subsequent addition of alkali until the end-point is attained. On addition of a little sodium hydroxide after the neutralization point, there will be a small concentration of OH^- ions and conductivity will once again rise, this being the result of OH^- ions having the second greatest mobility. The point corresponding to the minimum conductivity represents, therefore, the end-point of titration.

Attention is secondly focused on Figure 6.5 (B) which represents the titration curve of a weak acid against a strong base. The poor dissociation of the weak acid is reflected in the initial conductivity being low. The addition of alkali results in the formation of highly ionized sodium acetate and the conductance of the solution begins to increase.

$$CH_3COOH + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + H_2O \text{ (feebly ionized)}$$

Immediately following the end-points, further addition of sodium hydroxide introduces the fast-moving hydroxy ions and the conductivity value registers a sharp rise. The point at which the two curves intersect provides, therefore, the end-point.

Attention is thirdly focused on Figure 6.5 (C) which is obtained for the titration of a strong acid against a weak base. In this particular case, the solution conductance decreases rapidly, this result being due to the uptake of the fast-moving H^+ ions and their substitution by slow-moving NH_4^+ ions:

$$H^+ + Cl^- + NH_4OH \rightarrow NH_4{}^+ + Cl^- + H_2O \text{ (feebly ionized)}$$

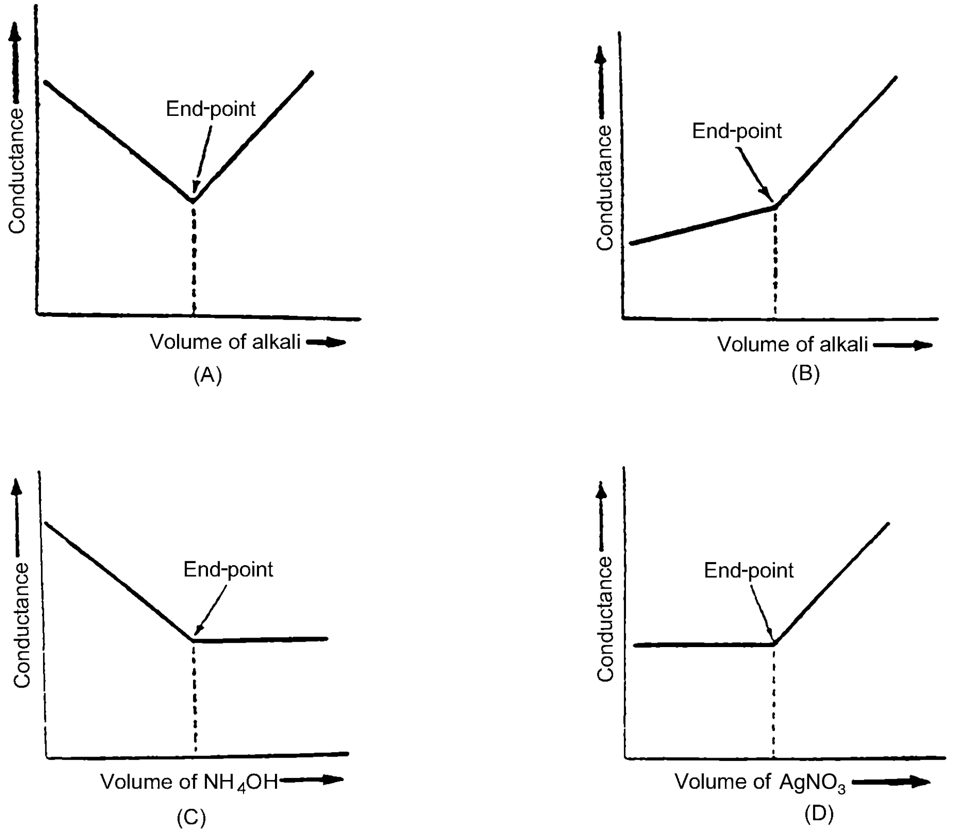

Figure 6.5 Conductometric titrations: (A) strong acid against strong base; (B) weak acid against strong base; (C) strong acid against weak base; (D) potassium chloride against silver nitrate.

After attaining the end-point, the addition of NH_4OH will not have any major influence on the conductance value, and the second curve will be appear as shown in Figure 6.5 (C).

Attention is fourthly focused on Figure 6.5 (D) which shows titration of potassium chloride against silver nitrate. Here, the change in conductivity on the addition of silver nitrate is minimal, as the mobilities of potassium and silver ions are of the same order and the curve is nearly horizontal.

$$Ag^+ + NO_3^- + K^+ + Cl^- \rightarrow K^+ + NO_3^- + AgCl \text{ (precipitation)}$$

The conductivity enhancement commences only after the end-point has been attained.

Attention is finally focused on the advantages of conductometric titrations, which include: (i) colored solutions where no indicator is found to function satisfactorily can be successfully titrated by this method; (ii) the method is useful for titrating weak acids against weak bases, which does not produce a sharp change in color with indications in ordinary volumetric analysis; and (iii) more accurate results are obtained because of the graphical determination of the end-point.

6.4
Galvanics

6.4.1
Redox Reactions

The study of chemical sources of electrical energy or chemical sources of current – known as electrochemics – originates from specific types of reaction known as reduction–oxidation (or redox) reactions. According to early views, oxidation was defined as the addition of oxygen or removal of hydrogen, whereas reduction was defined as the addition of hydrogen or removal of oxygen. No oxidation process can occur without a corresponding reduction process.

The description of redox reactions may afresh be carried out by introducing oxidation and reduction as an electron-transfer process. For this purpose, a process involving burning of magnesium in oxygen is considered, the reaction being written chemically as:

$$2\ \mathrm{Mg}\ (s) + \mathrm{O_2}\ (g) \rightarrow \mathrm{MgO}\ (s)$$

According to early definitions of oxidation and reduction, magnesium is oxidized as it has gone into combination with oxygen. Now, if the formation of magnesium oxide is treated on the basis of electronic configurations of magnesium and oxygen, it would be found that during oxide formation magnesium is transformed into its positive ion ($\mathrm{Mg} \rightarrow \mathrm{Mg^{2+}} + 2\ e^-$). The two electrons produced have been consumed to convert oxygen to negatively charged oxide ions ($\mathrm{O} + 2\ e^- \rightarrow \mathrm{O^{2-}}$ or $\mathrm{O_2}\ (g) + 4\ e^- \rightarrow 2\ \mathrm{O^{2-}}$). The burning of oxygen in chlorine may be outlined in a similar way. The electron configuration of magnesium (atomic number 12) is 2, 8, 2, while that of chlorine (atomic number 17) is 2, 8, 7. Each magnesium atom needs a stable configuration of 2, 8 by donating two electrons of its outermost shell to form a magnesium ion, $\mathrm{Mg^{2+}}$. However, each chlorine atom which contains seven electrons in the outermost shell, can accommodate only one of the two electrons donated by the magnesium atom. This implies that for each magnesium atom yielding a magnesium ion, there must be two chlorine atoms to form the chloride ions.

In the two examples cited above, the magnesium atom donates electrons to one oxygen atom or to two chlorine atoms. The productive number of electrons of the Mg atoms has fallen, steering a net positive charge close to the magnesium, while the productive number of electrons of the oxygen and chlorine has risen. Both of the above reactions are redox reactions, and these can now very well be described in terms of electron transfer. The redox reaction is one in which electrons are supplied from one reactant to another. Oxidation is dispossession of electron(s) or gain in positive valence, while reduction is gain of electron(s) or loss of positive valence. The reactant which acquires electron(s) from the other reductant is reduced and is called the *oxidizing agent*, while the reactant which parts with electron(s) to the other reactant is oxidized and is called the *reducing agent*. Further reference in the present context is drawn to an experiment in which a zinc strip is immersed in a solution of copper sulfate solution. The reaction commences, and the effects of the continuing reaction are readily observed. At first, the zinc strip turns a copper color as it gains a copper layer. As the layer builds up, the bluish coloration of the copper sulfate solution progressively fades. Careful inspection of the zinc after a period of time shows it to be pitted and corroded. The reaction occurring is represented by the equation

$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Cu\ (s) + Zn^{2+}\ (aq)$

The equation fully complies with all observations made. The copper ion precipitates as red copper on the zinc strip, and the color of the solution fades on account of this. Zinc metal dissolves and enters the solution as zinc ions; hence, the surface of the zinc metal shows pitting. Because a zinc ion solution is colorless, the increase in zinc ion concentration is physically observed as color fading. Energy is liberated, as indicated by the temperature of the solution rising by several degrees. With electrons positioned in their correct places, one can write, for the two processes, separate equations as shown below:

$Zn \rightarrow Zn^{2+} + 2\ e^-$ Oxidation

$Cu^{2+} + 2\ e^- \rightarrow Cu$ Reduction

Because electrons are neither products nor reactants in chemical reactions, the two processes are interdependent and neither can occur alone. The zinc metal dissolution must furnish electrons for the copper metal plating. The reaction of zinc and copper sulfate solution is a spontaneous reaction involving a transfer of electrons, i.e., is a spontaneous redox process. The spontaneity of the reaction is commonly explained by saying that zinc loses electrons more readily than copper or, alternatively, that Cu^{2+} ions gain electrons more readily than Zn^{2+} ions.

Most of the redox reactions can be expressed using two half-reactions as described for zinc and copper. However, for the complete reaction, the number of electrons lost must be equal to the number gained. This requirement sometimes needs adjustment; for instance, in case of aluminum metal taking out silver from a solution of silver nitrate, the following equations are set out:

$Al\ (s) \rightarrow Al^{3+}\ (aq) + 3\ e^-$

$Ag\ (aq) + e^- \rightarrow Ag\ (s)$

Before summing the two foregoing half-equations, it is necessary to adjust the second equation by multiplying each member involved with the equation by three. This process makes the number of electrons involved in the reduction of silver equal to the number of electrons which aluminum atom contributes by oxidation. The final picture emerges as:

Oxidation: $Al\ (s) \rightarrow Al^{3+}\ (aq) + 3\ e^-$

Reduction: $3\ Ag^+\ (aq) + 3\ e^- \rightarrow 3\ Ag\ (s)$

Redox: $Al\ (s) + 3\ Ag^+\ (aq) \rightarrow Al^{3+}\ (aq) + 3\ Ag\ (s)$

6.4.2
Electrochemical Cells, Reactions, and Electromotive Forces

The preceding section has introduced redox reactions as those involving transfer of electrons. It has particularly been noted that copper and zinc are in direct contact. So, the electron transfer occurs between the two entities over a distance of separation of the order of one or a few molecular diameters. Thus, the redox change is a chemical reaction wherein, as embodied in the description, oxidation and reduction always go side by side, or in other words, oxidation and reduction occur simultaneously. It is, however, entirely possible to implement a transfer of electrons from zinc metal to copper ions indirectly when the two are separated in different vessels by an arrangement in which a rod of zinc metal dips into zinc sulfate solution in one vessel, and a rod of copper metal in copper sulfate solution in the other vessel. A connecting wire joins the two rods externally. The zinc metal gives out electrons to copper ions through the externally connected wire and the copper rod dipped in the copper sulfate solution. The redox change occurring under these conditions is an electrochemical change. Electrolysis cases (see later) are also redox changes belonging to electrochemical types. The entire reaction involving zinc at copper can be presented as:

$$\mathrm{Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Cu\ (s) + Zn^{2+}\ (aq)} \qquad \text{(a)}$$

which in turn can be broken down into two half-equations presented as:

$$\text{Oxidation:} \quad \mathrm{Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2\ e^-} \qquad \text{(b)}$$

$$\text{Reduction:} \quad \mathrm{Cu^{2+}\ (aq) + 2\ e^- \rightarrow Cu} \qquad \text{(c)}$$

Any reaction of the type described herein can, in principle, form the basis of electricity generation. The only requirement is that site of oxidation (loss of electrons or de-electronation) be physically separated from the site of reduction (gain of electrons or electronation) so that the reaction cannot be completed without the passage of an electric current from one site to the other, except through the external circuit. If there is no external connection between the electrodes, equilibria will exist and each of the metals concerned will have a potential relative to the corresponding electrolyte. These potentials will be different for the two metals.

An arrangement of the system organized in the way described and leading to the generation of electricity from a spontaneously occurring redox reaction can be seen in an electrochemical cell. Although such a cell requires two electrodes for an electrochemical reaction to occur and its electrical consequences to be measured, the nature of the cells that can be constructed is best understood in terms of the individual electrodes. The electrode, including the electrode itself and the reagents that are involved with it, is called the half-cell, while the component of total chemical reaction that occurs in the half-cell is the half-reaction, or electrode reaction. When pairs of electrodes such as those of Cu-Zn are combined and are linked by an external electrical conductor, an electric current will flow and chemical reactions will take place in the two half-cells. Combination of the electrodes is implemented without complication if both electrodes can operate in the same solution, as shown in Figure 6.6. When this is not possible, a connection must be established that allows ionic conduction between the two half cells, but prevents mixing of the half-cell solutions. The experimental design described for the Cu-Zn system suffers from one important deficiency for sustained working. As electrons are lost by the zinc, the content of that container would acquire a net positive charge, while the contents of the other container would acquire a negative charge as the copper ions are taken away by reduction. For the reaction to occur, electrical neutrality must be maintained. It is, therefore, necessary that a linkage be made between the solutions that permits ionic conduction to take place between the half-cells, but disallows mixing of the two half-cell solutions. For this, a salt bridge is often used, and such a connecting device – which is usually indicated by a double vertical

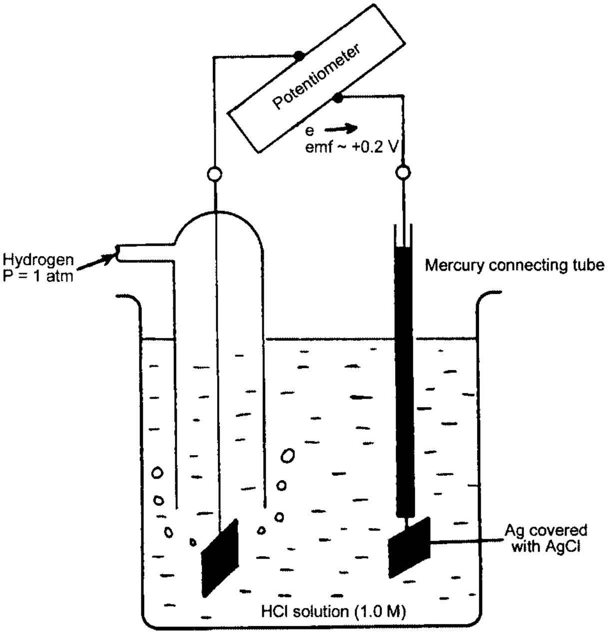

Figure 6.6 Electrode arrangement for an electrochemical cell in which both electrodes can function in the same solution. Description: The electrochemical cell is found to drive electrons from the hydrogen electrode to the silver electrode with an emf of about 0.2 V. This can be reported by writing the cell as: Pt | H_2 (1 atm) | HCl (1.0 M) | AgCl | Ag and assigning the emf as +0.2 V. If the cell to be written as: Ag | AgCl | HCl (1.0 M) } H_2 (1 atm) | Pt, the emf would be assigned as –0.2 V. In either instance, the emf values show that there is a tendency for electrons to be propelled through the external circuit from the hydrogen to the silver electrode.

line in a cell formulation – has no net effect on the cell reaction. The topic on the use of a salt bridge is set aside for the time being. Instead, for the present, it will be instructive to trace the path of electrical current in the Cu-Zn cell.

At the zinc electrode, electrons are produced by the oxidation half-reaction (b). This electrode, which pumps electrons into the external circuit, is labeled negative, and is the anode of the cell.

The reaction proceeds, sending electrons through the metallic conductor which externally connects the two electrodes contained in respective of containers. The details of the part of the circuit may be an electric motor to do work, or a heating coil to deliver heat energy, or a lamp to deliver light energy, or some other device that consumes electrical energy. If the electron current is prevented from flowing into the circuit by incorporating instead a device such as the voltameter it will cause an electrical potential difference (voltage) to build up.

Electrons pass through the external circuit into the copper electrode, where they are consumed in reducing Cu^{2+} ions in the solution to copper atoms. This is represented by the reduction half-reaction (c). The copper electrode which pulls electrons from the external circuit is labeled positive, and is the cathode of the cell.

The resultant effect of reactions (b) and (c), which are usually variously addressed as part-reactions, or half-reactions, or half-cell reactions, within the Zn-Cu cell is, of course, the spontaneous redox reaction (a). It is seen that electrons do not figure in the net cell reaction. Rather, they are generated at the anode and consumed at the cathode, and thus are not accumulated. The sum of the anodic and cathodic reactions is the overall chemical reaction for the cell ($CuSO_4 + Zn = ZnSO_4 + Cu$), and electrical energy is obtained from the chemical energy of this reaction. The cell is so designed that electron transfer from zinc atoms to copper ions occurs indirectly through an external circuit. In this way, the energy liberated by the reaction is used to perform electrical work rather than being dissipated as heat. The motor runs as long as the external conductor (wire outside the cell) is connected, zinc metal is present, and the copper ion concentration is maintained.

Two essential points concerning the design of a Zn-Cu cell are implied by equation (a):

1. The only species which need be present in the cell initially are the reactants, zinc atoms, and Cu^{2+} ions. In other words, the anode of the cell must be made of zinc and the solution surrounding the cathode must contain Cu^{2+} ions. On the other hand, the products of the reaction, copper atoms and Zn^{2+} ions, need not be present when the cell is set up. A platinum wire can be substituted for the copper rod; copper ions plate out as readily on platinum as on copper. Any positive ion which does not react with zinc can replace the Zn^{2+} ions surrounding the zinc electrode. A solution of Na_2SO_4 or KNO_3 works as well as a solution of $ZnSO_4$.

2. It is mandatory that Cu^{2+} ions do not come physically into contact with the zinc electrode. If this takes place in a situation where two solutions have inadvertently become mixed, the reaction will occur directly at the surface of the zinc on which copper will plate out and no emf will be obtained thereby short-circuiting the cell.

The way of preventing the Cu^{2+} ions formed at the cathode from diffusing over to the zinc anode is to interpose a barrier, and this can be achieved in two ways: (i) a porous partition and (ii) a porous pot. The barrier permits migration of ions while the cell is in use, but minimizes the random diffusion of ions that otherwise takes place when the cell is not connected.

An alternative way that goes into the making of the cell is to locate the two halves of the cell in separate containers. The two solutions are brought into contact in order to complete the electrical circuit and this contact, as noted earlier, is established by using a U-shaped tube which is referred to as a salt bridge.

It is relevant to present here some preliminaries as regards the salt bridge, this being a traditionally used and more convenient way than the porous partitioning medium in setting up a laboratory assemblage of an electrochemical cell. In this premise, attention is focused on the line formulae of the two cells as presented below:

$$Zn \mid ZnCl_2\ (c_1) \mid AgCl \mid Ag$$

$$Zn \mid ZnSO_4\ (c_1) \parallel CuSO_4\ (c_2) \mid Cu$$

The two vertical lines in the line formula for each of the cells presented above indicate use of a salt bridge. The first of the two cells has on the left side a combination consisting of zinc and zinc chloride solution at a concentration c_1, and on the right side a combination of silver chloride plated on silver. The second is formed with a combination of zinc and zinc sulfate at a concentration c_1 and of copper sulfate solution at a concentration c_2 and copper. An important difference between the two cells is that whereas the first cell holds phase boundaries only at the two electrodes, the second cell contains an additional boundary between the zinc sulfate and the copper sulfate solutions. This boundary is known as a liquid junction. Apart from making the cell irreversible, it generates a potential difference, known as a liquid junction potential. This potential difference originates from the circumstance that the rate of diffusion of Zn^{2+} ions from left to right across the boundary varyies from the rate of diffusion of Cu^{2+} ions from right to left, so that a potential gradient is established. Unless $c_1 = c_2$, an additional contribution to this potential may well originate from a difference between the rate of diffusion of sulfate across the boundary and the net rate of cationic diffusion. In any cell having a liquid junction, therefore, the overall potential difference across the cell is not purely a measure of the penchant for the occurrence of an oxidation–reduction reaction, but also involves a contribution from the liquid junction potential.

The foregoing text highlights the fact that at the interface between electrolytic solutions of different concentrations (or between two different electrolytes at the same concentration) there originates a liquid junction potential (also known as diffusion potential). The reason for this potential lies in the fact that the rates of diffusion of ions are a function of their type and of their concentration. For example, in the case of a junction between two concentrations of a binary electrolyte (e.g., NaOH, HCl), the two different types of ion diffuse at different rates from the stronger to the weaker solution. Hence, there arises an excess of ions of one type, and a deficit of ions of the other type on opposite sides of the liquid junction. The resultant uneven distribution of electric charges constitutes a potential difference between the two solutions, and this acts in such a way as to retard the faster ion and to accelerate the slower. In this way an equilibrium is soon reached, and a steady potential difference is set up across the boundary between the solutions. Once the steady potential difference is attained, no further net charge transfer occurs across the liquid junction and the different types of ion diffuse at the same rate.

It can be shown that the liquid junction potential, E_j, between two concentrations, c_1 and c_2, of a uni-univalent electrolyte (e.g., KCl, HCl) is provided by the following special case of an equation derived as:

$$E_j = (2\,t_+ - I)\,\frac{2.303\,R\,T}{F}\log\frac{a_1}{a_2}$$

where a_1 and a_2 are the appropriate activities in the bulk of the two solutions, and t_+ is the mean transfer number of the cation in the activity range considered. At 25 °C, and putting a_1/a_2 equal to c_1/c_2 to obtain results of approximate accuracy, the equation above becomes,

$$E_j = 0.0591\,(2\,t_+ - I)\log(c_1/c_2)$$

The two equations show that the nearer the cationic transport is to 0.5, the smaller is the liquid junction potential (other factors being unchanged). Among common electrolytes one of the highest numerical values of the factor $(2\,t_+ - I)$ is given by hydrochloric acid, at ≈ 0.65. Hence a potential difference of about 39 mV develops at 25 °C across the junction between 0.001 N and 0.01 N hydrochloric acid. In the case of potassium chloride solution, the numerical value of $(2\,t_+ - I)$ is only about 0.02, so that at 25 °C the potential difference between 0.001 N and 0.01 N solution is about 1 mV.

When the electrolytes on either side of a liquid junction are different, the mathematical analysis of the interfacial potential becomes complex. In nearly all these cases the potential is a function of the geometrical characteristics of the boundary itself. In one general case, however, i.e., for the junction between two uni-univalent electrolytes at the same concentration and having a common ion (e.g., the pair KCl, NaCl), the liquid junction potential is independent of the structure of the boundary and is provided by following equation:

$$E_\mathrm{j} = \frac{2.303\,R\,T}{F}\log\frac{\Lambda_1}{\Lambda_2}$$

where Λ_1 and Λ_2 are the equivalent conductivities of the two electrolytes at the concentration in question. As is evident from the equation above, the nearer to each other are the equivalent conductivities of electrolytes forming the boundary, the smaller is the liquid junction potential. In contrast, when the junction made with HCl and the chloride ion is common across the boundary, the liquid junction potential is relatively high owing to the unusually great equivalent conductance of hydrochloric acid. For example, the liquid junction potential between 0.1 N solutions of NaCl and KCl is calculated to be 0.059 log 128.96/106.74 = 0.0049 volts at 25 °C; the comparable junction potential between 0.1 N solutions of NaCl and HCl is, however,

$$0.059 \log 391.32/106.74 = 0.0333 \text{ volts}$$

at 25 °C, which is over sixfold greater.

Hardly any electrochemical cell is free of liquid junction potentials, and the measurement of arbitrary single electrode potentials is often rendered difficult by the inclusion of a liquid junction potential of unknown magnitude in the observation. The most usual procedure for reducing the magnitude of liquid junction potentials in electrochemical systems is to introduce a salt bridge. This consists of a narrow tube filled with a highly concentrated solution (often a saturated solution) of a salt whose cation and anion have close to the same mobility. The preferred salt is KCl, but NH_4NO_3 is often used when the adjacent solutions contain Ag^+ or some other ion that forms a precipitate with chloride ions. The salt solution is made up in a gel (e.g., agar) in order to decrease mixing with the solutions in the two half-cells. The salt bridge whose ends dip into the electrolytes contained in the electrochemical cell has in this way replaced one liquid junction by two (two liquid junctions instead of one): a liquid junction between the bridge and the $ZnSO_4$ solution; and another between the bridge and the $CuSO_4$ solution. The ion concentration in the salt bridge is, as has been pointed out, made very high, while the concentrations of $ZnSO_4$ and $CuSO_4$ solutions are usually relatively low. Thus, the two liquid junction potentials are largely determined by the relative rates of diffusion or ionic mobilities of the K^+ and the Cl^- (or of the NH_4^+ and the NO_3^- ions) into adjoining solutions, these being nearly equal. The liquid junction potential at each boundary in a salt bridge constituted as described is determined by an equation of the form,

$$E_\mathrm{j} = (2\,t_+ - I)\,\frac{2.303\,R\,T}{F}\log a_1/a_2$$

Hence, the advantage of using salts such as KCl or NH_4NO_3 is that the mobilities of the ions they contain are such as to make the ionic transport numbers close to 0.5. Thus, the factor (2 t_+ – I) in the equation shown above is near to zero, and the liquid junction potential nearly vanishes. It may be emphasized however, that this potential can never be completely eliminated. It is clear that most of the current is carried across the junction by K^+ and Cl^- ions. Current is drawn from the cell, and ions move slowly through the salt bridge to complete the circuit. The arrangement involving use of a porous pot or a porous partition or a salt bridge as described in the making of the cell is shown in Figure 6.7. The cell shown in Figure 6.7 (C) is considered without the salt bridge in place. The electrons released by zinc atoms can flow up to copper plate through the external circuit, where they will neutralize some of the Cu^{2+} ions from the solution. When this has occurred, the copper sulfate solution will for a short while acquire a negative charge due to loss of positive ions (Cu^{2+}). In the meantime, zinc sulfate solution will become positively charged with the new Zn^{2+} ions gained by it from the zinc plate. An accumulation of charges in the two solutions will prevent further flow of electrons, and the electrochemical changes or the redox reaction will stop. When a salt bridge is introduced, it provides a passage for flow of charge in the internal circuit. The negative ions move from the copper-plate side through the copper

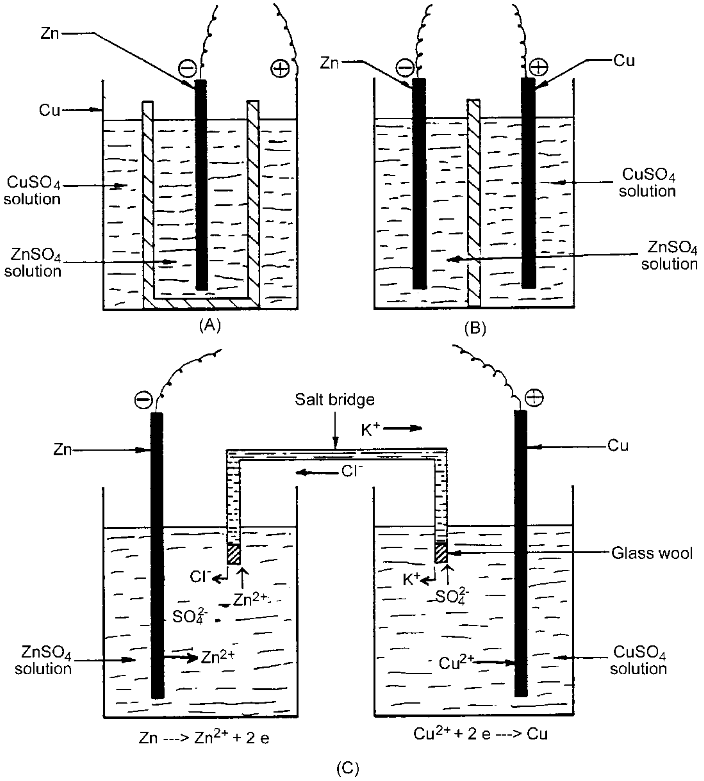

Figure 6.7 Different types of Daniell cell (Zn|Zn2$^+$||Cu^{2+}|Cu$^+$)
(A) with porous pot, (B) with porous partition, (C) with salt bridge.

sulfate solution, salt bridge, and zinc sulfate solution to the zinc plate. The positive ions move in the reverse direction, i.e., from the zinc-plate side to the copper-plate. Thus, a flow of electricity is maintained and an accumulation of charges is prevented when the salt bridge is introduced. Hence, while the salt bridge does not participate chemically in the cell reaction, it is a must if the cell is to operate. In short, the functions of the salt bridge are to: (i) connect the two half-cells; (ii) maintain electrical contact while avoiding direct diffusion of solutions between the two half-cells; and (iii) prevent the accumulation of positive and negative charges in the half-cells by allowing the ions to pass through.

In a general manner it may be recounted here that devices which implement direct conversion of a spontaneous chemical reaction – or in other words chemical energy – to electrical energy are called electrochemical cells. An electrode dipping into a solution, it may be recalled, is said to constitute a half-cell; the combination of two half-cells is a typical electrochemical cell. It would also be recalled that electrochemical cells are also called galvanic (or voltaic) cells. The particular cell formed with zinc dipped in zinc sulfate and copper dipped in copper sulfate which has actually formed the central figure in the presentation so far is a Daniell cell. This represents an important classical practical application of electrochemical cells. A great many simple electrochemical cells can be set up in a manner entirely analogous to the Daniell cell shown in Figure 6.7. One can, for example, devise cells in which the following spontaneous redox reactions serve as a source of electrical energy:

$$\mathrm{Ni\ (s) + Cu^{2+} \rightarrow Ni^{2+} + Cu\ (s)}$$

$$\mathrm{Zn\ (s) + 2\ H^{+} \rightarrow Zn^{2+} + H_2\ (g)}$$

In each case, the set up consist of two half-cells, each containing an electrode dipping into a solution of an appropriate electrolyte, separated by a salt bridge or similar device. Atoms of elements having a greater tendency to lose electrons (Ni, Zn) are oxidized at the anode, giving up electrons which travel through the external circuit to the cathode, where they combine with the cation (Cu^{2+}, H^+) which is most readily reduced. An illustrative list of cells with different types of electrode is shown in Table 6.9, while an illustrative list of various types of half-cell is shown in Table 6.10.

Yet another way of preventing Cu^{2+} ions from coming physically into contact with the zinc electrode is illustrated in the gravity cell shown in Figure 6.8. To form this cell, sufficient copper sulfate solution is added to the container to cover the copper electrode. A more dilute, less dense solution of zinc sulfate is then carefully poured over the copper sulfate. As long as the cell is not subjected to vibrations, the boundary between the layers may be maintained over long periods of time. Since their internal resistance is much lower than that of porous barrier or salt-bridge cells, a much larger current can be drawn from them. However, from the point of convenience, the use of a salt bridge to build a laboratory electrochemical cell remains unchallenged. No advance has yet been made to dislodge the salt bridge from its perch of prominence, and its electrochemically interesting features are briefly discussed in the following text.

It is important to discuss cell notation and conventions. Instead of drawing a complete diagram to present electrochemical cells, it is convenient to specify a cell in line formula form or, as may be said, shorthand form. The Cu-Zn cell is thus presented as:

$$\mathrm{Zn \mid Zn^{2+}\ (1\ M) \parallel Cu^{2+}\ (1\ M) \mid Cu}$$

Table 6.9 Representation of cells with different types of electrode.

Description of cell	***Cell formula***	***Half-reaction***		***Net cell reaction***
		Oxidation	***Reduction***	
Zinc and cadmium electrodes	$- \mathrm{Zn} \vert \mathrm{Zn}^{2+}(1\ \mathrm{M}) \vert\vert \mathrm{Cd}^{2+}\ (1\ \mathrm{M}) \vert \mathrm{Cd}\ +$	$\mathrm{Zn\ (s)} \rightarrow \mathrm{Zn}^{2+}\ \mathrm{(aq)} + 2\ \mathrm{e}^-$	$\mathrm{Cd}^{2+}\ \mathrm{(aq)} + 2\ \mathrm{e}^- \rightarrow \mathrm{Cd\ (s)}$	$\mathrm{Zn\ (s)} + \mathrm{Cd}^{2+}\ \mathrm{(aq)} \rightarrow \mathrm{Zn}^{2+}\ \mathrm{(aq)} + \mathrm{Cd\ (s)}$
Nickel and tin electrodes	$- \mathrm{Ni} \vert \mathrm{Ni}^{2+}(1\ \mathrm{M}) \vert\vert \mathrm{Sn}^{2+}\ (1\ \mathrm{M}) \vert \mathrm{Sn}\ +$	$\mathrm{Ni\ (s)} \rightarrow \mathrm{Ni}^{2+}\ \mathrm{(aq)} + 2\ \mathrm{e}^-$	$\mathrm{Sn}^{2+}\ \mathrm{(aq)} + 2\ \mathrm{e}^- \rightarrow \mathrm{Sn\ (s)}$	$\mathrm{Ni\ (s)} + \mathrm{Sn}^{2+}\ \mathrm{(aq)} \rightarrow \mathrm{Ni}^{2+}\ \mathrm{(aq)} + \mathrm{Sn\ (s)}$
Hydrogen and copper electrodes	$- \mathrm{Pt},\ \mathrm{H}_2\ \mathrm{(g)} \vert \mathrm{H}^+\ (1\ \mathrm{M}) \vert\vert \mathrm{Cu}^{2+}(1\ \mathrm{M}) \vert \mathrm{Cu}\ +$	$\mathrm{H}_2\ \mathrm{(g)} \rightarrow 2\ \mathrm{H}^+\ \mathrm{(aq)} + 2\ \mathrm{e}^-$	$\mathrm{Cu}^{2+}\ \mathrm{(aq)} + 2\ \mathrm{e}^- \rightarrow \mathrm{Cu\ (s)}$	$\mathrm{H}_2\ \mathrm{(g)} + \mathrm{Cu}^{2+}\ \mathrm{(aq)} \rightarrow 2\ \mathrm{H}^+\ \mathrm{(aq)} + \mathrm{Cu\ (s)}$
Copper and silver electrodes	$- \mathrm{Cu} \vert \mathrm{Cu}^{2+}(1\ \mathrm{M}) \vert\vert \mathrm{Ag}^+\ (1\ \mathrm{M}) \vert \mathrm{Ag}\ +$	$\mathrm{Cu\ (s)} \rightarrow \mathrm{Cu}^{2+}\ \mathrm{(aq)} + 2\ \mathrm{e}^-$	$2\mathrm{Ag}^+\ \mathrm{(aq)} + 2\ \mathrm{e}^- \rightarrow 2\mathrm{Ag\ (s)}$	$\mathrm{Cu\ (s)} + 2\mathrm{Ag}^+\ \mathrm{(aq)} \rightarrow \mathrm{Cu}^{2+}\ \mathrm{(aq)} + 2\ \mathrm{Ag\ (s)}$

Table 6.10 Various types of half-cell.

Type of electrodes	***Description of half-cell***
Metal	Metal in contact with a solution containing ions of the metal, e.g., silver in silver nitrate solution. Such a half-cell is represented as $\mathrm{Ag} \vert \mathrm{Ag}^+\ (c)$, where c is the silver-ion concentration. The reaction occurring at this electrode is solution or deposition of the metal, according to $\mathrm{Ag} \rightleftharpoons \mathrm{Ag}^+ + \mathrm{e}^-$.
Gas	These are constructed by placing a strip of nonreactive metals (usually platinum or gold) in contact with both the solution and a gas stream: (a) the hydrogen electrode consists of a platinum strip exposed to a current of hydrogen, and partly immersed in an acid solution. A potential is set up between the gas and the solution, the equilibrium involved being $\mathrm{H}_2 \rightleftharpoons 2\ \mathrm{H}^+ + 2\ \mathrm{e}^-$; (b) potentials also occur when the halogens are in contact with their ions in solution, the equilibrium in the case of chlorine being $\mathrm{Cl}_2 + 2\ \mathrm{e}^- \rightleftharpoons 2\ \mathrm{Cl}^-$.
Oxidation–reduction	An inert metal dips into a solution containing ions in two different oxidation states. An example consists of a platinum wire dipping into a solution containing ferrous and ferric ions. Such a cell is described by $\mathrm{Pt} \vert \mathrm{Fe}^{2+}\ (c_1),\ \mathrm{Fe}^{3+}\ (c_2)$. The comma is used to separate the two chemical species which are in the same solution. These electrodes are similar to the gas electrodes, except that the two species involved in the electrode reaction are ions. The electrode reaction in the example is $\mathrm{Fe}^{3+} + \mathrm{e}^- \rightleftharpoons \mathrm{Fe}^{2+}$, and there is the possibility of the electrode either donating or accepting electrons.
Metal insoluble-salt	These consist of a metal in contact with one of its slightly soluble salts; this salt in turn is in contact with a solution containing the anion of the salt. An example is represented as: $\mathrm{Ag} \vert \mathrm{AgCl} \vert \mathrm{Cl}^-\ (c)$. The electrode process at such an electrode as: $\mathrm{AgCl\ (s)} \rightleftharpoons \mathrm{Ag}^+ + \mathrm{Cl}^-$; $\mathrm{Ag}^+ + \mathrm{e}^- \rightarrow \mathrm{Ag\ (s)}$ or overall, $\mathrm{AgCl\ (s)} + \mathrm{e}^- \rightleftharpoons \mathrm{Ag\ (s)} + \mathrm{Cl}^-$. The electrode reaction involves only the concentration of Cl^- as a variable, in contrast with the $\mathrm{Ag} \vert \mathrm{Ag}^+$ electrode, which has the Ag^+ concentration as a variable. The most frequently electrode of this type is the calomel electrode (see text for description).
Metal insoluble-oxide	These are similar to the previous electrodes. An example is the antimony, antimony trioxide electrode, $\mathrm{Sb} \vert \mathrm{Sb}_2\mathrm{O}_3 \vert \mathrm{OH}^-$. An antimony rod is covered with a thin layer of oxide and dips into a solution containing OH^- ions. The electrode reaction is: $\mathrm{Sb\ (s)} + 3\ \mathrm{OH}^- \rightleftharpoons 0.5\ \mathrm{Sb}_2\mathrm{O}_3 + 1.5\ \mathrm{H}_2\mathrm{O\ (l)} + 3\ \mathrm{e}^-$.

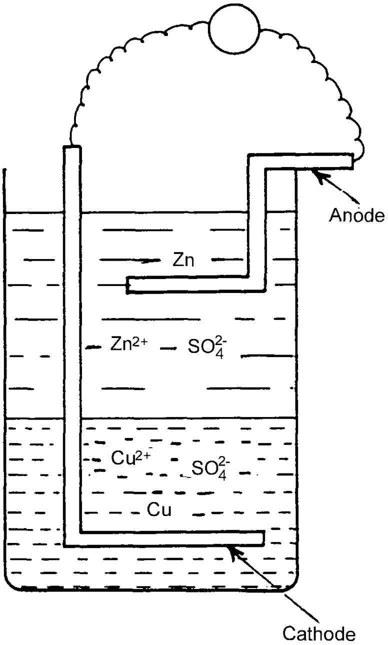

Figure 6.8 Gravity (Daniell) cell.

To describe in words the cell formula expressed above it may be said that the components of the cell are written in order, starting with the left-hand electrode and moving across the salt bridge to the right. The significance of single and double lines has been pointed out earlier. By convention, the electrode written to the left of the salt bridge in this cell notation is always taken to be the anode, and the associated half-reaction is always written as an oxidation. The right-hand electrode is therefore always the cathode, and the half-reaction is always taken as a reduction. It may be noted for the sake of remembrance that anode-half-reaction comes first in the cell notation, just as the letter a comes before c. The cell reaction corresponding to a given shorthand description is obtained by the addition of the half-equations after multiplying by any factor required for equalization of the number of electrons lost at the anode with the number gained at the cathode.

The conventions as described in the foregoing paragraph can be used to decide whether the cell reaction is actually spontaneous. In general, if an electrochemical cell is connected to a voltmeter, the electrode connected to the negative terminal of the meter must be the anode. If the shorthand cell notation shows that electrode on the left, then the corresponding cell must be spontaneous. If, on the other hand, the voltmeter shows that the right-hand electrode is releasing electrons, then the writing of the shorthand notation must have been backwards. This implies that the reverse of the cell reaction obtained by the rule specified must actually be occurring, and it is the reverse reaction which is spontaneous. Thus, by simply seeing which electrode in the cell loses electrons and which takes up them (that is, by finding which electrode is negative and which positive), the spontaneity of the cell reaction is determined.

6.4.3
Cell Electromotive Force

A prima facie understanding of the electromotive force of a cell is the difference of potential which implements a current to flow from an electrode of higher potential to one of lower potential. The electrical potential difference (commonly called voltage) between the two electrodes provides a quantitative index of just how spontaneous a redox reaction is. The potential difference is greatest when a large electrical resistance in the external circuit prevents any current from flowing. The maximum potential difference which can be measured for a given cell is defined as its electromotive force, abbreviated as emf and symbolized as *E*. The emf cannot be found out by voltameter connected between the two electrodes. This is because of the fact that during such measurement a part of the cell current is drawn and thereby there occurs a change in the emf as a result of the formation of reaction products at the electrodes and of alteration in the concentration of the electrolyte around the electrodes. The definition of emf implies the conduction of measurement of potential difference under the condition of the cell staying open, i.e., while no current is being drawn from the external leads. In practice, it is possible to measure emf under conditions in which the current drawn from the cell is so small as to be negligible. The method, devised by Poggendorf, uses a circuit known as a potentiometer.

If the unknown cell in the Cu-Zn cell is connected to the circuit, the emf measured is the combined potentials of two single electrode potentials for the two metals (zinc and copper) making up the cell, and it is impossible to state from the value of the emf measured what proportion is due either to the zinc, or to the copper.

In potentiometric measurements of emf, it is necessary to have a cell where emf is constant with time and is exactly known. For this purpose, a standard Weston cell is commonly employed. A diagram of a simplified potentiometer is shown in Figure 6.9. It consists of a

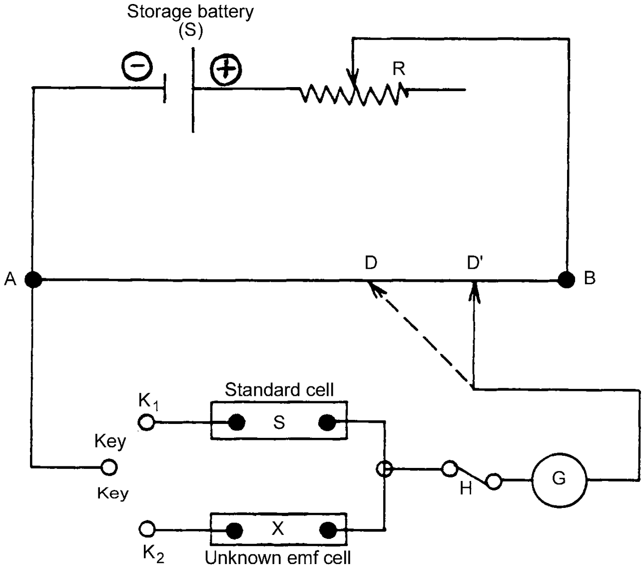

Figure 6.9 Measurement of the emf of a cell.

uniform wire *AB* of high resistance, and a storage battery of constant (but large) emf is connected to the ends *A* and *B* of the wire, through an adjustable resistance (*R*). The cell *X*, whose emf is to be determined, is included in another circuit by connecting the pole *A* through a galvanometer and sliding contact. The second circuit is completed by introducing key K_2. The sliding contact is moved along the wire *AB*, until point *D* is reached, when no current flows through the galvanometer. The position *D* is noted. The second circuit is then completed through a standard cell *S* of known emf by introducing key K_1. The sliding contact is again moved along the wire *AB*, until the point *D′* is noted. Then:

$$\text{Emf of cell, } E_x \propto \text{length } AD$$

and emf of the standard cell, $E_s \propto$ length *AD′*. Therefore,

$$E_x/E_s = \text{length } AD/\text{length } AD'$$

Thus, the unknown emf, E_x, of the cell can be calculated, if the emf of the standard cell E_s is known.

In the foregoing description dealing with cell emf measurement, the need to use a standard cell has been seen. A standard cell is one which is capable of giving constant and reproducible emf, and having negligible a temperature coefficient of emf. In other words, the standard cell is a source of unvarying potential. The present text refrains from stepping into describing the scientific and technical details of the prevailing standard cells, as many electrochemical texts have already dealt with them, and these may be consulted to obtain knowledge in this respect.

6.4.4
Standard EMFs and Electrode Potentials

A voltmeter joined between the two electrodes of a galvanic cell shows a characteristic voltage, which depends on the concentration and nature of participating reactants. For example, in the Cu-Zn cell, if Cu^{2+} and Zn^{2+} are at 1 mol dm^{-3} (1 M) concentrations and the temperature is 298 K, the voltage measured would be 1.10 V. This voltage is characteristic of the reaction as shown below:

$$Zn\ (s) + Cu^{+} \rightarrow Zn^{2+} + Cu\ (s)$$

It is instructive at the present stage to study the comparison of zinc and copper electrodes against the hydrogen electrode in order to delineate the very basic and centrally important ingredients on which the essence of electrochemistry is based. For this purpose, a galvanic cell is assembled to study the reaction as shown below:

$$Zn\ (s) + 2\ H^{+} \rightarrow H_2\ (g) + Zn^{2+}$$

It may be recalled that the cell is formed with a zinc bar dipping into an aqueous solution of a zinc salt and with hydrogen gas bubbling over a platinum electrode dipped into an acidic solution. A voltmeter is connected to the galvanic cell and it so happens that the zinc electrode is connected to the negative terminal of the meter and the positive terminal of the meter to the hydrogen electrode. The voltmeter reading shows that the anode compartment is that having the zinc electrode and the cathode compartment is that having the hydrogen electrode. At 298 K, when the concentrations of H^+ and Zn^+ are each at 1 M and when the pressure of the H_2 gas is 1 atm, the voltmeter is found to read +0.76 V. The deflection is in such a direction as to represent the fact that zinc has a greater tendency than H_2 to push electrons into the circuit. In other words, the half-reaction:

$$Zn\ (s) \rightarrow Zn^{2+} + 2\ e^-$$

possesses a greater disposition to take place than the half-reaction:

$$H_2\ (g) \rightarrow 2\ H^+ + 2\ e^-$$

to the extent of 0.76 V.

Having studied the Zn-H_2 galvanic cell, the next assembled galvanic cell needed to complete the present purpose, is to make use of the reaction as shown below:

$$H_2\ (g) + Cu^{2+} \rightarrow 2\ H^+ + Cu\ (s)$$

Adhering to the conditions given above in that at 298 K, the concentrations of Cu^{2+} and H^+ are 1 M and the pressure of H_2 is 1 atm, the voltmeter is found to read 0.34 V. The deflection direction is indicative of the fact that Cu has an inferior disposition to H_2 to emit electrons. In other words, in this case, the half-reaction:

$$Cu\ (s) \rightarrow Cu^{2+} + 2\ e^-$$

has an inferior disposition to occurrence than the reaction:

$$H_2\ (g) \rightarrow 2\ H^+ + 2\ e^-$$

by 0.34 V.

In all cells the voltage observed between two electrodes originates from two origins: an offering at the anode and an offering at the cathode. If either of these is known, the other is readily obtained by difference. However, it is not at all possible to measure the electrode potential of a separate electrode; after all, there must be two electrodes for any circuit. The accepted course is to score one electrode as a standard reference, accredit it a zero value, and subsequently refer all other electrode potentials to this dictatorially designated zero. As a reference, an international convention has consented on the standard hydrogen electrode (sometimes termed SHE). The understanding is that a zero value of the voltage will be fixed to it at 298 K, 1 atm H_2 pressure, and 1 M H^+ concentration. Thus, in a cell that has the SHE, the integral measured voltage is attributed to the half-reaction at the other electrode. Voltages thus fixed are called oxidation–reduction potentials, or redox potentials. If the half-reaction is conveyed with the electrons involved on the right, the accompanying voltage is called the oxidation potential. If, on the other hand, the half-reaction is conveyed with the electrons involved on the left, the accompanying voltage is called a reduction potential. A confusion exists as to whether electrode potential implies oxidation potential or reduction potential. The international recommendation is that electrode potential implies reduction potential, and it is this convention which is herein being adopted and thereby giving no room for confusion. Some half-reactions, together with their reduction potentials have been listed in Table 6.11. However, literature abounds with more extensive listings. The values given in Table 6.11 apply for the half-reaction comprehended from left to right (the signs need to be changed for the opposite direction). The forward reaction is a reduction

Table 6.11 Some standard electrode potentials 298 K.

Feature description	*Half-reaction (reduction)*	*Potential E^0_{red} (V)*	*Disposition towards disposition*	*Classification*	*Alternatively described feature*
↓ Increase in (i) tendency of oxidation; (ii) tendency to lose electrons; (iii) power as oxidizing agent.	$0.5\ F_2 + e^- \rightarrow F^-$	+2.87	↕ Ions reducible from aqueous solutions.	↕ (Cathodic) "Noble" end-	↑ Increase in (i) tendency of reduction; (ii) tendency to gain electrons; (iii) power as oxidizing agent.
	$Au^+ + e^- \rightarrow Au$	+1.69			
	$Cl_2 + 2\ e^- \rightarrow Cl^-$	+1.36			
	$Br_2 + 2\ e^- \rightarrow Br^-$	+1.09			
	$Pt^{4+} + 4\ e^- \rightarrow Pt$	+0.86			
	$Ag^+ + e^- \rightarrow Ag$	+0.80			
	$Fe^{3+} + 3\ e^- \rightarrow Fe^{2+}$	+0.77			
	$Cu^{2+} + 2\ e^- \rightarrow Cu$	+0.34			
	$H^+ + e^- \rightarrow 0.5\ H$	0.00	Reference		
	$Pb^{2+} + 2\ e^- \rightarrow Pb$	−0.13	↕ Ions reducible from aqueous solutions by virtue of overvoltage.	↕ "Base" end- (Anodic)	
	$Sn^{2+} + 2\ e^- \rightarrow Sn$	−0.14			
	$Ni^{2+} + 2\ e^- \rightarrow Ni$	−0.25			
	$Co^{2+} + 2\ e^- \rightarrow Co$	−0.28			
	$Fe^{2+} + 2\ e^- \rightarrow Fe$	−0.44			
	$Cr^{2+} + 3\ e^- \rightarrow Cr$	−0.74			
	$Zn^{2+} + 2\ e^- \rightarrow Zn$	−0.76			
	$Mn^{2+} + 2\ e^- \rightarrow Mn$	−1.18			
	$Al^{3+} + 3\ e^- \rightarrow Al$	−1.66	↕ Ions not reducible from aqueous solutions. Molten salt is needed.		
	$Mg^{2+} + 2\ e^- \rightarrow Mg$	−2.36			
	$Na^+ + e^- \rightarrow Na$	−2.71			
	$Ca^{2+} + 2\ e^- \rightarrow Ca$	−2.90			
	$K^+ + e^- \rightarrow K$	−2.92			
	$Li^+ + e^- \rightarrow Li$	−3.05			

process wherein an oxidizing agent, cited just to the left of each atom, is subjected to reduction to yield the reducing agent cited to the right. The arrangement in the table is such that the oxidizing agents are listed in order of decreasing strength (or disposition to be reduced). In other words, as one traverses from upper to lower, there is a decreasing disposition for the forward half-reaction to take place. For example, of the list provided, fluorine (F_2), at the top, is the best oxidizing agent as it possesses the greatest disposition to drive for electrons. The lithium ion, Li^+, in occupying the lowest position in the list, is the poorest oxidizing agent and possesses the minimum disposition to opt for electrons. The numerical values provided in Table 6.11 are devoted to aqueous solutions at 298 K in which the concentration of each dissolved species is 1 M. A negative value implies that the oxidizing agent is weaker than H^+, while a positive value implies that the oxidizing agent is stronger than H^+ (set at zero).

The tabulated presentation described in the foregoing presentation is called the electrochemical series, and it provides one of the rational schemes for the classification of metals. The higher the location of a metal in the electrochemical series, the higher is its reactivity, and the higher is the stability of its compounds. Thus, lithium: (i) forms positive ions most readily; (ii) forms the most stable compounds; and (iii) discharges its ion least readily. On the other hand, silver: (i) forms positive ions least readily; (ii) forms the least stable compounds; and (iii) discharges its ion most readily. The greater the tendency for a metal to ionize, the lesser will be the tendency for this ion to gain an electron or to discharge at the electrode. Hence, cations can be arranged in order of their increasing tendency to gain an electron, which is the same as the electrochemical series of metals.

Before dealing with various important applications of the electrochemical series with some practical examples, a break is given here to present a more detailed elaboration on the hydrogen electrode, reference electrodes, and some of the theoretical and general aspects pertaining to electrode potentials and free energy changes involved with cell reactions.

Each oxidizing agent in Table 6.11 is united in its half-reaction with a reduced form. For example, F_2 (g) is united with F^-. The reduced form is capable of serving as a reducing agent when the half-reaction is inverted. Thus, the reduction potentials in Table 6.11 also provide facts about relative disposition of reducing agents to get rid of electrons. If a half-reaction, such as the one at the very top of the table, possesses great disposition to move to the right, it possesses little disposition to move to the left; the reducing agent is a poor entity. Of the reducing agents listed (always to the right of the arrow), F^- is the poorest, and Li (s) is the greatest. The half-reaction:

$$\text{Li (s)} \rightarrow \text{Li}^+ + e^- \qquad +3.05\ \text{V}$$

which is the opposite of:

$$\text{Li}^+ + e^- \rightarrow \text{Li (s)} \qquad +3.05\ \text{V}$$

possesses a much greater disposition to take place than:

$$F^- \rightarrow 0.5\ F_2\ \text{(g)} + 2\ e^- \quad -2.87\ \text{V}$$

Table 6.11 lists, to the right of the arrows, reducing agents or disposition to electron loss or disposition to oxidation in order of increasing strength. Such a list is more popularly called the electromotive force, or emf, series. The maximum potential difference which can be measured for a given cell is called the electromotive force (abbreviated emf) and represented by the symbol E_{cell}. It may be recounted that the emf values reported in Table 6.11 are for those cells under specified standard conditions in which all the concentrations are 1 M and pressures are 1 atm. The emf of such a cell is said to be its standard electromotive force, and is given by the symbol E^0_{cell}.

6.4.4.1 Hydrogen Electrode

A general introduction to the hydrogen electrode can be made by stating the fact that solutions frequently contain hydrogen ions, and the study of such solutions by electrochemical methods would be facilitated if a rod of solid hydrogen could be used as a hydrogen electrode. This is impossible, simply because hydrogen ceases to be a solid above –259 °C. Fortunately, it has been shown that a plate of platinized platinum covered with a film of hydrogen can be used as an electrode just as though it were a rod of solid hydrogen. The film of hydrogen is maintained on the platinum by bubbling hydrogen gas through the solution in such a way that the platinum is both wetted with the solution and in contact with the hydrogen gas. The hydrogen electrode finally represents the fact that a gas can be induced to participate in an electrochemical reaction and that it represents an important example in the development of electrochemical data. There are many forms of hydrogen electrode, but one typical form of apparatus is shown in Figure 6.10 (A). The electrode is such that on the surface of the inert metal electrode the reagents H_2 (g), H^+ (aq), or H_3O^+ (aq) and e^-, the latter in the metallic conductor, can be accommodated. The description of the set-up is as follows. It consists of a small platinum strip coated with platinum black to adsorb the hydrogen gas. A platinum wire, welded to the electrode and sealed through a glass tube, establishes contact with the outer circuit. The platinum strip is surrounded by an outer glass tube which has an inlet for hydrogen gas at the top, and a number of openings at the base for the escape of the excess gas. The electrode is dipped in a dilute solution of an acid. Pure hydrogen is then introduced into it at 1 atm pressure. A part of the gas is adsorbed by the platinized electrode, while excess gas escapes through the openings. This results in an equilibrium between the adsorbed hydrogen on the electrode surface and the hydrogen ions in the solution.

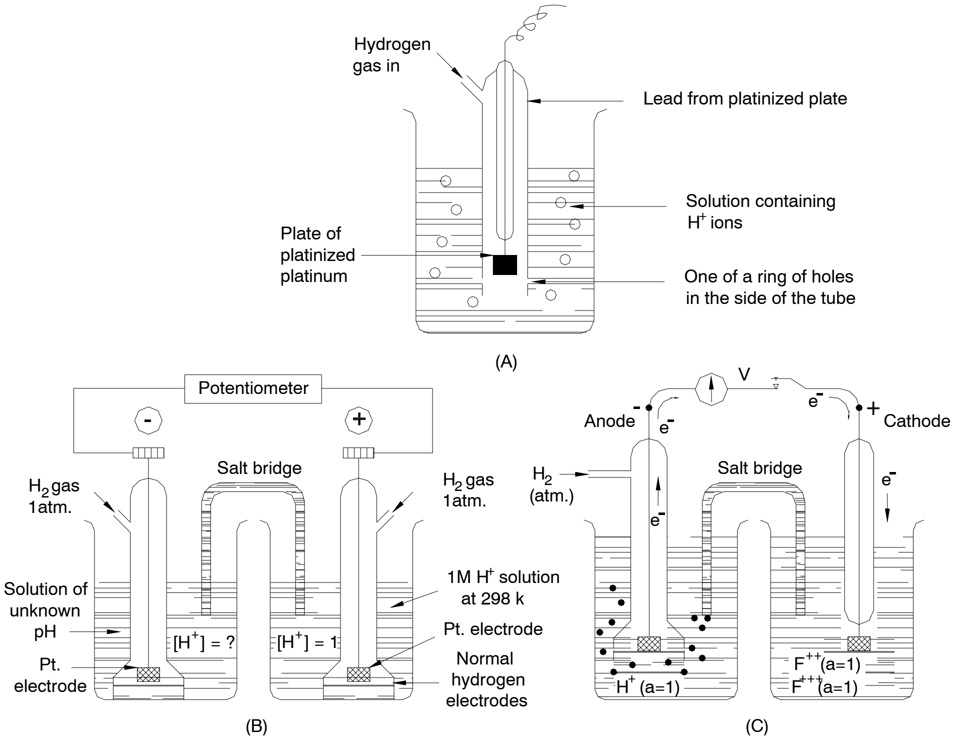

Figure 6.10 (A) A gas electrode in general and a hydrogen electrode in particular; (B) measurement of pH by hydrogen electrode; (C) galvanic cell.

$H^+ \text{ (aq)} + e^- \rightleftharpoons 0.5\ H_2$

The above is written, as is the convention, as a reduction reaction. The electrode assembly in which this reaction can proceed is indicated, are indicated by $Pt|H_2$ (P atm)$|H^+$ (C mole liter^{-1}). The interfaces between physical states is indicated by vertical lines, with an indication of the significant features of these states in a one-line formula. The symbol Pt is more restricted than necessary, being used here to mean any inert-metal electrode. The hydrogen electrode is given the name standard hydrogen electrode when in the electrode pure hydrogen at 1 atm pressure is bubbled through a solution at 25 °C containing hydrogen ions at unit activity. The electrode is thus $Pt|H_{2G}$ (1 atm)$|H^+_{aq}$ $(a_{H^+} = 1)$, and a solution of hydrogen ions containing H^+ at unit activity is 1.19 N HCl solution. Here, the electrode potential E_H is E^0_H, the standard hydrogen electrode potential and is given a value of zero volts. If the activity of hydrogen ions in the electrolyte is anything other than unity, using the Nernst equation the electrode potential of the hydrogen electrode is then

$$E_H = E^0_H + \frac{R\,T}{F} \ln a_{H^+}$$

the electrode reaction being

$H^+ \text{ (aq)} + e^- = 0.5\ H_2 \text{ (G)}$

At 25 °C, $E^0_H = 0$ and then the following equation can be written:

$$E_H = \frac{R\,T}{F} 2.303 \cdot \log_{10} a_{H^+} = -2.303 \frac{298\,R}{F}\ \text{pH}$$

Substituting for R (8.31 joules) and F (96,500 coulombs)

$E_H = -0.059$ pH at 25 °C

Thus, the electrode potential of the hydrogen electrode is dependent upon the pH of the electrolyte, or in other words hydrogen ion concentration in solution. Besides this, it also depends on the pressure of the gaseous hydrogen passing through the solution and over the platinum. Measurement of pH by a hydrogen electrode is shown in Figure 6.10 (B). Since the emf of the reference electrode is zero, the observed emf gives directly the emf of the half-cell containing the solution to be tested for pH.

$$E_{cell} = E_{right} - E_{left} = 0 - (-0.0591\ \text{pH})$$

$$\text{Therefore,}\quad \text{pH} = \frac{E_{cell}}{0.0591}$$

As an example of the numerous combinations of the hydrogen electrode with other electrodes, attention is drawn to Figure 6.10 (C) of a galvanic cell. The two redox couples or the half-cells to make up the cell and reactions taking place at the electrodes or the electrode reactions constituting the cell are presented below:

Half-cells and electrode reactions:

Anode $H_2 \rightarrow 2\ H^+ + 2\ e^-$

Cathode $2\ Fe^{3+} + 2\ e^- \rightarrow 2\ Fe^{2+}$

The cell reaction which represents the total chemical change accompanying the operation of the cell is the sum of the two electrode reactions, the sum of the anode reaction and the cathode reaction: $H_2 + 2\,Fe^{3+} \rightarrow 2\,H^+ + 2\,Fe^{2+}$

6.4.4.2 Reference Electrodes

Measurement of single electrode potential, as has been seen, involves first assembly of a cell by coupling the given electrode with another electrode, the potential of which is either arbitrarily fixed or is exactly known. This type of electrode of standard potential with which the potentials of all other electrodes are compared, is called a reference electrode. It has been shown that by knowing the emf of the assembled cell and the electrode potential of reference electrode, how the potential of the electrode in question can easily be compared. It has also been seen that the best reference electrode used is a standard hydrogen electrode and, by convention, its potential at all temperatures is taken as zero. As some limitations of the hydrogen electrode, mention may be made of: (i) the hydrogen electrode is readily affected by compounds of Hg, As, S and oxidizing agents such as Fe^{3+}, MnO_4^-, etc., and as a result this electrode cannot be used in solutions containing these ions; (ii) it cannot be used in the presence of ions of many metals; (iii) it cannot be used in solutions containing redox systems; and (iv) it is quite cumbersome to set up the system. One, therefore, witnesses the use of various subsidiary reference electrodes. Some of the important reference electrodes other than the hydrogen electrode are the calomel electrode, glass electrode, quinhydrone electrode and silver chloride electrode. Many electrochemical and physical chemistry texts exist which embody excellent descriptions of the different electrodes, and accordingly they will not be discussed at this point.

6.4.4.3 Free Energy Changes for Cell Reactions

In order to appreciate the relationship between the free energy change of a chemical reaction and the cell emf, a reaction such as that of zinc metal with dilute sulfuric acid is considered:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

If this reaction is implemented, for instance, in a calorimeter, an amount of heat, q', will be released and an amount of work, w', will be carried out by the expansion of the hydrogen gas along with other volume changes. According to the first law of thermodynamics, the change in the internal energy of the system can be written as

$$\Delta E = E_\mathrm{f} - E_\mathrm{i} = q' - w'$$

where E_f and E_i denote the energies associated with the final and the initial states. If a galvanic cell, such as that shown schematically in Figure 6.11 is now constructed, the same net reaction can be made to occur in such a way that the electrons will be compelled to flow through an external circuit, and the resultant electrical energy can be harnessed to perform useful work. In this particular cell, one electrode is made of zinc metal and the other of an inert metallic conductor such as platinum. These are placed in solutions containing $ZnSO_4$ and H_2SO_4 and are then connected externally by means of an electrical conductor. The same basic reaction will occur as before, but now it is noted that hydrogen gas is evolved from the surface of the platinum electrode rather than from the zinc electrode. The current flow in the external circuit occurs due to the oxidation reaction:

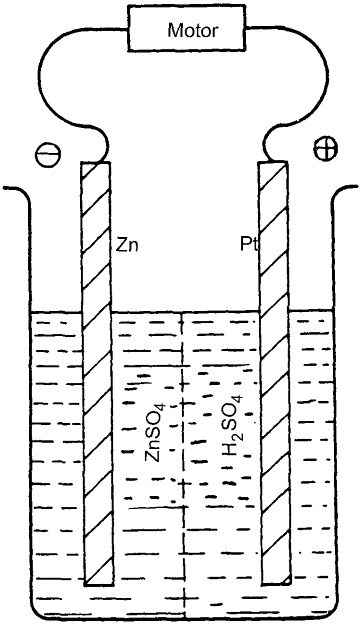

Figure 6.11 A schematic of a galvanic cell.

$$Zn = Zn^{2+} + 2\ e^-$$

which takes place at the zinc electrode–solution interface, and the reduction reaction:

$$2\ H^+ + 2\ e = H_2$$

which takes place at the platinum electrode-solution interface. The electrons released at the zinc electrode go through the external circuit to the platinum electrode where they participate in the reduction of the H^+ ions. This then, provides the total cell reaction

$$Zn + 2\ H^+ = Zn^{2+} + H_2$$

which can be considered to be made up of the two half-cell reactions. Again, it can be said that

$$\Delta E = q - w$$

but w is now made up of two parts – the work done against the atmosphere and the electrical work done in the external circuit. Consequently, ΔE can be expressed as

$$\Delta E = q - (w_e + P\,\Delta V)$$

It can be recalled from Chapter 3 that although the change in internal energy is independent of the path, the same is not true of the heat, q, and the work, w. If a large current flow is allowed, considerable heating effects will be observed as a consequence of the electrical resistance in the cell. On the other hand, if the current flow can be made imperceptibly small, the heating effect will be negligible. The great advantage of such cells in the study of free energy changes lies in the fact that they can be made to operate very nearly reversibly.

This can be accomplished by applying an electrical potential in the external circuit in such a manner that an emf occurs in opposition to that of the galvanic cell. The opposing emf is varied by means of a potentiometer until the current flow from the cell is essentially zero. Under these conditions, the cell may very well approach reversibility. This is readily tested by changing the direction of the current and allowing an infinitesimally small current flow in the opposite direction. If the cell is reversible, the cell reaction will proceed in the reverse direction with the same efficiency as in the forward direction. For a reversible reaction

$$\Delta G = -w_{\mathrm{net}} = w_{\mathrm{max}} + P\,\Delta V$$

and for the present system, w_{net} is the same as w_{e}, the electrical work carried out by the cell. Thus, it is observed that a relationship does exist between the free energy change of the system and the electrical work carried out by the reversible cell. This relationship becomes more useful when it is realized that the available electrical energy for a mole of the reactant is

$$w_{\mathrm{e}} = -n\,F\,E$$

where E is the emf of the cell, F is Faraday's constant, and n is the number of electrons changed per atom or ion. This, then, leads to the fundamental relationship

$$\Delta G = -n\,F\,E$$

and it is now seen that it is possible to relate the thermodynamic driving force of a reaction to the cell emf as well to the free energy change.

To provide a thermodynamic description of a system in which a chemical reaction is occurring it is usually not sufficient that temperature, pressure, and volume be specified. It is also required to specify the composition of the system in terms of the concentrations of the various components present. This leads to the free energy expression

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \Sigma\,\mu_{\mathrm{I}}\,\mathrm{d}n_{\mathrm{i}}$$

where S, V, T, and P have their usual significance, n_{i} is the number of moles of the *i*-th component, and μ_{i} is the chemical potential of this component and may be defined as

$$\mu_{\mathrm{i}} = \left(\frac{\delta G}{\delta n_{\mathrm{i}}}\right)_{T,P,n_{\mathrm{j}}}$$

If the conditions of constant temperature and pressure are imposed, the free energy expression will then become

$$(\mathrm{d}G)_{\mathrm{T,P}} = \mu_1\,\mathrm{d}n_1 + \mu_2\,\mathrm{d}n_2 + \mu_2\,\mathrm{d}n_2\,\ldots$$

If one considers the reaction in the galvanic cell to be

$$n_{\mathrm{a}}\,A + n_{\mathrm{b}}\,B = n_{\mathrm{c}}\,C + n_{\mathrm{d}}\,D$$

One can be more explicit and say that

$$(\mathrm{dG})_{\mathrm{T,P}} = \mu_{\mathrm{C}}\,\mathrm{d}n_{\mathrm{c}} + \mu_{\mathrm{D}}\,\mathrm{d}n_{\mathrm{d}} - \mu_{\mathrm{A}}\,\mathrm{d}n_{\mathrm{a}} - \mu_{\mathrm{B}}\,\mathrm{d}n_{\mathrm{b}}$$

which, when integrated, gives

$$\Delta G = \mu_{\mathrm{C}}\,n_{\mathrm{c}} + \mu_{\mathrm{D}}\,n_{\mathrm{d}} - \mu_{\mathrm{A}}\,n_{\mathrm{a}} - \mu_{\mathrm{B}}\,\mathrm{d}n_{\mathrm{b}}$$

assuming that the chemical potentials of the reactants and products remain constant. Now, since the chemical potential in terms of the activity is given by

$$\mu_I = \mu_0 + R\,T \ln a_i$$

it is possible to combine the above equations to give

$$\Delta G = n_c(\mu_C^0 + RT\ln a_C) + n_d(\mu_D^0 + RT\ln a_D) - n_a(\mu_A^0 + RT\ln a_A) - n_b(\mu_B^0 + RT\ln a_B)$$

or, on rearrangement

$$\Delta G = n_c\ \mu_C^0 + n_d\ \mu_D^0\ n_a\ \mu_A^0\ n_b\ \mu_B^0 + R\,T \ln \frac{(a_C)^{n_c}\ (a_D)^{n_d}}{(a_A)^{n_a}\ (a_B)^{n_b}}$$

Finally, one can say that

$$\Delta G = \Delta G^0 + R\,T \ln \frac{(a_C)^{n_c}\ (a_D)^{n_d}}{(a_A)^{n_a}\ (a_B)^{n_b}}$$

where ΔG^0 is the standard state free energy change.

The transition to the reversible emf of a galvanic cell is now quite straightforward. Combining the last equation with the equation $\Delta G = -n\ F\ E$, the Nernst equation could be obtained:

$$E = E^0 - \frac{R\,T}{n\,F} \ln \frac{(a_C)^{n_c}\ (a_D)^{n_d}}{(a_A)^{n_a}\ (a_B)^{n_b}}$$

The above important relationship now allows evaluation of the thermodynamic driving force of a redox reaction in terms of a measurable cell emf. Moreover, it is possible to utilize the relationship between the standard state potential and the standard state free energy to arrive at an expression for the equilibrium constant of a redox reaction in terms of the emf. Thus

$$E^0 = \frac{R\,T}{n\,F} \ln K$$

6.4.4.4 **Electrode Reaction Thermodynamics**

Attention is now confined to one of the electrodes of the Daniell cell, say the copper electrode. The reaction in this is:

$$Cu^{2+} + 2\ e^- = Cu$$

It represents the case of the reaction at the metal electrode in which ions of the same metal discharge at the electrode from the electrolyte. It can be said that copper ions in the electrolyte (copper sulfate solution) possess a free energy $G_{Cu(e)}$, and those in the copper metal electrode possess a free energy $G_{Cu(m)}$. Then, if a copper ion is to leave its place in the copper sulfate electrolyte structure and occupy a position in the structure of the copper electrode, the free energy change accompanying this process will be:

$$\Delta G = G_{Cu_{(m)}} - G_{Cu_{(e)}}$$

and the reaction, $Cu^{2+} + 2\ e^{-} = Cu$, could be written:

$$Cu^{2+}_{(e)} = Cu^{2+}_{(m)}$$

where $Cu^{2+}_{(e)}$ is the copper ion in the electrolyte, $Cu^{2+}_{(m)}$ the copper ion in the metallic electrode. From the Van't Hoff isotherm, the free energy change ΔG accompanying this reaction will be given by

$$\Delta G = \Delta G^{+} + R\,T \ln \frac{a_{Cu^{2+}_{(m)}}}{a_{Cu^{2+}_{(e)}}}$$

where 1 mole of ions is involved. The activity of a metal ion in a pure metal, $a_{Cu^{2+}}$ can be considered to be unity if the pure metal is in its standard state, and the activity of the metal ions in the electrolyte can be written as $a_{Cu^{2+}}$. The final equation can then be written as

$$\Delta G = \Delta G^{0} - R\,T \ln a_{Cu^{2+}}$$

and this represents the free energy change accompanying the discharge of one gram ion of the metal ion Cu^{2+} at an electrode of the metal Cu by $Cu^{2+} + 2\ e^{-} = Cu$. If $G_{Cu(e)}$ were less than $G_{Cu(m)}$, ΔG would be positive and the metal Cu would tend to go into the electrolyte as the ion Cu^{2+}.

After dealing with the thermodynamics of the reaction at the copper electrode it is relevant that the text next concentrates on the area of electrode potential, and here again, the term of reference is made to continue to rest on the copper electrode. The reaction such as ($Cu^{2+} + 2\ e^{-} = Cu$) must be associated with a driving force, depending on the value of ΔG. The measure of that driving force will provide a measure of the disposition of the Cu^{2+} ion to discharge at the copper electrode, or of the Cu^{2+} ion of the electrode to go in the electrolyte. An alternative course compromises the consideration of an electrical potential difference E between the copper ion's position in the copper sulfate solution and its position in the structure of the copper electrode. The work carried out in making an unit electrical charge through such a potential difference is equal to E units of electrical potential. This stipulation ensues from the definition. The charge bound with one gram ion Cu^{2+} is $2\ F$ coulombs, where F is the Faraday, so that if the potential difference between the electrolyte and electrode is E volts, the work carried out (w) in the supply of a charge of $2\ F$ coulombs through this potential difference is $E\ 2\ F$ joules,

$$w = E\ 2\ F$$

It is an out-and-out fact which figures prominently in classical thermodynamics that this electrical work carried out is equal, at constant pressure, to $-\Delta G$, the free energy change associated with the process

$$\Delta G = -w + P\,\Delta V$$

There is no measurable volume alteration attending this process, so that $\Delta V = 0$ and, using $w = E\ 2\ F$,

$$\Delta G = -E\ 2\ F$$

The units of the terms involved in the above relationship are ΔG in joules, while F is the Faraday (96,500 coulombs), and the number, 2, of course, represents the valency exhibited by the ion Cu^{2+} in the electrolyte. E is measured in volts and is known as the electrode potential of the electrode. Substituting for ΔG in $\Delta G = \Delta G^0 - R\,t \ln a_{Cu^{2+}}$,

$$-E\,2\,F = -E^0\,2\,F - R\,T \ln a_{Cu^{2+}}$$

or multiplying through by (–1/2 F)

$$E = E^0 + \frac{R\,T}{2\,F} \ln a_{Cu}^{2+}$$

where E^0 is termed the standard electrode potential of the electrode copper chosen in the present example. The preceding equation is known as the Nernst equation as applied to copper. In its general form, the Nernst equation for a reaction represented by

$$M^{Z+} + Z\,e^- = M$$

is as follows,

$$E = E^0 + \frac{R\,T}{z\,F} \ln a_{M^{z+}}$$

where Z is the valency exhibited by the ion M^{z+} in the electrolyte. When the ions M^{z+} are in their standard state of unit activity, $\ln a_{M^{z+}} = 0$ and E is equal to the standard electrode potential E^0. It must be borne in mind that the equations as given below:

$$\Delta G = \Delta G^0 + R\,T \ln \frac{a_{Cu^{2+}_{(m)}}}{a_{Cu^{2+}_{(e)}}}$$

$$\Delta G = \Delta G^0 - R\,T \ln a_{Cu^{2+}}$$

$$E = E^0 + \frac{R\,T}{2\,F} \ln a_{Cu}^{2+}$$

only apply to thermodynamically reversible processes. This implies that E is the reversible electrode potential, and only where the electrode is conducting thermodynamically reversibly can it appertain.

The text has so far confined attention to the electrode potential of only one metal and is henceforward extended to two electrodes. Copper continues to be one metal, and the other introduced into the consideration is zinc. If the copper and the zinc electrodes are placed in a common electrolyte holding ions of both metals, Cu^{2+} and Zn^{2+}, respectively, both electrodes will have an electrode potential, E_{Cu} and E_{Zn}, respectively.

The reversible electrode potential for Cu has been shown as:

$$E_{Cu} = E^0_{Cu} + \frac{R\,T}{2\,F} \ln a_{Cu}^{2+}$$

In similar way, the reversible electrode potential for Zn can be shown as:

$$E_{\mathrm{Zn}} = E^{0}_{\mathrm{Zn}} + \frac{R\,T}{2\,F}\ln a^{2+}_{\mathrm{Zn}}$$

These electrode potentials essentially measure the tendency of Cu and Zn ions to discharge at the electrodes respectively, and in the previous section it was seen that the more positive the electrode potential, the more negative ΔG, the free energy change accompanying the discharge process. This implies that the higher the value of E, the more the tendency for the metal ion to leave the electrolyte and discharge at the metal electrode. Thus, if $E_{\mathrm{Cu}} > E_{\mathrm{Zn}}$, metal ions Cu^{2+} will have a greater tendency to discharge at the Cu metal electrode, than Zn^{2+} ions at the Zn electrode.

In the Cu-Zn cell formed out of the two half-reactions as described, $E_{\mathrm{Cu}} > E_{\mathrm{Zn}}$, the electrode reaction at Cu will have a greater tendency to occur and this reaction will occur, as expressed previously as:

$$\mathrm{Cu}^{2+} + 2\,\mathrm{e}^{-} = \mathrm{Cu}$$

In the above process electrons will be consumed and will have to be generated by a net electron flow along the externally used connecting wire from the electrode Zn in the Cu-Zn cell. In order for electrons to be produced at the electrode Zn, the electrode reaction at Zn must be reversed:

$$\mathrm{Zn} = \mathrm{Zn}^{2+} + 2\,\mathrm{e}^{-}$$

The greater driving force ΔG_{Cu} of the reaction at Cu will therefore be driving the reaction at Zn contradictory to its intrinsic disposition, and the free energy change at Zn will be $-\Delta G_{\mathrm{Zn}}$. The sum of the reactions, $\mathrm{Cu}^{2+} + 2\,\mathrm{e}^{-} = \mathrm{Cu}$ and $\mathrm{Zn} = \mathrm{Zn}^{2+} + 2\,\mathrm{e}^{-}$; yield the overall reaction of the Cu-Zn galvanic cell. The free energy change ΔG accompanying the overall cell reaction, the redox reaction, is given by sum of the free energy of changes occurring at the Cu and Zn electrodes, and will develop an "electromotive force" (emf), E_{cell}.

$$\Delta G = \Delta G_{\mathrm{Cu}} - \Delta G_{\mathrm{Zn}}$$

and, from (the earlier expression $\Delta G = -E\,2\,F$)

$$\Delta G = -E_{\mathrm{cell}}\,2\,F$$

or

$$\Delta G_{\mathrm{Cu}} - \Delta G_{\mathrm{Zn}} = -E_{\mathrm{cell}}\,2\,F$$

or

$$-E_{\mathrm{Cu}}\,2\,F + E_{\mathrm{Zn}}\,2\,F = -E_{\mathrm{cell}}\,2\,F$$

or

$$E_{\mathrm{cell}} = E_{\mathrm{Cu}} - E_{\mathrm{Zn}}$$

Thus, through the example of the galvanic (Cu-Zn) cell, it has been shown that the emf of a cell is equal to the difference between the electrode potentials of the electrodes of which it is constructed. It may be recounted here that the thermodynamic text presented here supposes that all processes are thermodynamically reversible, so that E_{cell} is a measure of the reversible emf of the cell, and also supposes that no current flows in the circuit. It is therefore only a magnitude of the disposition of a given cell to effect an emf. In order to make the present section totally self contained, it may be repeated here that – using the definitions of anode and cathode in an earlier section – electrons are consumed at the electrode Cu, which is therefore the cathode and is positively charged, while electrons are generated at the electrode Zn, which is the anode and is negatively charged. It should be espied that the conventional current flow is in the opposite direction to the electron flow in the conductor.

6.4.4.5 **Reversible Electrodes and Cells**

If two zinc electrodes are set up in opposition to one another as in Figure 6.12 (A), the difference of potential between them, measured by a potentiometer or voltmeter, is zero. If an infinitesimally small external emf is applied to the electrodes so that A is positive and B is negative, a very small current flows round the circuit, and Zn atoms pass from A into solution as Zn^{2+} ions, and Zn^{2+} ions leave the solution and are deposited as Zn atoms on B. If the small emf is reversed so that B is positive and A is negative, the current flows in the opposite direction, and zinc is dissolved from B and deposited on A. An electrode such as the zinc electrode, which reacts thus to an infinitesimal applied emf, is known as a reversible electrode. The hydrogen electrode described earlier is a reversible electrode. If two molar hydrogen electrodes are set up in opposition to one another, Figure 6.12 (B), the

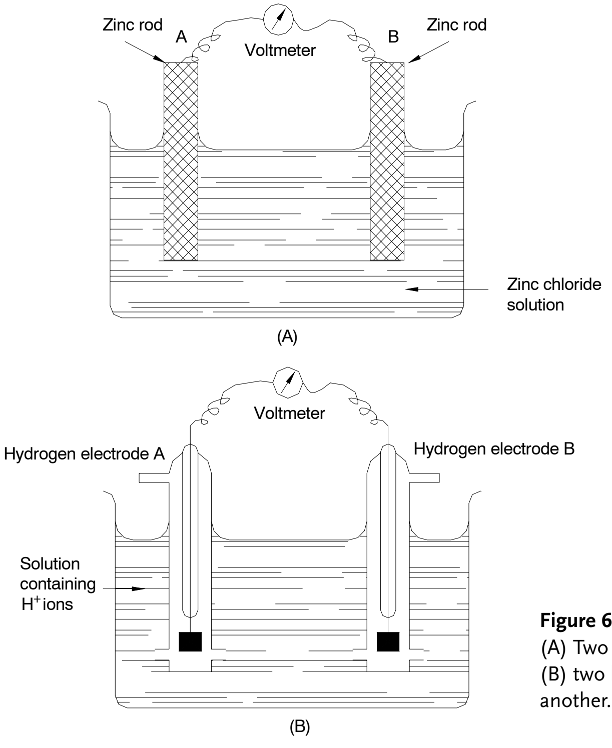

Figure 6.12
(A) Two zinc electrodes opposing one another; (B) two hydrogen electrodes opposing one another.

difference of potential between them is zero. If an infinitesimally small emf is applied to the cell so that A is positive and B is negative, hydrogen gas ionizes at A and passes into solution as H^+ ions, and H^+ ions leave the solution at B and become hydrogen gas. If the small emf is reversed, gaseous hydrogen dissolves at B and is liberated at A.

It is relevant to follow up the description given above on reversible electrodes with attention focused on the potential difference of a cell. The potential difference measured under reversible conditions, is called the electromotive force, or emf, of the cell, E. It is clear that if a cell is reversible then it is implied that the half-cells of which it is composed are also reversible.

A reversible cell must satisfy the following two conditions: (i) when an emf exactly equal to the cell emf is applied externally so as to oppose the latter, the chemical reactions occurring inside the cell stop and (ii) when the externally applied emf is decreased by an infinitesimally small amount, then a current should flow from the cell; however, when the externally applied emf is increased by an equally small amount, the same current should flow through the cell in the opposite direction and any chemical or other reaction occurring when the cell produces current should be exactly reversed. Any cell in which these two conditions are not satisfied is known as an irreversible cell. As an example, one may consider a cell comprising zinc and silver electrodes immersed in a solution of sulfuric acid. Connecting these two electrodes by a conducting wire leads to the dissolution of zinc with the evolution of hydrogen and the cell reaction is

$$\mathrm{Zn\ (s) + 2\ H^+\ (aq) \rightarrow Zn^{2+}\ (aq) + H_2\ (g)}$$

If the cell is now connected to an external opposing source whose potential is slightly greater than its own (i.e., the cell potential) silver dissolves at one electrode while hydrogen is evolved at the other electrode and the reaction becomes:

$$\mathrm{2\ Ag\ (s) + 2\ H^+\ (aq) \rightarrow 2\ Ag^+\ (aq) + H_2\ (g)}$$

It is to be noted that zinc is not deposited on the zinc electrode. In the case of this cell, the second condition of reversibility is not satisfied even though the first condition may be satisfied. The cell is, therefore, irreversible. As an additional example of cell irreversibility mention may be made of the cell having a liquid junction.

6.4.4.6 Applications of Electrochemical Series

Having introduced matters pertaining to the electrochemical series earlier, it is only relevant that an appraisal is given on some of its applications. The coverage hereunder describes different examples which include aspects of spontaneity of a galvanic cell reaction, feasibility of different species for reaction, criterion of choice of electrodes to form galvanic cells, sacrificial protection, cementation, concentration and temperature effects on emf of electrochemical cells, clues on chemical reaction, caution notes on the use of electrochemical series, and finally determination of equilibrium constants and solubility products.

The potential of a half-reaction is a measure of the disposition of that half-reaction to take place, no matter what the other half of the complete reaction is. Thus, the potential of any complete reaction can be obtained by adding potentials of its two half-reactions. The potential so obtained is a measure of disposition of the complete reaction to occur, and provides the voltage measured for a galvanic cell which was the overall reaction. For example, the entries in Table 6.11 for Ni and Ag electrodes are:

Ni^{2+} (aq) + 2 e^- → Ni (s) $E^0 = -0.25$ V

Ag^+ (aq) + e^- → Ag (s) $E^0 = +0.80$ V

one of the reactions must occur as an oxidation. Reversing the half-reaction with the more negative potential always provides a positive voltage for the cell. In the example considered, the nickel couple is reversed, with a change in sign of its standard potential:

Ni (s) → Ni^{2+} (aq) + 2 e^- $E^0 = +0.25$ V

2 Ag^+ (aq) + 2 e^- → 2 Ag (s) $E^0 = +0.80$ V

on summing up the two

Ni (s) + 2 Ag^+ (aq) → Ni^{2+} + 2 Ag (s)

and the voltage of the reaction is

$E^0_{\text{cell}} = 0.25 + 0.80 = +1.05$ V

The positive value of the standard voltage obtained in the example indicates that the cell reaction shown is spontaneous. Thus, the standard potentials in Table 6.11 can be used to predict whether a particular reaction will occur, or not. The advantage of Table 6.11 is that it provides quantitative as well as qualitative information. It not only conveys that nickel is a stronger oxidizing agent than silver (because nickel is positioned below silver in the electrochemical series), but it also conveys how much stronger, in terms of the cell emf of +1.05 V.

It will be noted that in the silver half-reaction, the coefficients have been multiplied by two in obtaining the balanced redox reaction. The reason for this may be readily understood by taking into account the half-reactions presented below:

Ag^+ + e^- → Ag (s)

2 Ag^+ + 2 e^- → 2 Ag (s)

The energy change in the second half-reaction is twice that in the first one, but the charge transferred is also doubled, from a mole of electronic charge to two moles. A voltage is the energy released per coulomb of charge transferred, so the energy change transferred is identical for both reactions. The energy change and charge transferred are both extensive properties, but the cell voltage is an intensive property. Whence two half-reactions are integrated to yield a balanced redox equation, the standard voltages are added, ignoring any constant multipliers. It must be borne in mind that this feature of additivity of voltages for half-reactions is right only in the case when the resulting equation is a balanced redox reaction.

The table of standard reduction potentials assists in the determination as to whether species can react with each other, or not. This can be substantiated by considering the reaction of hydrogen with two metals, copper and zinc. In order to determine whether or not a reaction takes place spontaneously under standard conditions, one calculates the standard potential using hydrogen ions and the metal as reactants.

2 H^+ (aq) + 2 e^- → H_2 (G); $E^0 = 0.00$ V

Cu (s) → Cu^{2+} (aq) + 2 e^-; $E^0 = -0.34$ V

Addition: 2 H^+ (aq) + Cu (s) → Cu^{2+} (aq) + H_2 (G); $E^0 = -0.34$ V

For the other metal, zinc

$2\,H^+\,(aq) + 2\,e^- \rightarrow H_2\,(G);\qquad E^0 = 0.00\ V$

$Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2\,e^-;\qquad E^0 = -0.76\ V$

Addition: $2\,H^+\,(aq) + Zn\,(s) \rightarrow Zn^{2+}\,(aq) + H_2\,(G);\ E^0 = 0.76\ V$

These calculations readily convey that zinc can be oxidized by hydrogen (generating gaseous hydrogen), and this ensues from the fact that the reaction is associated with a positive potential as written. The negative sign for the potential of the reaction between copper and hydrogen ion implies that acid is in no way in a position to dissolve copper by oxidizing it. It is therefore not a surprise that one finds water pipes usually made of copper. Any oxidation–reduction reaction for which the overall potential is positive works to occur spontaneously as conveyed. This can be decided simply from the relative placements of the two half-reactions. For example, in Table 6.11 any oxidizing agent works to react voluntarily with any reducing agent placed below it in the emf series. Thus, F_2 oxidizes Cu, H_2, Fe, and so on, but refrains from oxidizing Br, Cl^-, and so on. Similarly, Mn reduces Fe^{2+}, H^+, Cu^{2+}, and so on, but refrains from reducing Al^{3+}, Mg^{2+}, Ca^{2+}, and so on. All these may be regarded as an alternatively described concentration process that is described later in this section.

In choosing electrode metals for a galvanic cell, it must be borne in mind that the further the metals are apart in the electrochemical series, the greater is the emf of the cell. It is, however, impractical to choose metals from the opposite ends of the series to construct galvanic cells. It has been seen that most galvanic cells use zinc for the negative pole and copper or carbon for the positive pole. Obviously, carbon does not figure in the series because it does not form ions. Between any selected pair of electrodes, the one with a more negative electrode potential forms the negative pole of the cell, while the other with a less negative or positive electrode potential forms the positive pole when two are coupled together.

Sacrificial protection may be described typically through the cell of the type presented below:

$$Zn \mid Zn^{2+}(a_{Zn^{2+}} = 1) \parallel Fe^{2+} \mid (a_{Fe^{2+}} = 1) \mid Fe$$

$E^0_{Zn} = -0.76$ V, and $E^0_{Fe} = -0.44$ V. If the zinc and the iron electrodes connected by an electrical conductor are dipped into standard electrolytes in this cell, then iron would serve as the cathode ($Fe^{2+} + 2\,e^- \rightarrow Fe$) and zinc as the anode ($Zn \rightarrow Zn^{2+} + 2\,e^-$). The result would be a tendency for zinc to dissolve in the electrolyte, and this process is known as the galvanic corrosion of a less noble metal (zinc) in comparison with the more noble metal iron in this system. The reversible emf of the corrosion cell would be

$$E^0_{cell} = E^0_{Fe} - E^0_{Zn} = -0.44\ V - (-0.76)\ V = 0.32\ V$$

If zinc is replaced by tin, the corresponding cell can be represented as

$$Fe \mid Fe^{2+} \parallel Sn^{2+} \mid Sn$$

because

$$E^0_{Sn} = -0.14\ V,\quad \text{and}\quad E^0_{Fe} = -0.44\ V$$

In this case iron would serve as the anode ($Fe \rightarrow Fe^{2+} + 2\ e^-$) and tin as the cathode ($Sn^{2+} + 2\ e^- \rightarrow Sn$). In this situation, iron tends to dissolve in the electrolyte, and this process is also known as galvanic corrosion of the less noble metal (which is iron in this case) in comparison with the more noble metal (tin) in this system. The reversible emf of the corrosion cell would be:

$$E^0_{\text{cell}} = E^0_{\text{Sn}} - E^0_{\text{Fe}} = -0.14\ \text{V} - (-0.44)\ \text{V} = 0.30\ \text{V}$$

Thus, in the case of iron coated with zinc (galvanized sheet), zinc would protect iron by sacrificing itself, i.e., by anodically dissolving in the corroding media. However, in the case of iron coated with tin (tinned sheet), tin would protect iron against corrosion by virtue of its own corrosion-resistance properties; however, any flaw in the coating would enhance the corrosion of iron since it is anodically disposed to tin according to their placements in the electrochemical series.

The cell reactions shown below typically represents cementation reactions which are used to purify solutions:

$$Cu^{2+} + Ni = Ni^{2+} + Cu$$

$$Ni \mid Ni^{2+} \parallel Cu^{2+} \mid Cu; \qquad E^0_{\text{cell}} = E^0_{\text{Cu}} - E^0_{\text{Ni}} = 0.34\ \text{V} - (-0.25)\ \text{V} = 0.59\ \text{V}$$

$$Cu^{2+} + Fe = Fe^{2+} + Cu$$

$$Fe \mid Fe^{2+} \mid Cu^{2+} \parallel Cu; \qquad E^0_{\text{cell}} = E^0_{\text{Cu}} - E^0_{\text{Fe}} = 0.34\ \text{V} - (-0.44)\ \text{V} = 0.78\ \text{V}$$

$$Au^{2+} + Zn = Zn^{2+} + Au$$

$$Zn \mid Zn^{2+} \parallel Au^{2+} \mid Au; \qquad E^0_{\text{cell}} = E^0_{\text{Au}} - E^0_{\text{Zn}} = 1.35\ \text{V} - (0.76)\ \text{V} = 2.11\ \text{V}$$

$$Co^{2+} + Zn = Zn^{2+} + Co$$

$$Zn \mid Zn^{2+} \parallel Co^{2+} \mid Co; \qquad E^0_{\text{cell}} = E^0_{\text{Co}} - E^0_{\text{Zn}} = -0.28\ \text{V} - (-0.76)\ \text{V} = 0.48\ \text{V}$$

Thus nickel powder and scrap iron can be used to remove copper from aqueous solutions; likewise, zinc dust and zinc powder can be used to remove gold from aqueous cyanide solutions and the cobalt impurity present in zinc-bearing aqueous solutions. In general, each metal displaces those following it, and is displaced by those preceding it in the series. Using the same rule, it is possible to anticipate whether or not an acid will dissolve a metal. Metals preceding hydrogen in the series can liberate hydrogen from acids and form salts. On the other hand, metals coming after hydrogen will not be attacked by an acid, unless the action involves oxidation. Copper and silver are not attacked by hydrochloric acid. However, nitric acid and hot concentrated sulfuric acid will attack most of the metals, the action being one involving oxidation if the metal occupies a place below hydrogen in the series. Some more interesting consequences arising from the series may be mentioned here: (i) none of the metals (except lead and tin) preceding hydrogen occurs free in nature, while all metals coming after hydrogen, occur in the free state; (ii) the farther apart the two elements are in the series, the more likely are they to form stable compounds; and (iii) elements close to one another in the series either do not combine at all, or form unstable compounds.

The electrode potentials discussed earlier are standard potentials and, as such, describe disposition to react at fixed concentration. For precise work, it is the chemical activity rather than concentration of the species that is to be taken into account. The term, chemical activity, has no units; it is a quantity which is dimensionless and defined as the ratio of the effective concentration of a species divided by the concentration in a standard reference state. The activity for most purposes can well be represented for dissolved species by molarity, or in dilute solutions by molarity, and by atmospheres of pressures for species that are gaseous. The present intention is to determine the disposition of a reaction when concentrations are altered. Applying the Le Chatelier principle, it can qualitatively be recorded that increasing the concentration of a reactant indulges its disposition to react, while reducing the concentration of a product indulges the disposition toward production of that product. A quantitative answer of the presently laid down intention is given by Nernst equation as shown below:

$$E = E^0 - \frac{R\,T}{n\,F} \ln J$$

which, as may be recalled, relates E, the potential for a reaction under conditions which are not standard, to E^0, the standard potential for that reaction at unit concentrations with R in the relationship representing the gas constant, T the temperature, n the number of electrons transferred in the reaction, and F the Faraday. Putting in the proper constants and shifting over to base-10 logarithms, the equation at 298 K turns out to be as follows:

$$E = E^0 - \frac{0.0591}{n} \log Q$$

where Q, which is a form of description as mass expression, is constituted by multiplying together the concentration of each species on the right-hand side of the chemical equation raised to a power equivalent to the coefficient of the species in the balanced chemical equation, and dividing by the concentration of each species on the left-hand side of the equation, raised to the proper power. For the half-reaction:

$$2\,H^+ + 2\,e^- \rightarrow H_2\,(g)$$

the Nernst equation at 298 K provides:

$$E = E^0 - \frac{0.0591}{n} \log \frac{P_{H_2}}{[H^+]^2}$$

where P_{H_2} stands for the concentration or pressure of hydrogen gas and $[H^+]$ the concentration of hydrogen ion, the dissolved species in moles liter^{-1}. For the hydrogen half-reaction $E^0 = 0$, and therefore the relationship finally is:

$$E = 0.00 - 0.0296 \log \frac{P_{H_2}}{[H^+]^2}$$

At standard conditions, where $P_{H_2} = 1$ and $[H^+] = 1$ M, the term, $P_{H_2}/[H^+]^2$ is equal to 1 (which implies its logarithm is 0), and the end result is $E = 0.00$ V. As a subsequent example, in pure water the hydrogen ion concentration is $1.0 \cdot 10^{-7}$ M. Substituting $P_{H_2} = 1$ and $[H^+] = 1.0 \cdot 10^{-7}$, one obtains the following:

$$E = 0.00 - 0.0296 \log \frac{1.0}{(1.0 \cdot 10^{-7})^2} = -0.41 \text{ V}$$

The circumstance that this potential is less than zero discerns that the half-reaction, $2\,H^+ + 2\,e^- \rightarrow H_2$ (g) has less disposition to more to the right in pure water than in 1 M acid.

Taking another example to illustrate the dependency of emf on concentration (temperature effect is not considered, as in the previous example), reference may be drawn to the familiar Cu-Zn cell a shown in standard notation as:

$$\text{Zn (s)} \mid \text{Zn}^{2+} \text{(aq)} \mid \text{Cu}^{2+} \text{(aq)} \mid \text{Cu (s)}$$

The electrode potential of the right half-cell is

$$E_{\text{right}} = E^0_{\text{right}} + \frac{R\,T}{2\,F} \ln\,[\text{Cu}^{2+}\text{ (aq)}]$$

Similarly, the electrode potential of the left half-cell can be written. The cell emf E can be written as

$$\begin{aligned} E &= E_{\text{right}} - E_{\text{left}} \\ &= E^0_{\text{right}} + \frac{R\,T}{2\,F} \ln\,[\text{Cu}^{2+}\text{ (aq)}] - E^0_{\text{left}} - \frac{R\,T}{2\,F} \ln\,[\text{Zn}^{2+}\text{ (aq)}] \\ &= E^0_{\text{right}} - E^0_{\text{left}} + \frac{R\,T}{2\,F} \ln \frac{[\text{Cu}^{2+}\text{ (aq)}]}{[\text{Zn}^{2+}\text{ (aq)}]} \end{aligned}$$

Consequent to substitution of the value of the standard electrode potentials as obtained from entries in Table 6.11 and conversion of natural logarithm to the base 10 logarithm, the following relationship is obtained:

$$\begin{aligned} E \text{ (in volts)} &= 1.1 + \frac{2.303\,R\,T}{2\,F} \log \frac{[\text{Cu}^{2+}\text{ (aq)}]}{[\text{Zn}^{2+}\text{ (aq)}]} \\ &= 1.1 + \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}\text{ (aq)}]}{[\text{Zn}^{2+}\text{ (aq)}]} \end{aligned}$$

Here, $[\text{Cu}^{2+}\text{ (aq)}] = 0.05$ M and $[\text{Zn}^{2+}\text{ (aq)}] = 0.5$ M

at 298 K (with values substituted for R, T, and F). The concentration of copper sulfate is considered to be 0.05 M, and that of zinc sulfate to be 0.5 M at 298 K. The emf of the cell can be calculated by substituting the values of R, T, n, F and the concentrations of Cu^{2+} and Zn^{2+} ions in the above equation.

Therefore, $E = 1.1 + \frac{0.059}{2} \log \frac{0.05}{0.5} = 1.1 + \frac{0.059}{2} \log \frac{1}{10} = 1.07$ V

The electrochemical series table provides important clues as regards the chemical reaction. The evolution of hydrogen by the reaction of zinc and dilute sulfuric acid is facilitated by the impurity of copper or graphite in zinc. Copper and zinc form a local electrochemical cell in which copper helps in converting H^+ ions to hydrogen gas, leaving the zinc surface free for action on solution.

$$Zn \rightarrow Zn^{2+} + 2\,e^-$$

$$Cu + 2\,e^- + 2\,H^+ \rightarrow Cu + H_2\uparrow$$

Decreasing the concentration of the metallic ions or of hydrogen ions in solution makes the electrode potential of the corresponding metals more negative. For this reason, it is possible to plate nickel from a weak acid solution, for the relatively high nickel ion concentration makes the potential of nickel more positive than that of hydrogen ions in the dilute acid solution and nickel plating will occur unless an excessively high current density is used by applying too high a voltage. By using complex ions in cyanide solutions in silver and gold plating it is possible to make the concentration of silver ions so low that the potential becomes more negative and thus approaches that of iron, thereby greatly reducing the difficulty due to deposition by immersion.

The principle of the displacement of one metal by another, or in other words of the displacement of nobler by base or not so noble metals, as described earlier, must be applied with due caution, without neglecting other effects that may not be immediately obvious from consideration of the electrochemical series. Some of these effects are illustrated in the following. Although the position of lithium is above that of sodium in the series, lithium cannot displace sodium from common salt solutions since both of these metals occupy positions higher up than hydrogen and will displace this element from the solution. It must be borne in mind, therefore, that the series applies to aqueous solutions, and the hydrogen ion, which is present in these solutions, can also take part in the displacement reactions.

The electrochemical series corresponds only to the standard condition, i.e., for unit activity of the ions, since a change to another ionic concentration can alter the order of the electrode potentials of the elements very markedly. The case of nickel plating mentioned earlier may be taken as typically illustrative of the many practical examples of the effects and the consequences of nonstandard conditions. It must also be mentioned in the context of the examples of displacement reactions provided earlier that the concentrations and the electrode potentials frequently vary during a displacement reaction.

The potentials pertinent to the series correspond to a temperature of 25 °C. In many cases, ion displacement equilibria lie so far towards one side of the equation that no significant change in the position of the equilibrium arises because of the altered potential conditions at temperature other than 25 °C.

Considerable practical importance attaches to the fact that the data in Table 6.11 refer to electrode potentials which are thermodynamically reversible. There are electrode processes which are highly irreversible so that the order of ionic displacement indicated by the electromotive series becomes distorted. One condition under which this situation arises is when the dissolving metal passes into the solution as a complex anion, which dissociates to a very small extent and maintains a very low concentration of metallic cations in the solution. This mechanism explains why copper metal dissolves in potassium cyanide solution with the evolution of hydrogen. The copper in the solution is present almost entirely as cuprocyanide anions $[Cu(CN)_4]^{3-}$, the dissociation of which by the process

$$[\mathrm{Cu(CN)_4}]^{3-} \rightleftharpoons \mathrm{Cu} + 4\ \mathrm{CN^-}$$

is very small.

The data of Table 6.11 create a wealth of information on the free energies of inorganic reactions. Although reported as emfs, these data are readily transformed into free energies by the expression $\Delta G^0 = -n\ F\ E^0$. Such free-energy data are of considerable utility in determining equilibrium properties and, in particular, the equilibrium constant for the overall cell reaction. The possibility of the reduction of ferric ion to ferrous ion by zinc as a reductant is considered as an example. The reaction in which one would be interested might be executed in the cell

$$\mathrm{Zn}\ |\ \mathrm{Zn^{2+}}\ ||\ \mathrm{Fe^{3+}},\ \mathrm{Fe^{2+}}\ |\ \mathrm{Pt}$$

and the electrode reactions and the emfs are:

$$\mathrm{Fe^{3+}} + \mathrm{e^-} \rightleftharpoons \mathrm{Fe^{2+}}; \qquad E^0_{\mathrm{Fe^{2+}|Fe^{3+}}} = 0.77$$

$$0.5\ \mathrm{Zn} \rightleftharpoons 0.5\ \mathrm{Zn^{2+}} + \mathrm{e^-}; \qquad -E^0_{\mathrm{Zn|Zn^{2+}}} = 0.76$$

On summation of the two shown above:

$$\mathrm{Fe^{3+}} + 0.5\ \mathrm{Zn} \rightleftharpoons \mathrm{Fe^{2+}} + 0.5\ \mathrm{Zn^{2+}}; \quad E^0 = +1.53\ \mathrm{V}$$

The cell emf is expressed as:

$$E = 1.534 - \frac{0.05915}{1} \log \frac{a_{\mathrm{Fe^{2+}}} (a_{\mathrm{Zn^{+}}})^{0.5}}{a_{\mathrm{Fe^{3+}}}}$$

At equilibrium, the cell would be able to do no useful work, and its emf must then be zero. For equilibrium activities of the variable reagents of the summed up equation shown ($\mathrm{Fe^{3+}}$ + 0.5 Zn), one therefore has $E = \mathrm{O}$ and

$$1.534 = \frac{0.05915}{1} \log \left[\frac{(a_{\mathrm{Fe^{2+}}})\,(a_{\mathrm{Zn^{2+}}})^{0.5}}{(a_{\mathrm{Fe^{3+}}})} \right]_{\mathrm{equil}}$$

or

$$\left[\frac{(a_{\mathrm{Fe^{2+}}})\,(a_{\mathrm{Zn^{2+}}})^{0.5}}{(a_{\mathrm{Fe^{3+}}})} \right]_{\mathrm{equil}} = K = 8 \cdot 10^{25}$$

The result displays that basically all the iron will be reduced to the ferrous state by zinc.

There are some illustrations of cells wherein the overall reaction corresponds to the solution of an insoluble salt. In such cases the equilibrium constant that can be demarcated is a solubility product. This can be shown by the cell:

$$\mathrm{Ag}\ |\ \mathrm{Ag^+}\ |\ \mathrm{Br^-}\ |\ \mathrm{AgBr\ (s)}\ |\ \mathrm{Ag}$$

The electrode reactions and the emfs are:

$$\mathrm{AgBr\ (s) + e^- \rightleftharpoons Ag + Br^-}; \qquad E^0_{\mathrm{Ag|AgBr|Br^-}} = +0.07$$

$$\mathrm{Ag \rightleftharpoons Ag^+ + e^-}; \qquad -E^0_{\mathrm{Ag|Ag^+}} = -0.80$$

On summing up the two shown above:

$$\mathrm{AgBr\ (s) \rightleftharpoons Ag^+ + Br^-}; \qquad E^0 = -0.73$$

The cell emf is expressed as:

$$E = -0.73 - \frac{0.05915}{1} \log (a_{\mathrm{Ag^+}})(a_{\mathrm{Br^-}})$$

The solubility of silver bromide is very low, and if no other ions are present in discernible amounts, the activity coefficients will be adequately close to unity to permit the activities to be displaced by concentrations. Again, at equilibrium the emf of the cell will be zero and

$$0.73 = -0.05915 \log ([\mathrm{Ag^+}]\,[\mathrm{Br^-}])_{\mathrm{equil}}$$

or

$$([\mathrm{Ag^+}][\mathrm{Br^-}])_{\mathrm{equil}} = 4.8 \cdot 10^{-13}$$

The foregoing two examples have been taken to convey that the data of Table 6.11 can very well be used to determine the equilibrium constant for any reaction which is the overall reaction for a cell assembled with electrodes contained in the electrochemical series table.

6.4.5
Cell Types

There have principally been two main pathways by which cells have been described. One description begins from the very basic elements relating to the fact that when two suitable half-cells are combined, an electrochemical cell results. The combination is built by bringing the solutions in the half-cells into communication, so that ions can pass between them. If these two solutions are similar, no liquid junction is present, and one has a cell with an absence of transference (Figure 6.6). If the solutions are dissimilar, the transport of ions across the junction will bring about irreversible changes in the two cells, and one has a cell with presence of transference.

The decrease in free energy (–$-\Delta G$) which provides the driving force in a cell may ensue either from a chemical reaction or from a physical change. In particular, one often studies cells in which the driving force is a change in concentration (almost always a dilution process). These cells are called concentration cells. The alteration in concentration can take place either in the electrolyte or in the electrodes. As examples of alterations in concentration in electrodes, mention may be made of amalgams or alloy electrodes with different concentrations of the solute metal and in gas electrodes with different pressures of the gas.

In addition to the above, cells are also described from the point of view of their operational aspects. This factor points towards cells being grouped into two categories: primary and secondary. In primary cells, chemical energy is converted into electrical energy with a reduction in the free energy of the system. It is desirable that this loss in free energy manifests itself entirely as electrical energy outside the cell, but this ideal is never attained in practice because the internal resistance of a cell is not zero and the reactions occurring within the cell are never completely reversible. Primary cells, while in the process of converting chemical energy into electrical energy, are said to be discharging. This process (i.e., discharging) can occur only once and the original chemical state of the cell cannot be regained by passing electricity back through the cell from an external source. This means that primary cells cannot be charged electrically, and once discharged, have no further electrical use. The most common type of primary cell is the Leclanche dry cell, often called the "dry cell" or "battery". Secondary cells or accumulators (the name by which they are often known) are similar to the primary cells, except that such systems can be reversed, and the products of the electrochemical reactions can be reconverted into the reactants by feeding back through the cell an amount of electricity at least equal to that taken out during the period the cell has discharged. The chemical reaction taking place in a secondary cell can thus be reversed any desired number of times, and the same materials can be used for storing or delivering electrical energy over and over again. The products of electrolysis remain on the electrodes in this case. Although galvanic cells of the Daniell cell type are reversible, they cannot be used for prolonged periods of time as accumulators because the two electrolytes, which are usually separated by a diaphragm, tend to mix and thus promote self discharge. It may thus generally be stated that, in principle, all electrode reactions are reversible. In most practical cases secondary reactions and, or, physical changes occur when a current is withdrawn from a cell, so that the passage of a reverse current does not restore the cell fully to its original state. The primary cell, the Leclanche cell, and the secondary cell, the lead-acid accumulator, are recognized as the classical prototype electricity stores in the field of electrochemical science and technology. The lead-acid accumulator is one of the most well-known secondary cells.

The list of different types of cells must include fuel cells; these have a commercial identity and their general principles will be described later.

One is by now familiar with the equation that expresses the reversible potential of an electrode as a function of the activities of participants in the electrode reaction. If the activities of resultants (or products) of the electrode reaction are standardized and taken arbitrarily to be unity, this equation or expression takes the form of one in which the electrode potential is a function of the activity of one type of ion only. It should clearly be possible to construct two similar electrodes to take up reversible potentials corresponding to different activities of this one type of ion, and emf of the cell formed by the combination of such a pair of electrodes should, therefore, take up a potential determined by both the activities concerned. Cells of this type, in which the reversible emf is a function of the different activities of one participant in the electrode reaction, are termed concentration cells.

Concentration cells may be classified into two main groups: (i) electrode-concentration cells and (ii) electrolyte-concentration cells. Of the two, those belonging to the second category are by far the most important.

Electrode-concentration is based on dilution of the electrode material itself. For the electrode material to be engaged in such a process, it must have a changeable concentration. Amalgams or alloy electrodes with different concentrations of solute metal, and gas electrodes with different pressures of gas belong to this classification. The given description of electrode-concentration cells may be conveyed by the following cell notation:

$\mathrm{Zn}\ (a_1)\ |\ \mathrm{Zn}^{2+}\ (c_1)\ |\ \mathrm{Zn}^{2+}\ (c_1)\ \mathrm{Zn}\ (a_2)$

To describe a specific example of electrode-concentration cells, it is possible to consider two zinc amalgams at different concentrations, dipped into a solution containing zinc ions:

$(\mathrm{Hg})\ \mathrm{Zn}\ (a_{\mathrm{Zn}} = a_1)\ |\ \mathrm{Zn}^{2+}\ (c_1)\ |\ \mathrm{Zn}^{2+}\ (c_1)\ |\ (\mathrm{Hg})\ \mathrm{Zn}\ (a_{\mathrm{Zn}} = a_2)$

The electrode reactions are:

$\mathrm{Zn}^{2+} + 2\ \mathrm{e}^- \rightleftharpoons \mathrm{Zn}\ (a_2);\quad \mathrm{Zn}\ (a_1) \rightleftharpoons \mathrm{Zn}^{2+} + 2\ \mathrm{e}^-$

The cell reaction is obtained by adding the electrode reactions shown above:

$\mathrm{Zn}\ (a_1) \rightleftharpoons \mathrm{Zn}\ (a_2)$

No chemical change takes place, and the reaction comprises the transfer of zinc from an amalgam of one concentration to that of another concentration. The emf of such a cell, which necessarily possesses $E^0 = 0$, is:

$$E = -\frac{R\,T}{2\,F} \ln \frac{a_1}{a_2}$$

Assuming the concentrations of zinc in the amalgam to be very small and the solution fairly ideal, the activity terms in the above equation can be replaced by concentration terms, and the final relationship can be expressed as:

$$E = -\frac{R\,T}{2\,F} \ln \frac{c_1}{c_2}$$

The zinc will be inclined to depart spontaneously from the high-activity amalgam to that with a corresponding low activity. For example, if c_1, is greater than c_2, E is positive and the reaction advances in the direction specified. It may be added that metals in mercury constitute fairly ideal solutions, and that the emfs are almost correctly calculated by using concentrations instead of activities.

As has been pointed out, another interesting type of electrode-concentration cell is that comprising two hydrogen electrodes working at different pressures and remaining immersed in a solution of hydrochloric acid. The cell may be represented as:

$\mathrm{Pt}\ |\ \mathrm{H}_2\ (p_1)\ |\ \mathrm{HCl}\ (c)\ |\ \mathrm{H}_2\ (p_2)\ |\ \mathrm{Pt}$

At the left electrode: $0.5\ \mathrm{H}_2\ (p_1) \rightarrow \mathrm{H}^+\ (a_{\mathrm{H}^+}) + \mathrm{e}^-$

At the right electrode: $\mathrm{H}^+\ (a_{\mathrm{H}^+}) + \mathrm{e}^- \rightarrow 0.5\ \mathrm{H}_2\ (p_2)$

The overall change is accordingly $0.5\ \mathrm{H}_2\ (p_1) \rightarrow 0.5\ \mathrm{H}_2\ (p_2)$, the moving over of one equivalent of hydrogen from pressure p_1 to p_2. The emf corresponding to the overall cell reaction can be written as:

$$E = -\frac{R\,T}{2\,F} \ln \frac{p_2}{p_1}$$

Electrolyte-concentration cells are based on electrolyte dilution, and have two identical electrodes that are immersed in two solutions of the same electrolyte containing ions of the electrode material at two different activities. Electrolyte concentration cells are classified as: (i) cells without liquid junctions and (ii) cells with liquid junctions.

Present attention is first focused on the electrolyte concentration cells without liquid junctions. Such cells can be explained with two cells of the type

$\mathrm{Pt} \mid \mathrm{H_2} \mid \mathrm{HCl}\ (c) \mid \mathrm{AgCl\ (s)} \mid \mathrm{Ag}$

each of which has a working reaction:

$0.5\ \mathrm{H_2} + \mathrm{AgCl} \rightarrow \mathrm{Ag} + \mathrm{H^+}\ (c) + \mathrm{Cl^-}\ (c)$

If two such cells electrically joined through their silver electrodes are treated in the countered mode,

$\mathrm{Pt} \mid \mathrm{H_2} \mid \mathrm{HCl}\ (c_1) \mid \mathrm{AgCl} \mid \mathrm{Ag{-}Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}\ (c_2) \mid \mathrm{H_2} \mid \mathrm{Pt}$

The total reaction is now the summation of the two simple cell reactions. Provided that the pressure of hydrogen is the same for both terminal electrodes, the electrode reactions can be integrated to contribute:

Right cell: $\mathrm{Ag} + \mathrm{H^+}\ (c_2) + \mathrm{Cl^-}\ (c_2) \rightleftharpoons 0.5\ \mathrm{H_2} + \mathrm{AgCl}$

Left cell: $0.5\ \mathrm{H_2} + \mathrm{AgCl} \rightleftharpoons \mathrm{Ag} + \mathrm{H^+}\ (c_1) + \mathrm{Cl^-}\ (c_1)$

Total reaction: $\mathrm{H^+}\ (c_2) + \mathrm{Cl^-}\ (c_2) \rightleftharpoons \mathrm{H^+}\ (c_1) + \mathrm{Cl^-}\ (c_1)$

The total reaction therefore contains no chemical change and comprises only the transfer of HCl from a concentration c_2 to a concentration c_1. The emf of the entire cell is conveyed as:

$$\begin{aligned} E &= -\frac{0.059}{1} \log \frac{(a_{\mathrm{H^+}})_1\,(a_{\mathrm{Cl^-}})_1}{(a_{\mathrm{H^+}})_2\,(a_{\mathrm{Cl^-}})_2} \\ &= -0.118 \log \frac{[a_\pm]_1}{[a_\pm]_2} \end{aligned}$$

It is observed that the spontaneous process takes HCl from a greater activity (or concentration) to a lesser activity (or concentration). If, for instance, c_2 is greater than c_1 and therefore $(a_\pm)_2$ is greater than $(a_\pm)_1$, the emf will be positive and the reaction will advance in the direction in which it is expressed. One can apply such concentration cells to ascertain the activity of an electrolyte at one concentration, or in a solution having other ions compared with the activity of an electrolyte in another solution.

The next focus is on the electrolyte-concentration cells with a liquid junction. The dilution of HCl, which was the subject of the discussion above, can also be realized in a cell with a liquid junction, as shown in Figure 6.13. It is presupposed that the two HCl solutions of different concentration can be brought together and averted from mixing. The flowing of two streams of solution synchronously sometimes attains this. One then can establish the cell:

$\mathrm{Pt} \mid \mathrm{H_2} \mid \mathrm{HCl}\ (c_1) \mid \mathrm{HCl}\ (c_2) \mid \mathrm{H_2} \mid \mathrm{Pt}$

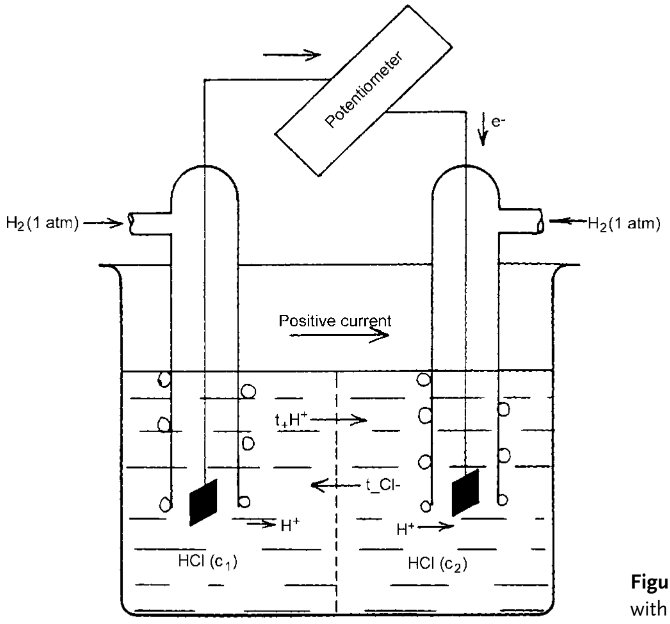

Figure 6.13 An electrochemical cell with a liquid junction.

The emf of the cell can be related to the total reaction that takes place when 1 Faraday of current flows. The reactions which take place at the electrodes and those which take place at the liquid junction can be expressed separately. The electrode reactions are:

Reaction at right electrode: $H^+ (c_2) + e^- \rightarrow 0.5\ H_2$
Reaction at left electrode: $0.5\ H_2 \rightarrow H^+ (c_1) + e^-$
Total reaction: $H^+ (c_2) \rightarrow H^+ (c_1)$

The junction reaction is better understood by reference to Figure 6.13. As the current flows according to the set convention, 1 Faraday of positive charge must transmit through the cell and therefore across the junction. The portion of current carried by the ions is written in terms of their transference numbers, and t_+ equiv. of H^+ goes to the right whereas t_- equiv. of Cl^- goes to the left. The junction reactions are therefore as follows:

$t_+\ H^+ (c_1) \rightarrow t_+\ H^+ (c_2)$ or $(1 - t_-)\ H^+ (c_1) \rightarrow (1 - t_-)\ H^+ (c_2)$
and
$t_-\ Cl^- (c_2) \rightarrow t_-\ Cl^- (c_1)$

The electrode reaction and the junction reactions are now integrated to provide the total cell reaction as represented below:

Electrode reaction: $H^+ (c_2) \rightarrow H^+ (c_1)$

Junction reactions: $H^+ (c1) - t\!-\ H^+ (c1) \rightarrow H+ (c2) - t\!-\ H^+ (c2)$
$t\!-\ Cl^- (c2) \rightarrow t\!-\ Cl^- (c1)$

Total cell reaction: $t_-\ [H^+ (c_2) + Cl^- (c_2)] \rightarrow t_-\ [H^+ (c_1) + Cl^- (c_1)]$

The emf of this cell, which possesses $E^0 = 0$, can now be expressed as:

$$E = -\frac{0.059}{1}\log\frac{[(a_{\mathrm{H^+}})_1\,(a_{\mathrm{Cl^-}})_1]^{t_-}}{[(a_{\mathrm{H^+}})_2\,(a_{\mathrm{Cl^-}})_2]^{t_-}}$$

$$= 0.118\,t_-\,\log\frac{[a_\pm]_1}{[a_\pm]_2}$$

The emf of the cell, contrary to that in the absence of a liquid junction, depends on the transference numbers. Such cells are usually identified as concentration cells with presence of transference, the second one in the electrolyte concentration cell classification list. This system, as has been seen, contains a liquid junction across which it is possible for direct transport of ions to occur.

In addition to the various types of concentration cells described above there is one form of the concentration cell which has certain important applications in metallurgy; this is the oxygen concentration cell. The cell is represented schematically as:

Pt, O_2 (g, at pressure p_1) | $CaO - ZrO_2$ or $Y_2O_3 - ThO_2$ | O_2 (g, at pressure p_2), Pt

Over wide ranges of temperature and oxygen pressure, calcia-stabilized zirconia (i.e., zirconia in the fluorite structure stabilized by forming a solid solution with (5 to 10% calcia)) conducts exclusively by O^{2-} ion migration and the conductivity is usually high. As Ca^{2+} replaces Zr^{4+} in the cation lattice there will be corresponding vacancies in the anion lattice through which the O^{2-} anions may easily move. Thus ZrO_2 plus CaO acts as an oxygen conductor. A similar behavior is observed in the case of thoria, stabilized in the fluorite structure by the addition of yttria. Both of these solid solutions have been used as electrolytes in oxygen concentration cells. The cell reaction is:

O_2 (g, at pressure p_1) $\rightarrow$ O_2 (g, at pressure p_2)

and the cell emf, E, is given by

$$E = -\frac{\Delta G}{4\,F} = -\left(\frac{R\,T}{4\,F}\right)\ln\frac{p_2}{p_1}$$

At a given temperature, the cell emf, E, is related to the oxygen pressures, p_1 and p_2, at the electrodes and a knowledge of any two of these three quantities (E, p_1 and p_2) is sufficient to evaluate the third. For example, by fixing the oxygen pressure, p_1, by using an equilibrated mixture of a suitable metal and its oxide, and by measuring the emf, E, the oxygen pressure at the other electrode, p_2, may be determined. This facility has many consequences: in fundamental studies as well as in practical applications.

As regards fundamental studies, the measurement of equilibrium oxygen pressures can lead to the determination of the free energy of a compound or the activity of a component in an alloy. Examples of practical applications include the measurement of oxygen potentials of mattes in flash smelting furnaces; of oxygen partial pressures in process gases; and of oxygen potentials in steel baths to monitor changes in oxygen activity and thus effect process control in the course of smelting, tapping, refining, and casting.

In addition to the oxygen ion conducting solid electrolytes mentioned above, there are solid electrolytes such as fluorite (CaF_2) which conduct F^- ions, the so-called β-alumina (which is actually a sodium aluminate with the approximate composition: ($Na_2O \cdot 10\ Al_2O_3$) which has a high conductivity for alkali ions, Na^+ ions, for example, and glasses containing potassium or silver which exhibit high conductivities for iron and silver ions, respectively. These solid electrolytes also have applications similar to those described for calcia-stabilized zirconia.

Apart from use in metallurgical research and measurements, solid electrolytes have also been put to use as heating elements in electrical resistance furnaces. In order to prevent electrolysis from occurring, alternating currents must be used. In contrast to metallic heating elements, they may be used in air at around 2000 °C. In view of the fact that their conductivity must be very low at room temperature, there is a need for them either to be kept continuously warm, or to be preheated with an auxiliary heating element.

6.4.5.1 **Commercial Galvanic Cells**

Very few of the cells formed by pairing the electrodes in Table 6.11 may be used for everyday sources of electric current. The simple reason for this deficiency is that most such cells can only supply a very small current per unit area of the electrode and so must be very large in order for them to be useful. A less serious difficulty is that they all involve solutions, many of which are not benevolent and which must be contained in a sturdy, splash-proof container. Neither of these two problem areas are confronted in commercial galvanic cells which are designed to deliver large currents, at steady voltages, at least for a brief period. These cells are called batteries and, as pointed out earlier, they are classified into primary (nonchargeable) cells and secondary (storage, or rechargeable) cells. The subject of fuel cells is discussed in a later section of this chapter.

6.4.5.1.1 **Primary Cells**

The Leclanché cell is a leading example of primary cells. The functioning of the cell and its various modifications or variations can be appreciated by having a general awareness as to the basic requirements of a primary cell. These are: (i) an anode of a relatively basic metal which is reasonably stable in moist air and exhibits no tendency toward or can be prevented from passivation in the cell; (ii) an aqueous, highly conducting electrolyte which does not spontaneously dissolve the metal of the anode at any significant rate with the cell on open circuit; and (iii) a relatively noble cathode. There is another constituent of the cell known as a cathodic depolarizer. The cathodic reaction in a primary cell may be regarded essentially as the discharge of hydrogen from a water molecule in a nearly neutral or alkaline solution. The hydrogen evolution reaction is usually highly irreversible and is associated with a considerable activation overpotential. The hydrogen discharge reaction is facilitated by making available at the cathode a readily reproducible material to remove the adsorbed hydrogen atoms. The type of depolarizer commonly used is a metallic oxide; hence, the steps in the cathodic reaction of most primary cells may be expressed as:

$$M + H_2O + e^- = MH + OH^-$$

$$2\,MH + O \rightarrow H_2O + 2\,M$$

where M is the cathode metal; the oxygen atom is usually derived from a metallic oxide, which is reduced to a lower oxide or to its parent metal as a result of the reaction.

The Leclanché cell (also known as the dry cell) is frequently used to power flashlights, watches, calculators, and a number of other portable devices. Despite the name dry cell, this battery does contain an electrolyte solution but only in the form of dense paste. There are two versions of this cell, the acid version and the alkaline version.

The acid version of the cell was patented in 1866 by the French chemist George Leclanché, and is shown schematically in Figure 6.14 (A). The cell, in shorthand notation, corresponds to:

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+}, \mathrm{NH_4}^{+} \mid \mathrm{MnO_2}\ (aq), \mathrm{C}$$

The reaction at the negative pole (in this case the anode) is the formation of Zn^{2+} ions ($Zn - 2\,e^{-} \rightarrow Zn^{2+}$) which pass into the solution and combine with chloride ions to form zinc chloride. The reaction at the positive pole (in this case the cathode) is the discharge of the incoming ammonium ions. After discharge, they break up into ammonia and hydrogen, the former remaining dissolved while the latter is oxidized to water by the manganese dioxide present. The overall chemical reaction taking place in the cell is represented as

$$\mathrm{Zn} + 2\,\mathrm{NH_4Cl} = \mathrm{ZnCl_2} + 2\,\mathrm{NH_3} + \mathrm{H_2}$$

The oxidation of hydrogen by manganese dioxide takes place according to the reaction:

$$\mathrm{H_2} + 2\mathrm{MnO_2} = \mathrm{Mn_2O_3} + \mathrm{H_2O}$$

The reactions described above indicate that when a current is drawn from the cell, the zinc rod is used up and the manganese dioxide is reduced. The reduced oxide is, however,

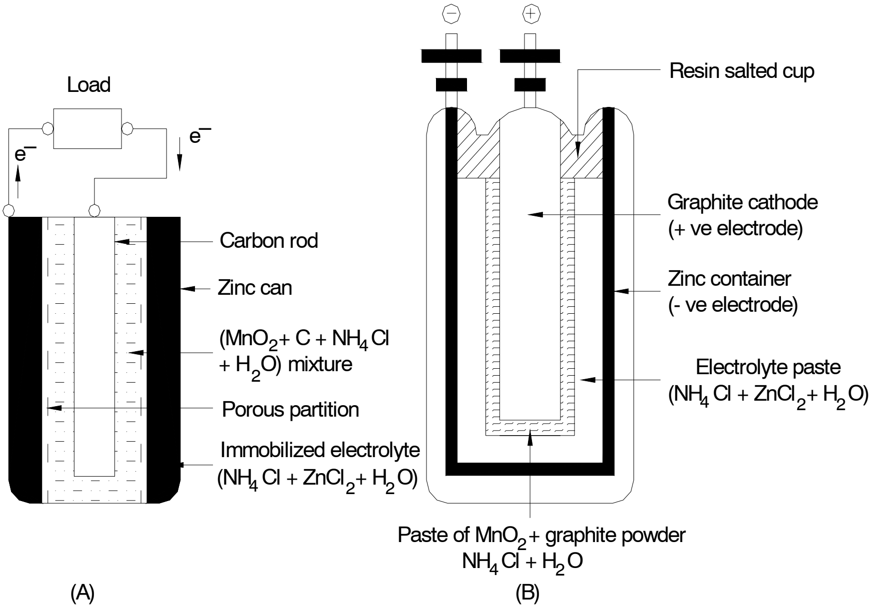

Figure 6.14 Schematics of (A) Leclanché cell and (B) dry cell.

slowly oxidized back to the dioxide by atmospheric oxygen ($2\ Mn_2O_3 + O_2 = 4\ MnO_2$). The cell is suited chiefly for intermittent service.

The most important form of development based on the Leclanché cell is the so-called dry cell, the manufacture of which for use in portable radio sets, pocket torches, and for similar purposes has become an important industry. A schematic of the cell is shown in Figure 6.14 (B). It consists of a zinc sheet container which acts as the negative electrode and furnishes zinc ions to the semi-solid electrolyte which fills the cell. A carbon (graphite) rod placed at the center of the cell with its axis parallel to the length of the cell serves as the positive electrode. It acts as an inert electrode and is surrounded by a paste consisting of MnO_2 and powered graphite. The cell is filled with the electrolyte which is a paste of NH_4Cl and $ZnCl_2$ prepared in water. The term "dry" in the nomenclature of the cell is a "misnomer", since moisture is indispensable to the operation of the cell. Water is present in the paste and there is no free liquid as such. On this account, it is called a dry cell. The reaction occurring at the zinc electrode (i.e., negative electrode) is: $Zn \rightarrow Zn^{2+} + 2\ e^-$, while that taking place at the carbon electrode (i.e., positive electrode) is: $2\ MnO_2 + 2\ NH_4^+ + 2\ e^- \rightarrow Mn_2O_3 + H_2O + 2\ NH_3$ (aq). Oxidation of zinc takes place at the negative electrode and reduction of MnO_2 to Mn_2O_3 occurs at the positive electrode (in MnO_2, the oxidation state of Mn is +4 and in Mn_2O_3 it is +3 and hence, reduction). The overall reaction is:

$$Zn + 2\ MnO_2 + 2\ NH_4^+ \rightarrow Zn^{2+} + Mn_2O_3 + H_2O + 2\ NH_3$$

The resulting water helps to extend the life of the dry cell by providing moisture for the movement of the ionic species. A second reaction, that extends the usefulness of this cell, is the formation of an amine complex of zinc ions in the cell:

$$Zn^{2+} + 4\ NH_3 \rightarrow [Zn(NH_3)_4]^{2+}$$

This shifts the equilibrium at the zinc electrode to the right and reduces the concentration of Zn^{2+} ions. Dry cells are designed for intermittent service only to avoid accumulation of H_2 gas at the positive electrode and polarization. The cell is covered and sealed at the top by wax or resin, which prevents moisture or paste from coming out. The use of manganese in excessive amounts leads to an excessive rise in cell resistance, while the use of carbon in large amounts dilutes the depolarizer and reduces cell performance. The addition of zinc chloride to ammonium chloride in the electrolyte has several purposes and effects. The chemical is hygroscopic and undergoes some hydrolysis in aqueous solution; its presence permits the moist electrolyte to dry only slowly, and the slight acidity it imparts to the electrolyte helps in maintaining the cell voltage. The ammonia produced during the cell reactions is absorbed by zinc chloride, and excessive gas production is thereby prevented. Among the disadvantages of using chloride mention may be made that it causes the viscosity of the electrolyte to increase and its thermal conductivity to decrease. Therefore, excessive use of this chemical should not be made in cells meant for delivering heavy currents.

The Leclanché dry cell with zinc replaced by magnesium offers considerable advantages. In the electromotive series, magnesium occupies a more basic position as compared to zinc ($E^0_{Zn} = -0.76$ V; $E^0_{Mg} = -2.38$ V), and this means that the voltage of a magnesium cell is greater than that of a similar zinc cell.

In the alkaline version, NH_4Cl is replaced by KOH as the electrolyte. Under alkaline conditions the half-reactions can be represented by:

Anode: $Zn\ (s) + 2\ OH^- \ (aq) \rightarrow ZnO\ (s) + H_2O\ (l) + 2\ e^-$

Cathode: $2\ MnO_2\ (s) + H_2O\ (l) + 2\ e^- \rightarrow Mn_2O_3\ (s) + 2\ OH^-\ (aq)$

Total cell reaction: $Zn\ (s) + 2\ MnO_2\ (s) \rightarrow ZnO\ (s) + Mn_2O_3\ (s)$

Unlike the acid cell, the alkaline cell maintains a constant voltage as discharge occurs. In this case, it may be noted, the reactants and products are all in solid forms, and this makes the value of the reaction quotient in the Nernst equation equal to 1. The cell voltage therefore does not alter. Although alkaline dry cells are expensive to produce, they last longer than acid cells. In both the acid and alkaline cells, the zinc casing is used up, and towards the end of a Leclanché cell's life holes may develop in the casing, exposing the environment to the rather corrosive contents. Modern design dry cells no longer use a zinc electrode as the outer casing, and so leaking seldom poses a problem.

There have been a number of versions or modifications of the original Leclanché cell and a summary of these is shown in Table 6.12. The primary cells described herein and the variations thereof, it may be recounted, are not rechargeable. Indeed it is dangerous to attempt generally to charge the primary cells, using a battery charger, as a build-up of gas during the recharging operation may lead to explosive effects.

According to the given organization of presentation on commercial galvanic cells the present text now concentrates on secondary cells. Accumulators (also known as storage cells) are by far the oldest traditional example of secondary cells. Secondary cells may be distinguished from primary cells by the fact that they can be recharged. Primary cells cannot function as accumulators simply because the electrode processes in them are not reversible; at the positive pole of a Leclanché cell, for example, chlorine would be evolved should any attempt be made at recharging.

Table 6.12 Some modified versions of Leclanché cells.

Name	*Essential features*	*Cell chemistry*
Alkaline manganese cell	Consists of Zn anode and MnO_2 cathode with KOH as the electrolyte is saturated with zincate ions	$Zn + 2\ MnO_2 + 2\ H_2O \rightarrow Zn(OH)_2 + 2\ MnO\ (OH)$ $\upharpoonleft\downharpoonright$ $ZnO + H_2O$
Mercury cell	Consists of Zn anode and HgO cathode with KOH containing ZnO as the electrolyte	$Zn + HgO + H_2O \rightarrow Zn(OH)_2 + Hg$ $\upharpoonleft\downharpoonright$ $ZnO + H_2O$
Silver-zinc cell	Consists of Zn anode and AgO or Ag_2O cathode with KOH as the electrolyte	$Zn + AgO + H_2O \rightarrow Zn(OH)_2 + Ag$ $\upharpoonleft\downharpoonright$ $ZnO + H_2O$ $Zn + Ag_2O + H_2O \rightarrow Zn(OH)_2 + 2\ Ag$ $\upharpoonleft\downharpoonright$ $ZnO + H_2O$
Copper oxide cell	Consists of Zn anode and CuO as cathode with alkaline electrolyte	$Zn + OH^- + CuO \rightarrow Cu + HZnO_2^-$

6.4.5.1.2 **Secondary Cells**

Lead storage cells in the first instance may be regarded as the most common of all secondary cells. They represent probably the most famous example among the numerous oxidation–reduction reactions that have been made into useful sources of electric current. The chemical principles involved have not changed since its first appearance. The technical developments relating to improvements in structure and efficiency have, however, been considerable. However, for an understanding of the working principle of the cell it is sufficient to refer to its basic features which are electrodes of lead (Pb) and lead oxide (PbO_2) dipped into a strong aqueous solution of H_2SO_4. The shorthand description of the cell is as follows:

$$\text{Pb, PbSO}_4\text{ (s)} \mid \text{H}_2\text{SO}_4\text{ (20\%)} \mid \text{PbSO}_4\text{ (s), PbO}_2\text{ (s), Pb}$$

when the cell discharges, the reactions can be put forward as follows:

Anode: $\text{Pb (s)} + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + \text{H}^+ + 2\,\text{e}^-$

Cathode: $\text{PbO}_2\text{ (s)} + \text{HSO}_4^- + 3\,\text{H}^+ + 2\,\text{e}^- \rightarrow \text{PbSO}_4\text{ (s)} + 2\,\text{H}_2\text{O (l)}$

Total cell reaction: $\text{Pb (s)} + \text{PbO}_2\text{ (s)} + 2\,\text{HSO}_4^- + 2\,\text{H}^+ + 2\,\text{e}^- \rightarrow 2\,\text{PbSO}_4\text{ (s)} + 2\,\text{H}_2\text{O (l)}$

In the discharge mode, as represented by the total reaction, Pb and PbO_2 are depleted, and the concentration of H_2SO_4 is diminished. Since the density of solution has a bearing on the concentration of H_2SO_4 measurement of the density can be used as a simple way to enumerate how far the cell has undergone discharge. The battery can be recharged and thus resorbed to its original condition. To perform this, a direct current is passed through the cell in the reverse direction and this reverses the reactions. The picture can very well be presented as provided below:

$$\text{Pb (s)} + \text{PbO}_2\text{ (s)} + 2\,\text{HSO}_4 + 2\,\text{H}^+ \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} 2\,\text{PbSO}_4\text{ (s)} + 2\,\text{H}_2\text{O}$$

The storage cells are in essence electrolytic cells during charging which implements nonspontaneous reaction, and galvanic cells during discharging which implements spontaneous reaction. Although the battery can usually be discharged and recharged several thousand times, it does not endure forever, particularly if it is allowed to stand for sometime when discharged. Repeated quick-charging can lead to dislodging of Pb, PbO_2, and $PbSO_4$ from the electrodes. This collects as a sludge beneath the battery, often short-circuiting one or more cells. Discharged batteries are also susceptible to freezing, since the sulfuric concentration is low. In the event of freezing occurring, the electrodes may warp and touch one another.

While the lead accumulator described above may be called an acid storage cell, the nickel-iron Edison cell is essentially an alkaline cell which has evolved as a result of a search for an accumulator which is lighter than the lead accumulator. The term alkaline battery also includes the nickel (Ni) cadmium (Cd) cell. Broadly speaking, their functioning is very much analogous to the charging and discharging modes by which accumulators operate. The Ni-Cd battery is used for small appliances, tools, and calculators. The anode in this cell is made of Cd metal, the cathode contains Ni(IV) oxide, NiO_2, and the electrolyte is a strong solution of KOH. The discharge reactions are written as:

Anode: $Cd\ (s) + 2\ OH^- (aq) \rightarrow Cd(OH)_2\ (s) + 2\ e^-$

Cathode: $NiO_2\ (s) + 2\ H_2O + 2\ e^- \rightarrow Ni(OH)_2\ (s) + 2\ OH^- (aq)$

Total cell reaction: $Cd\ (s) + NiO_2\ (s) + 2\ H_2O \rightarrow Cd(OH)_2\ (s) + Ni(OH)_2\ (s)$

The insoluble hydroxides of Cd and Ni deposit on the electrodes. Hence, quick reversals of half-reactions occur during recharging. These batteries are costlier than lead storage batteries, but they have a longer term of existence.

The list of different types of cells must include fuel cells. The bulk of the electrical energy to date has been generated by generators propelled by steam turbines run on the heat produced by burning coal, oil, or natural gas. Here, chemical energy is first converted into heat, which is subsequently used to raise steam. The conversion of chemical into electrical energy in this case is indirect, and such a process is much less efficient than the direct conversion process occurring in a galvanic cell. Since the combustion of a fuel is an oxidation–reduction reaction, there is no reason in principle as to why it cannot be accomplished in a galvanic cell. The cells devised to carry out this operation are referred to as fuel cells. A somewhat oversimplified description of fuel cells is that here the reactants, which ordinarily are gases, are introduced continuously to the electrodes, where they undergo half-reactions of oxidation and reduction. By contrast to a conventional fuel, where only limited quantities of oxidizing agent and reducing agent are available, a continuous supply of both is provided to a fuel cell, and the reaction product is continuously removed. The basic design principles are the same as for any galvanic cell. There are two electrode compartments, each containing the reactants shown in the respective half-reactions. In the present case two of the reactants are gases and must be bubbled into the cell from the exterior. The first really workable fuel cell uses the reaction between gaseous hydrogen and oxygen for electrical energy generation. Hydrogen enters the cell through a porous carbon electrode, and oxygen is delivered to a similar electrode. The electrolyte is usually a warm alkaline aqueous solution of potassium hydroxide, and the two electrode reactions (or half-reactions) in the alkaline medium can be expressed as:

Anode: $H_2\ (g) + 2\ OH^- (aq) \rightarrow 2\ H_2O\ (l) + 2\ e^-$

Cathode: $0.5\ O_2\ (g) + H_2O\ (l) + 2\ e^- \rightarrow 2\ OH^- (aq)$

Since the reaction between hydrogen and oxygen is very slow at room temperature, catalysts are incorporated in the carbon electrodes. At the anode, suitable catalysts are finely divided into platinum or palladium; at the cathode, cobaltous oxide, or silver. The two half-reactions shown above yield the overall result as:

$$H_2\ (g) + 0.5\ O_2\ (g) \rightarrow H_2O$$

Unless removed, water produced by the reaction will progressively dilute the electrolyte making the cell nonfunctional. The necessity thus arises to keep the electrolyte warm enough so that water evaporates as it is generated by the cell reaction. Fuel cells have an important advantage over all other devices where fuel combustion occurs to obtain useful energy: their efficiency. The H_2-O_2 cell illustrated herein generates 200 kJ of electrical energy per mole of hydrogen consumed. If the hydrogen were burned and the heat utilized to produce electrical energy in a conventional power plant, only half as much energy would be ob-

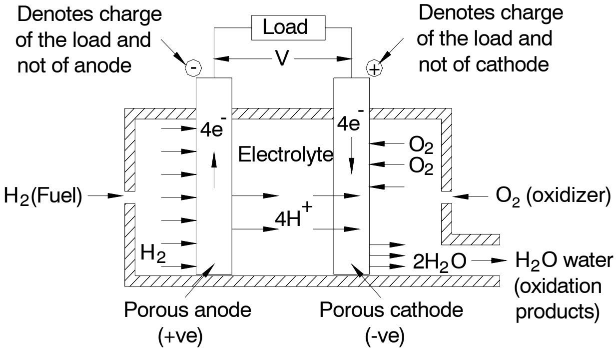

Figure 6.15
Simple H_2-O_2 fuel cell.

tained; the remainder would be wasted as heat. The major disadvantage of H_2-O_2 and other fuel cells, as for example, cells consuming methane or other hydrocarbons and oxygen, is their high cost. In part, this is attributed to the high temperature required, 200–300 °C. Although fuel cells have been available for a number of years, they are still too expensive to compete economically with other present modes of energy production. It is clear from the given description that the fuel cell may succinctly be described as a system which consists of a nonconsumable anode, cathode and an electrolyte (invariant), fuel and oxidant supply system, and suitable control. A schematic diagram of a H_2-O_2 fuel is shown in Figure 6.15. The recognition that the gaseous hydrogen serving as fuel and gaseous oxygen as oxidizer is apparent in the given description of the principles governing electrical energy supply from fuel cells. The advantages of hydrogen as a fuel in the cell are purely electrochemical. The relative case and simplicity of the electrode reaction, and the innocuous nature of the reaction (product) which are again very apparent in the given description may be cited as among the most important advantages. Oxygen is the only oxidant in these systems. This is cheap, convenient, and readily available.

6.5
Electrolytic Cells

An electrolytic cell essentially consists of two or more electrodes dipping into an electrolyte. These electrodes are connected to an external electric power source. When the current is switched on, the anode becomes positively charged, while the cathode becomes negatively charged. Thus, during electrolysis the cations or the positively charged ions move towards the cathode and the anions or the negatively charged ions migrate towards the anode. As mentioned earlier, an electrolytic cell differs from a galvanic cell in that it requires an external source of electric power to bring about a chemical reaction. In a galvanic cell the reaction occurs spontaneously. The main points of difference between the two types of cells, the electrolytic cell and the galvanic cell, are summarized in Table 6.13.

In order to outline broadly the mechanism of electrolysis, the behavior of ions of a dissolved salt during electrolysis may be illustrated by the account of the electrolysis of a solution of zinc chloride (Figure 6.16). When zinc chloride is dissolved in water, one zinc ion and two chloride ions are produced from one molecule of salt. The zinc ion will carry two

Table 6.13 Summary of the difference between electrolytic and galvanic cells.

Type of electrochemical cell	*Anode*		*Cathode*		*Means of implementing reaction*	*Remarks*
	Sign	*Reaction*	*Sign*	*Reaction*		
Electrolytic[1]	Positive	Oxidation $Cl^- \rightarrow Cl + e^-$	Negative	Reduction $H^+ + e^- \rightarrow H$	Imposition of electric current	Current used
Galvanic[2]	Negative	Oxidation $Zn \rightarrow Zn^{2+} + 2\ e^-$	Positive	Reduction $Cu^{2+} + 2\ e^- \rightarrow Cu$	Spontaneous process	Current generated

[1] Electrolysis of hydrochloric acid is considered.
[2] Daniell cell is considered.

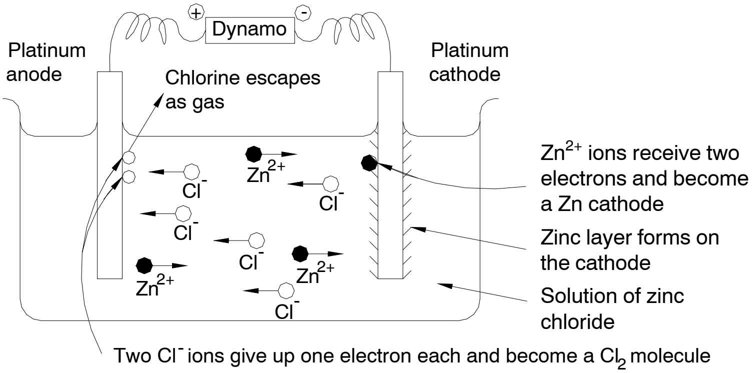

Figure 6.16 Electrolysis of zinc chloride solution using platinum electrodes.

positive charges so that the solution is electrically neutral. This is representative of the fact that the solution of electrolyte remains electrically neutral because equal quantities of positive and negative charge of electricity are produced. The current enters and leaves the solution by means of platinum electrodes. The platinum serves as a metallic electrical conductor only, and itself undergoes no chemical reaction during the electrolysis. The electrodes are dipped into the solution of zinc chloride and connected to a source of electrical energy (the algebraic difference between the discharge potentials of zinc and chlorine for the particular concentrations of zinc chloride solution used in the cell; if the applied emf is lower than this, no action occurs). The positively charged Zn^{2+} ions in the solution migrate to the negatively charged electrode. When a Zn^{2+} ion touches the electrode it accepts two electrons and is converted to a Zn atom which forms part of a film of zinc metal that gradually covers the platinum. The change may be expressed by the equation:

$$Zn^{2+} + 2\ e^- = Zn$$

The negatively charged Cl^- ions migrate to the positively charged electrode. When a Cl^- ion comes into contact with the electrode, an electron passes from the ion to the electrode, leaving momentarily an atom of chlorine. The atom immediately combines with another chlorine atom to form a molecule of chlorine which is liberated as gas as depicted below:

$Cl^- - e^- = Cl$; $Cl + Cl = Cl_2$

The electrode at which positive ions leave the solution (or at which negative ions enter the solution) is the cathode. The electrode at which negative ions leave the solution (or at which positive ions enter the solution) is the anode.

The theory of electrolysis is continued with one additional example in which a solution of hydrochloric acid contained in a container is considered. The dissociation of acid will cause the solution to have chlorine and hydrogen ions. It is shown below:

$HCl \rightleftharpoons H^+ + Cl^-$

The water in which the acid is dissolved will also be ionized to a very slight extent. It is shown below:

$H_2O \rightleftharpoons H^+ + OH^-$

The ions will be at motion in the solution, but the motion will be entirely random so that there is no flow of electricity in any particular direction. A pair of electrodes placed in the solution is now taken into account. The anode is the electrode connected to the positive terminal of the battery so that it will have a positive electric charge. The cathode, connected to the negative terminal of the battery, will have a negative electric charge. As the like charges repel each other, and unlike charges attract, the negatively charged chlorine ions will be repelled by the cathode but attracted by the anode, while positively charged hydrogen will move to the cathode. The ions moving to the anode are called anions, and those moving to the cathode are called cations. When positively charged hydrogen ions – initially derived from the acid but a few from the water – reach the cathode, they receive an electron from the cathode and become neutral hydrogen atoms which combine to become molecules of hydrogen gas. The Cl^- ions which the acid releases, plus a few OH^- ions which the water releases, reach the anode. The chlorine ions are more ready to part with electrons to the anode than are the hydroxy ions, and are discharged more easily (they are in fact the only ions discharged). They then combine to form molecules of chlorine gas as described in the previous example of electrolysis of zinc chloride solution. Although pointed out elsewhere in the present chapter, it may be mentioned in passing that when sodium chloride is dissolved in water there will exist in the solution Na^+, Cl^-, H^+, and OH^- ions. Of the Cl^- and OH^- ions, it is the Cl^- ions which are more readily discharged at the anode. Of the Na^+ and H^+ ions, it is H^+ ions which are more readily discharged at the cathode. Thus, when a solution of sodium chloride is electrolyzed, hydrogen gas is given off at the cathode and chlorine gas at the anode. The removal of hydrogen ions at the cathode results in further dissociation of water molecules so that as fast as hydrogen ions are removed, fresh hydrogen ions are formed. The hydroxy ions which are formed at the same time as the hydrogen ions will accumulate in the solution and are responsible for its alkaline properties. Since ions of metals and hydrogen are always positively charged they will always travel to and be discharged at the cathode. Ions of nonmetals – except hydrogen – are always discharged at the anode. The actual substance produced at the electrodes in electrolysis depends upon the nature of the solution and upon the nature of the electrodes, for in some cases the primary product of electrolysis is changed because it reacts with the electrode at which it is released. Illustrations abound in respect of all these particular aspects in the text, and hence the matter is not being pursued any further at this stage of presentation. It is interesting to compare the mechanism of electrolysis (in which an electric current from some external source, such as a dynamo, is passed through the solution) with the mechanism of a galvanic cell which is itself generating a current. Figure 6.17 is a pictorial representation of the changes which occur in a galvanic cell composed of a zinc chloride and a chlorine electrode immersed in a solution of zinc chloride. At the zinc electrode, Zn atoms ionize and enter the solution as Zn^{2+} ions; electrons are left on the zinc electrode. Since Zn^{2+} ions (positive) enter the solution from the zinc, the zinc electrode is the anode. At the chlorine electrode, Cl_2 molecules receive electrons from the electrode and become Cl^- ions. Here the Cl^- ions (negative) enter the solution, and hence by definition the chlorine electrode is the cathode. The solution becomes positively charged near the anode, and negatively charged near the cathode. The Cl^- ions in solution migrate to the positive region near the anode and not to the anode itself; the Zn^{2+} ions migrate to the negative region near the cathode. The points concerning the definitions used in describing both electrolysis and galvanosis that must be emphasized are: (i) the solution is the point of reference in defining both electrode potential and anode and cathode; (ii) the cathode and anode are not defined by the sign of the electrode; they are the points at which positive ions respectively leave or enter the solution; and (iii) the definitions of cathode and anode apply both to a cell in which electrolysis is taking place, and to a galvanic cell generating an electric current. It should be noted that the anode in Figure 6.16 is positive, whilst that the anode in Figure 6.17 is negative. The manner in which a galvanic cell operates and the way in which it differs from an electrolytic cell as has been described can best be summarized by a schematic diagram shown in Figure 6.18. As regards terminologies used in connection with galvanic and electrolytic cells, it may be seen that plus and minus terminals have been shown in galvanic and electrolytic cells. A cathode is always the electrode where reduction takes place, and an anode where oxidation occurs. Electrons leave at the anode and enter at the cathode. The direction of electron flow is in the direction opposite to that of positive electricity. In an electrolytic cell, the current flows from the positive electrode to the negative electrode within the cell; in a primary cell such as the galvanic one it flows from the positive electrode, or pole, to the negative pole outside the cell.

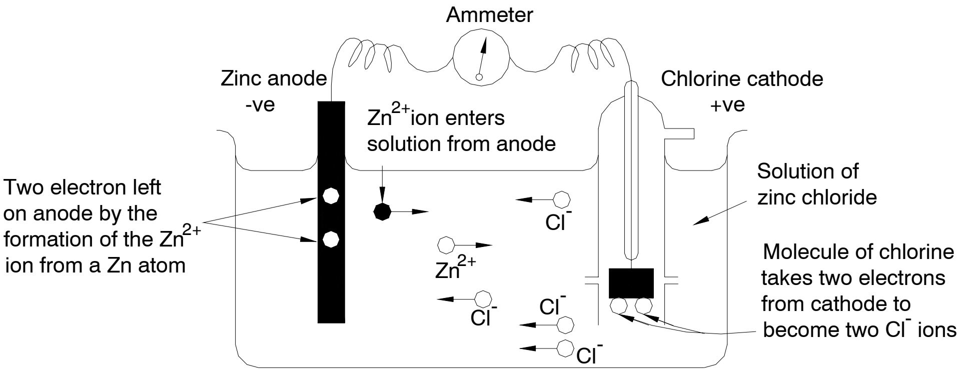

Figure 6.17 Production of an emf in a cell consisting of a zinc electrode and a chlorine electrode in zinc chloride solution.

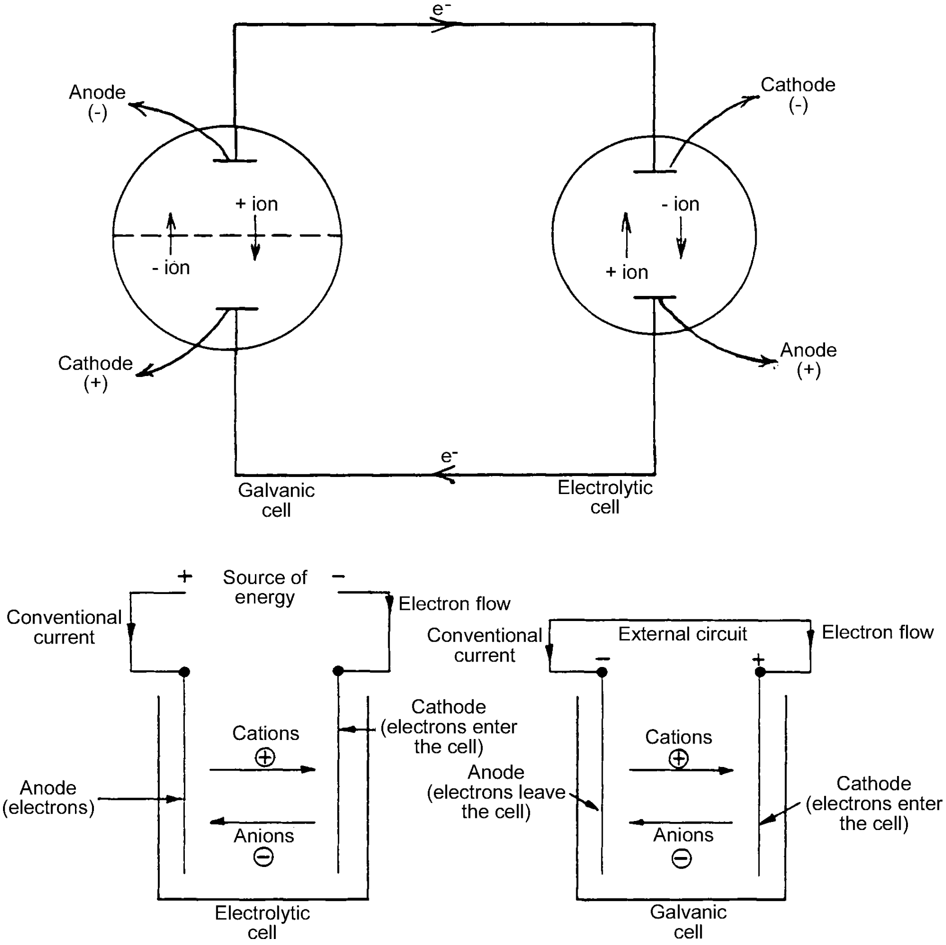

Figure 6.18 Galvanic cell operationally differing from an electrolytic cell (two methods of representation are shown).

6.5.1
Faraday's Laws

One of the first scientists to place electrochemistry on a sound scientific basis was Michael Faraday (1791–1867). On the basis of a series of experimental results on electrolysis, in the year 1832 he summarized the phenomenon of electrolysis in what is known today as Faraday's laws of electrolysis, these being among the most exact laws of physical chemistry. Their validity is independent of the temperature, the pressure, the nature of the ionizing solvent, the physical dimensions of the containment or of the electrodes, and the voltage. There are three Faraday's laws of electrolysis, all of which are universally accepted. They are rigidly applicable to molten electrolytes as well as to both dilute and concentrated solutions of electrolytes.

Faraday's first law of electrolysis states that the chemical decomposition during electrolysis takes place only at the surfaces of the electrodes.

Before describing the two other Faraday's laws of electrolysis, it will be useful to provide an understanding of the two very intimately connected terms; they are being presented from the very elementary levels. A typical equation such as $Al^{3+} + 3\,e^- \rightarrow Al$ can be interpreted on the atomic scale as meaning that one aluminum ion is converted by three electrons into one aluminum atom, or on the larger scale as meaning one mole of aluminum ions is converted by three moles of electrons into one mole of aluminum atoms. Moles of atoms, molecules, or ions can be measured out through weighing, but moles of electrons correspond to a certain amount of electricity. One mole of electrons is 1 Faraday (1 F) of electricity. Thus it can be seen that 3 F of electricity are required to deposit one mole of aluminum atoms. As an additional example mention may be made of the evolution of diatomic gases. One mole of hydrogen atoms is produced from one mole of hydrogen ions (H^+) by 1 F, but one mole of hydrogen gas (hydrogen molecules, H_2) requires 2 F since $2\,H^+ + 2\,e^- \rightarrow H_2$. 1 F is the quantity of electricity needed to deposit one mole of singly charged ions, half a mole of doubly charged ions, and one third of triply charged ions. Meters measuring the number of Faradays of electricity are few and far between. However, ammeters measuring electrical flow rate in amperes and clocks are common enough, and these can be used to measure Faradays in a slightly less direct manner. Users of electric currents mostly care little for moles, and choose to measure quantities of electricity in coulombs. One coulomb of electricity passes when current of one amp flows for one second. Thus, amps · seconds = coulombs. Coulombs are related to Faradays by the ungainly figure of 96,500 = 1 F. The coulomb is the practical unit of quantity of electricity, and the Faraday is taken as the bigger unit of quantity of electricity.

Faraday's second law of electrolysis states that the amount of any substance deposited or dissolved from an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte. Thus, according to the law, if the weight of the substance deposited (W) by passing a quantity (Q) of electricity, then $W = Z\,Q$, where Z is a proportionality constant called the electrochemical equivalent. This is how the second law is mathematically expressed. When $Q = 1$ coulomb, $W = Z$. Thus, Z, the electrochemical equivalent, is the weight of the substance deposited or dissolved by unit quantity of electricity (1 coulomb of electricity). Every substance has a definite electrochemical equivalent, i.e., Z is a constant characteristic of the substance liberated, evolved, or dissolved at an electrode. It is known that 1 coulomb of electricity liberated 0.001118 g of silver from a silver nitrate solution. So, the electrochemical equivalent of silver is 0.001118 g. If the same quantity of electricity (Q) is passed through two different electrolytes and the weights of two substances (say A and B) of electrochemical equivalents Z_A and Z_B liberated at an electrode (say cathode) are W_A and W_B, respectively, then

$$W\mathrm{A} = Z\mathrm{A}\,A \quad \text{and} \quad W\mathrm{B} = Z\mathrm{B}\,Q \quad \text{or} \quad \frac{W_A}{W_B} = \frac{Z_A}{Z_B}$$

Faraday's third law of electrolysis states that when the same quantity of electricity is passed through different electrolytes, the amounts of the different substances deposited, evolved at, or dissolved from the electrodes are directly proportional to their chemical equivalent weights.

The law may be expressed in an another fashion by stating that the same quantity of electricity is required to liberate 1 g-equiv. of any product of electrolysis. This quantity of electricity is known as the Faraday, and is 96,500 coulombs. To elaborate, let the passage of the same quantity of electricity through two solutions, one of copper sulfate and the other of silver nitrate, be considered. According to Faraday's third law, the ratio of the weights of the copper and the silver deposited is equal to the ratio of the equivalent weights of these two metals. Ionically, the deposition reaction for the two metals considered can be shown as

$$Cu^{2+} + 2\,e^- \rightarrow Cu \quad \text{and} \quad Ag^+ + e^- \rightarrow Ag$$

It is seen from the deposition reactions given above that the positive charge on copper ion is twice that on the silver ion. This implies that twice the quantity of electricity will be needed to liberate one mole of copper as for the liberation of one mole of silver. In the light of the relationship of the amount of element liberated during electrolysis and the charge on its ions, Faraday's third law may be stated as: when the same quantity of electricity is passed through solutions of different electrolytes, the relative numbers of moles of the elements deposited or liberated are inversely proportional to the charge on the ions of each of the element, respectively. The least quantity of electricity needed to liberate a mole of a univalent element which gives rise to slightly charged ions is 96,500 coulombs or 1 F. Thus, one Faraday will liberate one mole of hydrogen ions, one mole of sodium ions, one mole of potassium ions. The cathode reaction in such a case is $M^+ + e^- \rightarrow M$ (M = hydrogen or a univalent metal). So, to discharge one mole of unipositive ions, the charge carried by one mole of electrons is required. Therefore, one Faraday is equal to the charge carried by one mole or $6.023 \cdot 10^{23}$ electrons. It has already been mentioned that the electrochemical equivalent is the weight deposited by 1 coulomb of electricity and that 96,500 coulombs deposit 1 g-equiv. The g-equiv. (equivalent weight expressed in grams) of a substance is, therefore, 96,500 times the electrochemical equivalent (g-equiv. = 96,500 · electrochemical equivalent).

It will be interesting to express this through an equation which represents a combined form of Faraday's second and third laws. If W be the weight in grams of a substance (of equivalent weight E) deposited or dissolved at an electrode by Q coulombs of electricity, then

Based on the first law $W \propto Q$ (when E remains unchanged)
Based on the second law $W \propto E$ (when Q remains unchanged)

Therefore, $W \propto Q\,E$ or $W = Q\,E/F$ (where F is the proportionality constant).

When $Q = F$, then $W = E$. That is, F represents a definite quantity of electricity which is required to deposit or dissolve 1 g-equiv. of any substance in electrolysis. Inserting the value of the Faraday, Faraday's laws may be expressed by the following important form:

$$W = \frac{Q\,E}{96{,}500} = \frac{c\,t\,E}{96{,}500}$$

where c is current in amperes and t is time in seconds. The above relationship is obeyed so rigidly that it may be applied to measure the quantity of electricity or of current strength.

Significance of the Faraday's laws, $e = F/N$; relationship between the Faraday, Avogadro's number and the charge on the electron: Besides the practical applications so far described, Faraday's laws have an important significance in so far as theoretical interest goes. The laws have introduced the concept of atomic nature of electricity.

From the laws, it is known that the discharge of one g-equiv. of any ion (either positive or negative) necessitates the passage of 1 F of electricity. It means that 1 g-equiv. of an ion carries 1 F (or 96,500 coulombs) of electricity. Now, 1 g-ion of any ion is numerically equal to 1 g-atom of the element from which the ion is formed by gain or loss of electrons, and is therefore equal to product of 1 g-equiv. of the ion and its valency. (1 g-ion = 1 g-equiv. of the ion · valency.) If the valency of the ion is n, it may reasonably be stated that 1 mole or 1 g-ion will contain n g-equiv. and consequently will carry nF coulombs of electricity. Again, the number of individual ions in 1 g-equiv. is equal to the Avogadro's number N being equal to $6.023 \cdot 10^{23}$. So, the charge carried by a single ion is $n\ F/N$. Since n is an integer (1 for an univalent ion, 2 for a bivalent ion, 3 for a trivalent ion and so on), it is clear that a univalent ion carries the F/N, a bivalent ion 2 F/N, and a trivalent ion 3 F/N, and so on. It follows that the charge carried by a single ion is the same (where $n = 1$) or a multiple of a fundamental unit charge F/N. This outcome from Faraday's laws leads to the conclusion that electricity, like matter, is discrete or atomic in nature and that F/N is regarded as the atom or unit of electric charge. This unit of electric charge F/N has been found to be identical with the charge of an electron, the negative change, i.e., $e = F/N$. By substituting the values of F and N, one obtains

$$e = \frac{96{,}500}{6.023 \cdot 10^{23}} = 1.602 \cdot 10^{-19} \text{ coulombs}$$

The relationship $N = F/e$ provides an excellent method of calculating an accurate value of Avogadro's number from the values of Faraday and the experimentally determined electronic charge, e.

Since a Faraday is equal to the product of Avogadro's number and the electronic charge ($F = N \cdot e$), it amounts to the fact that a Faraday contains the same number of unit electric charges as the number of molecules in a mole. Hence, a Faraday (F) may be regarded as a mole of electricity.

Finally, it may be added that Faraday's laws have explained in a simple manner the phenomenon of electrolysis. According to these laws, the equivalent amounts of cations and anions are discharged at the cathode and the anode respectively, for a given quantity of electricity. This implies that when an electrolyte in solution or in fused state is electrolyzed, the number of electrons taken up by cations at the cathode must be equal to the number of electrons given up simultaneously at the anode. Now, a hydrogen ion is produced by the loss of the single electron of the hydrogen atom. The charge carried by a hydrogen ion is taken to be the unit of the positive electricity. On the basis of Faraday's laws, the charge carried by 1 g-ion of hydrogen ions equals to 96,500 coulombs. Therefore, the charge carried by one hydrogen ion is as follows:

$$\frac{96{,}500}{6.023 \cdot 10^{23}} = 1.602 \cdot 10^{-19} \text{ coulombs}$$

Thus, the charge of an electron is equal but opposite to that carried by a hydrogen ion. The calculated result of the quantity of electricity carried by a single ion shows that where the gram-ionic weight of an ion is numerically identical with the gram-equivalent, that is when the ion is univalent, the ion carries a charge equal to that of an electron. It can be shown similarly that bivalent and trivalent ions carry two or three electronic charges, respectively. These results go to provide definite support to the electronic theory of valency.

There are several reasons for apparent deviations from Faraday's laws, and why current efficiencies of less than 100% are encountered. Among these, mention may be made of the following:

a) Recombination of primary electrode products: in the mercury cell, the primary cathodic product, sodium, amalgamates with the cathode, but if precautions are not taken to prevent contact with chlorine, the primary anodic product, chlorine, recombines with sodium. This adversely influences the yield.
b) Instability of the primary electrode products. In the example provided in (a), the sodium amalgam is an unstable product in that it has a propensity for reacting with moist air. Because of this it is necessary to have a provision for the protection of the product if the current efficiency of its production is not to decrease.
c) Chemical or physical reactions with electrodes or electrolytes: there are many examples that appear in the text with regard to this aspect, and the inclusion of one more by way of elaboration would be redundant.
d) Unproductive simultaneous electrode reaction: these commonly arise from the deposition or the dissolution of some extraneous material present as an impurity or even as a necessary component of the electrolyte.
e) Generation of heat: the amount of heat generation in an electrolytic cell is directly proportional both to the resistance of the current path and to the square of the current. Thus, other factors being equal, the current efficiency is raised by an increase in the conductivity of the electrolyte and by a decrease in the current, the latter being the more important variable since heat reduced is proportional to its square.
f) Mechanical losses: there can be mechanical loss of the substances formed at the electrodes depending upon the structure of the deposit. This factor can be present with both fused and aqueous electrolytes.

6.5.2
Decomposition Voltage

The electrode processes that are reversible provide values for the equilibrium emfs of cells, which are related to the thermodynamic functions. The condition of reversibility is practically obtained by balancing cell emf against an external emf until only an unappreciable current passes through the cell, in order that the cell reactions proceed very slowly. It may, however, be pointed out that for many of the applications of electrometallurgy, it is clearly necessary to consider more rapid reaction rates. In that situation there is necessarily a departure from the equilibrium condition. Either the cell reactions occur spontaneously to produce electric energy, or an external source of electric energy is used to implement chemical reactions (electrolyses).

The electrolysis of a strong solution of hydrochloric acid is considered. Platinum electrodes are dipped into the solution and connected (through a device for changing the voltage) to an external source of electrical energy, such as a storage battery or other appliance. The arrangement is shown in Figure 6.19 (A). If one gradually increases the applied volt-

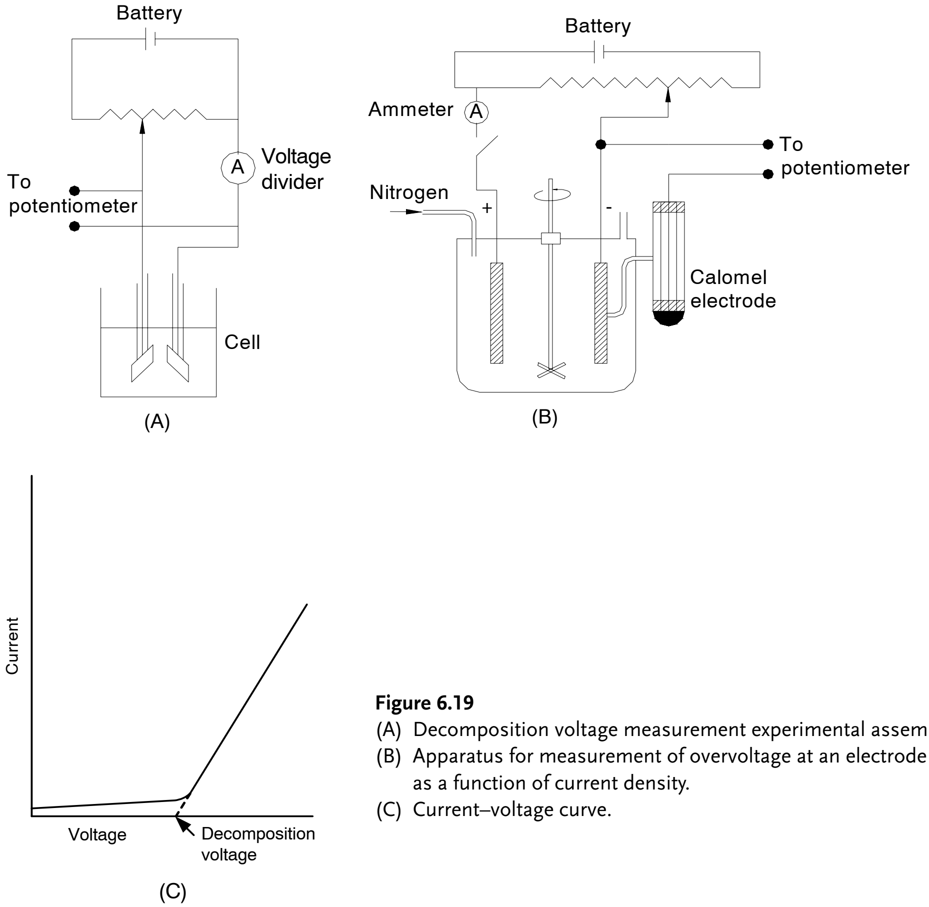

Figure 6.19
(A) Decomposition voltage measurement experimental assembly.
(B) Apparatus for measurement of overvoltage at an electrode as a function of current density.
(C) Current–voltage curve.

age and measures the current flowing through the cell as a function of the potential difference across the electrodes, the typical result shown in Figure 6.19 (C). The plot is of current per unit area of electrodes (called the current density) versus applied voltage. The current density is found to be very small until a certain definite voltage is reached; thereafter the current density–voltage curve is found to rise steeply. The voltage at which the current commences to flow freely corresponds to that condition at which bubbles of gas are first discharged from the electrodes – this is called the decomposition voltage of the solution.

A definite decomposition voltage occurs for the following reason. As soon as there is a potential difference between the electrodes, H^+ ions move to the cathode and Cl^- ions to the anode. The ions are discharged, forming layers of adsorbed gas on the inert metal surfaces. This essentially amounts to having a hydrogen electrode and a chlorine electrode in place of the two platinum electrodes. The outcome is a typical chemical cell:

$$\mathrm{Pt} \mid \mathrm{H_2} \mid \mathrm{H^+\,Cl^-}\,(a) \mid \mathrm{Cl_2} \mid \mathrm{Pt}$$

One could have used hydrogen and chlorine from external sources to construct a cell of this type, and the cell reaction would be

$$H_2 + Cl_2 \rightarrow 2\ HCl$$

The reversible emf of such a cell at 25 °C is given by the Nernst equation as:

$$E = E^0 - 0.059 \log (a_{\pm})^2_{HCl}$$

From the electrochemical series table, $E^0 = 1.3595$ V. If the solution is one molal, the mean activity coefficient of HCl is $\gamma_{\pm} = 0.82$. Therefore, the reversible emf of the cell is:

$$E = 1.3595 - 0.118 \log (0.82) = 1.3697\ \text{V}$$

This is the difference in potential that one must use from an external source in order to balance the driving force of the forward cell reaction. If one uses a potential difference just in excess of this value, one can bring a reversal of the cell reaction and commencement of the electrolysis of the HCl solution, $2\ HCl \rightarrow H_2 + Cl_2$.

If one begins with two inert electrodes in the HCl solution, one can expect to come across same situation as soon as enough H^+ has discharged at the cathode and enough Cl^- at the anode to transform these electrodes into a hydrogen and a chlorine electrode, respectively. Therefore, for electrolyzing the HCl solution, one must use at least enough potential difference to overcome the reversible emf of the cell that is developed by this polarization of the inert electrodes. This emf is known as the back-emf of the electrolytic cell. In this particular case, the measured decomposition is 1.370 V (with platinized platinum electrodes). In other cases the decomposition voltage may exceed the reversible back-emf.

The curve in Figure 6.19 (C) conveys the fact that there is a small current through the cell even below the decomposition voltage. This is called the diffusion current. There is a slow diffusion of ions away from the polarized electrodes, and a small current of ions must stream toward the electrodes at any applied voltage in order to keep them under polarized condition.

In the example just studied, the electrolysis of HCl solution, the ions that transport the current (H^+ and Cl^-) are also the ones that are discharged at the electrodes. In other cases, however, the main ionic transporters of current may not be of the same species as the ions that are discharged. An excellent example is the electrolysis of $CuSO_4$ solution between platinum electrodes. A one molal $CuSO_4$ solution is quite acid so that the positive current transporters are both Cu^{2+} and H^+ ions. The main negative transporter is the SO_4^{2-} ions. The solution contains, however, a small concentration of OH^- ions. In order to determine which ions will be discharged at the electrodes, it is necessary to consider standard electrode potentials of the concerned species:

$$H_2 \mid H^+ = 0.0; \quad Cu \mid Cu^{2+} = 0.337; \quad O_2 \mid OH^- = 0.401; \quad S_2O_8^{2-} \mid SO_4^{2-} = 1.98$$

The electrode reactions that take place in the electrolysis of $CuSO_4$ will be those that proceed most readily, and in the absence of the effects due to irreversibility, these are the reactions which possess the greatest driving force, or emf E. At the cathode the reactions possible are

$$Cu^{2+} + 2\ e^- \rightarrow Cu \qquad E^0 = 0.337$$

$$H^+ + e^- \rightarrow 0.5\ H_2 \qquad E^0 = 0$$

Thus, if Cu^{2+} and H^+ are existing at unit activity, the reduction of Cu^{2+} is easier than the reduction of H^+, and Cu^{2+} ions must be discharged in preference to H^+, until the Cu^{2+} concentration has dropped to such a point that the E for its half-cell reaction is less then that for the $H^+|H_2$ half-cell.

The different reactions at the anode are:

$$2\ OH^- \rightarrow H_2O + 0.5\ O_2 + 2\ e^- \qquad E^0 = 0.401$$

$$2\ SO_4{}^{2-} \rightarrow S_2O_8^{2-} + 2\ e^- \qquad E^0 = 1.98$$

In fact, the oxygen electrode is not irreversible, but the discharge potential SO_4^{2-} ion is so much on the high side that the OH^- ions are discharged preferentially, even in extremely dilute $CuSO_4$ solution.

If the assumption is presently made that the oxygen electrode is not irreversible, it is possible to calculate from the Nernst equation the ratio of activities of OH^- and SO_4^{2-} that must be present before SO_4^{2-} would begin to be discharged. In this context it is important to identify the numerical values that are obtained from the available data. These are presented below:

$$\Delta G^0 = 1.198 - 0.40 = 1.58 = \frac{R\,T}{2\,F} \ln \frac{a_{SO_4^{2-}}}{a_{OH^-}} = \frac{0.0592}{2} \log \frac{a_{SO_4^{2-}}}{a_{OH^-}}$$

$$a_{SO_4^{2-}} / a_{OH^-} = 10^{50}$$

The calculated value above shows that even with an unthinkably low concentration of OH^- ions, the question of discharge of SO_4^{2-} ions does not arise at all. The SO_4^{2-} ions transport almost all the negative charge across the electrolyte, but the work of giving up the electron to the anode is taken over by the OH^- ions and produce OH radicals. This radical having no independent existence reacts with another of its type and gives rise to oxygen at the anode:

$$OH^- - e^- \rightarrow OH$$

$$OH + OH \rightarrow H_2O + 0.5\ O_2$$

6.5.3
Polarization and Overvoltage

Here, an electrochemical cell working under irreversible conditions is considered. Its emf invariably moves away from the equilibrium value, and if the cell is serving as a battery or source of electricity, then its voltage drops below the equilibrium value. If, on the other hand, the cell is in a place where electrolysis is occurring, then the voltage to be applied must exceed the equilibrium value.

Part of this voltage difference is required to overcome the cell resistance and is equal to the IR product. The corresponding electric energy $I^2\ R$ is dissipated as heat. This is similar to the frictional losses that occur in mechanical processes that are irreversible.

In addition to this, one distinguishes that there are two other sources of voltage difference. One has its origin within the electrolyte of the cell, and the other is referred to rate processes taking place at the electrodes. The former is called concentration polarization, while the latter is called overvoltage.

As its name suggests, concentration polarization originates from concentration gradients within the electrolyte of the operating cell. As an example, a cell consisting of a copper anode and a platinum cathode in a solution of copper sulfate is considered. When a current passes, copper dissolves at the anode and deposits upon the cathode. If the current is appreciable, the solution in the vicinity of the cathode becomes relatively impoverished of copper ions. Correspondingly, due to dissolution of copper anode there is an increase in the vicinity of copper anode. This situation leads to the development of concentration gradient within the cell. This gradient is equivalent to a concentration cell of the type discussed earlier ($Pt|H_2|HCl(c)|AgCl\ (s)|Ag$, the cell type described as an example of the electrolytic concentration cell without involving both liquid junction and transference). The concentration cell generates a back emf in opposition to the applied emf, giving rise to a definite tendency for the concentrations of the anolyte and catholyte to be equalized by deposition of copper on the anode, and dissolution of copper from the cathode. The existence of the effects just described may be readily illustrated by a simple experiment in which a copper rod is placed vertically in a cell containing a lower layer of a concentrated aqueous solution of cupric sulfate and a weaker solution of the same salt above it. If after a time the copper rod is removed, it will be noted that a copper deposit has been laid down from the lower, stronger solution, whilst copper has been dissolved anodically from that portion of the rod immersed in the upper, weaker solution. Similarly, the Daniell cell may exhibit concentration polarization since on generating current the zinc electrode dissolves, thereby increasing the concentration of zinc ions in its vicinity and thereby making the potential of this electrode less negative; whilst at the copper electrode, copper is plated out and the concentration of cupric ions in its vicinity reduced thereby rendering this electrode less positive. In this specific case, concentration polarization may be minimized by employing saturated aqueous solutions of cupric sulfate and zinc sulfate containing crystals of these salts; thus, concentration changes come down to a minimum and the cell emf remains practically constant when supplying current. If potassium cyanide is added to the copper sulfate solution in the Daniell cell, the copper ions are nearly all removed to form complex ions $Cu(CN)_4^{3-}$, and the direction of the current changes sign. On account of low concentration of copper ions, copper dissolves and zinc ions are driven out of the solution as metallic zinc. In general, the magnitude of concentration polarization is small since it may be pointed out from Nernst equation that a tenfold change of ionic concentration only results in a change of 0.058 V or 0.029 V for univalent and bivalent ions, respectively. Concentration polarization can be minimized by vigorous stirring of the electrolyte, which destroys the concentration gradients developed by electrolysis, or by increasing the temperature which also tends to decrease the polarization by accelerating the diffusion of electrolyte ions within the cell, or by both, or by increasing the salt concentration, but it cannot be entirely eliminated.

As regards overvoltage, this essentially concerns electrode kinetics. The phenomenon of overvoltage arises from a slow attainment of equilibrium at the electrodes, i.e., a slowness either in transfer of electrons to, or in the acceptance of electrons from ions in the solution. Thus, a free energy of activation is required for the reaction to proceed and the excess applied voltage acts to provide this free energy. The effect may be seen for most electrode processes, but for deposition or solution at metal electrodes it is usually not large at all. Much more significant are the overvoltages needed for the liberation of gaseous hydrogen or oxygen, which may reach one volt or more on certain metals. In order to provide a gen-

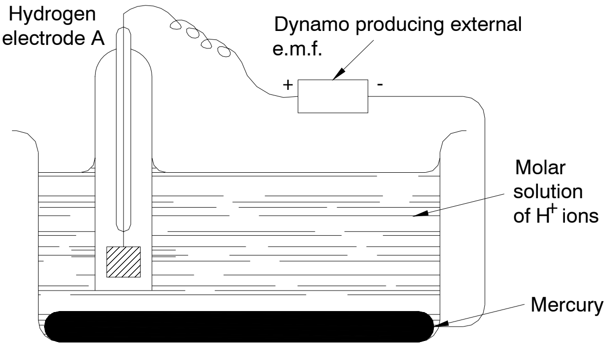

Figure 6.20 Cell with a mercury electrode.

eral understanding of overvoltage reference is drawn to Figure 6.20 which is essentially the hydrogen electrode B in Figure 6.12 (B) replaced by a layer of mercury on the floor of the cell. In this condition, the cell no longer consists of two reversible electrodes, for it is observed when the mercury is made the negative electrode and that the applied emf must attain a measurable value before gaseous hydrogen is observed to escape from the mercury surface. Mercury is therefore said to possess an overvoltage. The overvoltage or overpotential of a metal is measured by the potential difference that must be applied between an electrode of the metal and a molar solution of H^+ ions in which it is immersed, in order just to cause the evolution of hydrogen gas. Based on this principle the overvoltage or overpotential can essentially be measured with the apparatus shown in Figure 6.19 (B). An auxiliary reference electrode, e.g., normal calomel, is placed close to the electrode being investigated (to minimize IR drop) and the potential of the electrode at which the gas is being discharged is measured as a function of current density. The solution is agitated in order to eliminate concentration polarization. The matter of overvoltage may alternatively be described by taking reference to the hydrogen electrode, whose potential, as it would be recalled, is arbitrarily taken as zero. It would also be recalled that it uses platinum as the metal in contact with the hydrogen gas and the hydrochloric acid solution. If a metal other than platinum is used, a different potential difference is set up, or, expressed in another way, a definite potential difference must be applied to such a metal immersed in a normal solution of hydrogen ions in order that evolution of hydrogen gas may just occur. This potential difference (the normal hydrogen electrode again being taken as zero) is known as the overvoltage or overpotential of the metal. The values of hydrogen overvoltages of some metals are shown in Table 6.14. The sign of overpotential must be positive because it diminishes the tendency of the positive H^+ ions to undergo discharge at the metallic electrode. It may be added that overvoltage effects are also noted in the liberation of oxygen. As an example, mention may be made of oxygen voltage of iron metal anode in dilute sulfuric acid is of the order of 0.24 V.

The explanations of the products obtained as a result of the electrolysis can be given on the basis of the known values of the electrode potentials and of overvoltages. A representative example may be taken here focusing attention only on overvoltages. Because of the high hydrogen overvoltage, it is possible to plate metals from solutions in which their reversible discharge potentials are well below that of hydrogen ion. A cell consisting of plati-

Table 6.14 Hydrogen overvoltage of metals.

Metal	***Current density, amp cm^{-2}***	
	0	***0.10***
Gold	0.02	0.77
Iron	0.08	0.82
Polished platinum	0.09	0.39
Silver	0.15	0.90
Nickel	0.21	0.89
Copper	0.23	0.82
Lead	0.64	1.20
Zinc	0.70	1.06
Mercury	0.78	1.18

N.B.: The values for zero current density are for lowest c.d at which bubble formation could just be observed, usually about $5 \cdot 10^{-5}$ amp cm^{-2}. At higher current density the overvoltage increases.

num electrodes in a solution of zinc ions and hydrogen ions at unit activity is considered. The reversible potentials of the two half-cells are represented as:

of the zinc: $Zn^{2+} + 2\,e^- \rightarrow Zn$; $E^0 = -0.76$

of the hydrogen: $2\,H^+ + 2\,e^- \rightarrow H_2$; $E = 0.00$

If H^+ ions were discharged at its reversible potential, H_2 should be liberated at a lower voltage than that required to plate out zinc. The overvoltage of hydrogen on zinc, however, amounts to about 1.06 V at 0.7 amp cm^{-2} (Table 6.14), so that in an actual electrolysis, zinc will first be deposited on the cathode. The hydrogen ion will not be discharged rapidly until the zinc concentration has dropped to such a level that the emf of the zinc half-cell lies above the hydrogen overvoltage.

The hydrogen overvoltage has a limited range, however, and fails to prevent the evolution of hydrogen when an attempt is made to electrolytically deposit metals which occupy positions towards the top of the electrochemical series. The electrochemical series (Table 6.11) may thus be divided into three sections. The metals appearing below hydrogen in the series (e.g., copper, silver, etc.) are characterized by high reduction potentials. This implies that they can be readily electrodeposited from an aqueous solution – in other words, they are difficult to oxidize. Such metals are called noble metals. At the other end of the electrochemical series, well above hydrogen, there are metals such as lithium, magnesium, and titanium, which are characterized by low reduction potentials. They cannot be electrodeposited from an aqueous solution. Their great propensity for oxidation and non-amenability to reduction have earned them the name of base metals. In principle, all metals appearing above hydrogen should be called base metals; however, the phenomenon of hydrogen overvoltage confers a certain amount of "nobility" on the metals from lead to manganese in the series. All these metals can be electrodeposited from an aqueous electrolyte. In the case of these metals, in practice, the cell emf is usually so high that some evolution of hydrogen accompanies metal deposition. This hydrogen evolution should be minimized by maintaining the cell emf at a level as low as practicable, by ensuring that there are no potential catalysts present in the system, and by keeping the acidity (implying thereby the hydrogen ion activity) low.

The different factors responsible to influence the hydrogen overvoltage for a metal are:

1. Current density: the hydrogen overvoltage increases linearly with the current density.
2. Temperature: the hydrogen overvoltage decreases with increasing temperature. It can be zero at higher temperatures. For example, the hydrogen overvoltage on nickel is zero at 90 °C.
3. Pressure: at elevated pressures, the value of the hydrogen overvoltage changes only very slightly; but at lower pressures, it increases sharply on certain metals, as for example in the case of copper, nickel, and mercury cathodes.
4. Cathode material: the hydrogen overvoltage value varies from one cathode material to another. It can be quite high at certain electrodes made of lead and tin.
5. Cathode surface: the hydrogen overvoltage is smaller on rough unpolished surfaces than on smooth, shining, polished surfaces.
6. The pH: the hydrogen overvoltage, with other conditions remaining unchanged, varies with the pH of the electrolyte. First it increases with increasing pH value and then decreases again in alkali solutions.
7. Foreign elements: the hydrogen overvoltage is greatly influenced by the presence of foreign ions in the electrolyte. In general, specific adsorbed anions bring down the hydrogen overvoltage while specific adsorbed cations cause the hydrogen overvoltage to be increased. This is an instance where the effect of anions is not entirely electrostatic but also chemical.

The two identified cathodic processes during electrolysis of aqueous electrolytes are metal deposition and hydrogen evolution. The three cases that can arise are: (i) only metal deposition will occur if the hydrogen voltage is more negative, for all values of current density, than the voltage required for metal deposition; (ii) hydrogen will only deposit if the metal voltage is more negative, for all values of current density, than the voltage required for hydrogen evolution; and (iii) hydrogen and metal will deposit if the voltage required for deposition is the same for both. These three states of affairs are presented in Figure 6.21. It has already been seen that the hydrogen overvoltage can make the deposition of zinc possible. The same is true for some other metals (lead, tin, nickel, cadmium, iron) which are just above hydrogen in the electrochemical series. If overvoltages are not present, then clearly situations (ii) and (iii) described above will apply during electrolysis of aqueous salts of these metals. It is in order in the current text content to refer to once again the example of electrodeposition of zinc from solution containing zinc ions at unit activity. The potential needed to deposit zinc from this particular solution is –0.76 V. The hydrogen potential depends on the pH of the electrolyte and can be calculated from the equation, $E = -0.059$ pH. For the acidic solution of pH value 1, $E = -0.059 \cdot 1 = -0.06$ V. The depositional potential of metal (–0.76 V) is more negative than hydrogen (–0.06 V). This means that hydrogen should deposit first but this does not occur on account of the fact that zinc requires excess overvoltage (–0.70 V) at the zinc cathode (Table 6.14). Thus total potential required for hydrogen deposition becomes –0.76 V due to overvoltage. This potential is same as that needed for metal deposition. Thus, both zinc and hydrogen may be expected to deposit simultaneously. In order to deposit zinc, the hydrogen overvoltage should be further increased by

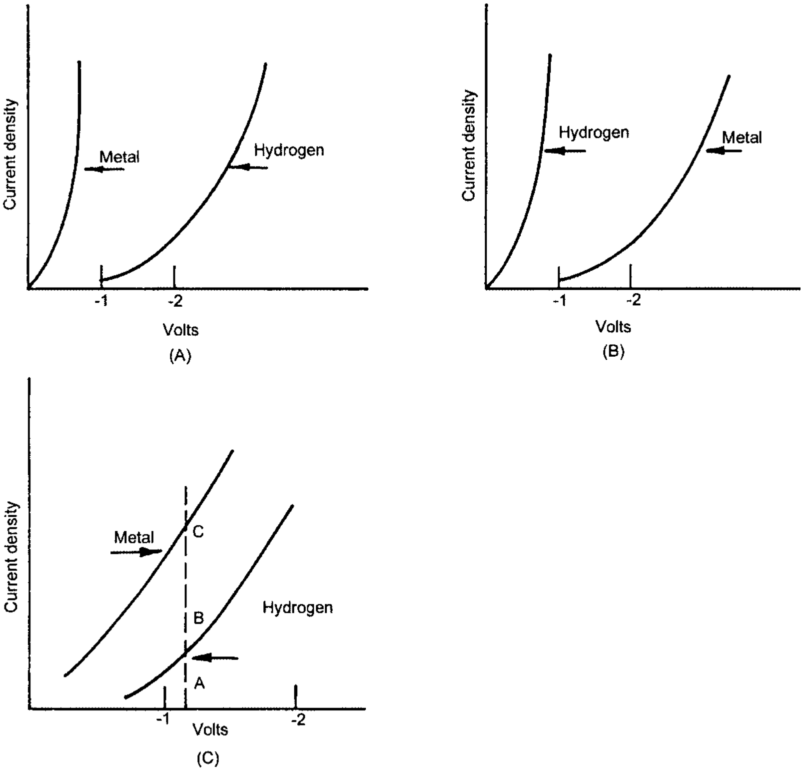

Figure 6.21 Different conditions of deposition of metal (M) and of hydrogen.
(A) Overvoltage of H_2 and M showing condition for M deposition.
(B) Overvoltage of M and H_2 showing condition for deposition of H_2.
(C) Overvoltage of H_2 and M showing condition for their simultaneous deposition.

making adjustments of the bath conditions. These have been pointed out earlier. A number of other situations may be mentioned to show that the property of overvoltage has an important bearing on the products obtained as the result of the electrolysis. For example, if a potential difference of less than 0.78 V is applied to a mercury cathode immersed in a normal solution of hydrogen ions, then no hydrogen will be evolved. Furthermore, if a solution containing both hydrogen ions and lead ions is electrolyzed, using a lead cathode, the lead ions will be discharged and lead will be deposited in preference to hydrogen since the potential difference which must be applied to discharge lead ions is 0.126 V (Table 6.11) and that required to liberate hydrogen on a lead electrode is 0.64 V (Table 6.14). Like hydrogen overvoltage, there also exist metal overvoltages in cathodic processes. The deposition of metal occurs relatively with small overvoltage, this being particularly low for metals such as zinc, copper, and cadmium, whereas metals such as cobalt, nickel, and iron shown high overvoltages. It may be mentioned here that increases in metal overvoltages are comparatively small. The overvoltage of a metal is increased when the metal can occur as a complex ion. For instance, silver shows a higher overvoltage in a cyanide solution than in a silver nitrate solution.

It may also be mentioned here that overvoltages are associated with anodic processes and these are significant with regard to oxygen evolution. The evolution of halogen occurs with relatively small overvoltages. The oxygen overvoltage is defined as the difference in potential between an oxygen electrode at equilibrium and one being oxidized with an external current. The factors affecting the oxygen overvoltage are:

a) Current density – the oxygen overvoltage increases with increase in current density.
b) Temperature – an increase in temperature results in a decrease of the oxygen overvoltage (more oxygen is liberated).
c) The pH – the oxygen overvoltage is independent of the pH in acid solutions whereas in alkaline solutions it varies with the pH.
d) The electrode material – the oxygen overvoltage is different for different materials; it is seen to attain higher values on such metals as gold and platinum and lower values on such metals as copper and nickel. This behavior is opposite to what is observed in the case of the hydrogen overvoltage.

The elements at the upper end of the electromotive series are very active chemically, whereas those at the lower end are quite inert. For instance, water will combine with sodium and potassium, but aqua regia is required to dissolve gold. Therefore, the metals toward the upper end of the series are never found free in nature. The active characters of these metals have provided them sufficient opportunity to combine with other elements; however, gold, platinum, and even copper (as has already been mentioned in Chapter 2), are found in nature in the native form. For the same reason, the compounds containing elements at the upper end of the series are quite stable. The oxides of the metals lying above manganese cannot be completely reduced even in a current of hydrogen, whereas the oxides of silver, mercury, gold, and platinum can be reduced by heating in atmosphere. Likewise, corrosion of the metals residing at the upper end of the series takes place quite readily. All the metals above copper oxidize fairly easily in the atmosphere, but metals below copper do not do so.

6.5.4
Electrode Reactions

The various possible electrode reactions at the cathode and at the anode in electrolytic cells have been shown in Table 6.2. It has been pointed before that the outcome of an electrolytic process can be made on the basis of knowledge of electrode potentials and of overvoltages. The selection of the ion discharged depends on the following factors: (i) the position of the metal or group in the electrochemical series; (ii) the concentration; and (iii) the nature of the electrode. Examples provided hereunder deliberate on these aspects.

A cell with two platinum electrodes and containing two electrolytes – a mixture of zinc chloride and cadmium bromide in solution – is considered to illustrate the principles behind the order in which discharging process for different ions occur. When the electrodes are connected to the poles of a dynamo the cathode becomes coated with the metal being deposited in the electrolysis, and it is then a reversible electrode with respect to that metal. The anode becomes a reversible electrode with respect to either bromine or chorine. If an emf gradually increasing from zero is applied to the cell, electrolysis begins as soon as the emf is great enough to discharge at the cathode the cation with the least negative charge potential, and at the anode the anion with the least positive discharge potential. The discharge potentials in volts, for solutions at molar concentration, of each of the four ions in solution in the cell in are: (the potentials are provided in the parentheses after the corresponding reactions expressed according to the convention being followed): $Cl^- \rightarrow Cl + e^-$ (+1.36 V); $Br^- \rightarrow Br^+$ (+1.07 V); $Zn^{2+} + 2\,e^- \rightarrow Zn$ (–0.76 V); $Cd^{2+} + 2\,e^- \rightarrow Cd$ (–0.401 V). From these values it can easily be appreciated that bromine appears at the anode, and cadmium at the cathode. The emf required just to bring about the electrolysis is $-0.401 - (1.07) = -1.471$ volts. The emf cannot exceed this value so long as Br^- ions and Cd^{2+} ions are present in molar concentration. In practice, the concentrations of these ions fall as electrolysis proceeds, and the emf rises. After a time, bromine and chlorine are liberated simultaneously at the anode, and cadmium and zinc at the cathode.

An increase in the concentration of an ion species tends to promote its discharge. For example, in concentrated hydrochloric acid, containing OH^- (from water) and Cl^- as negative ions, the concentration of Cl^- is overwhelmingly the greater of the two. In this situation, Cl^- ions are preferentially discharged by coming into contact with the anode where each ion loses an electron and becomes a neutral atom of chlorine. Pairs of these atoms combine to form molecules of gaseous chlorine. However, if the acid is very dilute, some discharge of OH^- ions also takes place. As the acid is diluted, no point will be encountered at which chlorine ceases to be produced and oxygen entirely replaces it. Instead, a mixture of the two gases will evolve, with the proportion of oxygen gradually increasing. The present example typically illustrates the fact that in some specific cases the order of discharge indicated by the electrochemical series may be reversed by a concentration effect.

The nature of the electrode may sometimes influence the choice of the ion for discharge. As an example, reference may be drawn to the contrasting results obtained when a solution of sodium chloride in water is subjected to electrolysis using: (i) a platinum cathode and (ii) a mercury cathode. The solution contains Na^+ ions and Cl^- ions from sodium chloride and H^+ ions and OH^- ions from water. When a platinum cathode is used, both Na^+ and H^+ ions migrate to it. The H^+ ion, being lower in the electrochemical series, discharges in preference to the Na^+ ion and becomes a hydrogen atom by accepting an electron. Hydrogen molecules are then formed by the combination of the atoms in pairs. In other words, hydrogen discharges in preference to sodium and this occurrence is simply because the tendency of the hydrogen ions to gain electrons is greater than that of the sodium ions. The discharge of H^+ ions disturbs the ionic equilibrium of water, and more water ionizes to restore the situation. The occurrence of excess OH^- ions so produced, along with the incoming Na^+ ions, is equivalent to an increase in the concentration of sodium hydroxide. In summary, the cathode product is 1 volume of hydrogen, with the solution becoming alkaline due to the presence of sodium hydroxide. The anode product is 1 volume of chlorine (in practice it will be less than 1 volume as some oxygen is always produced). When a mercury cathode is used, the electrolysis results in the formation of a solution of metallic sodium in the mercury cathode; there is no evolution of hydrogen. If the sodium amalgam is subsequently removed from the cell, covered with a dilute solution of sodium chloride, and placed in contact with an iron rod, hydrogen is evolved from the surface of the iron and sodium goes into solution as Na^+ ions. The Na^+ ions, together with the OH^- ions left in the water when H^+ ions are liberated as hydrogen gas, constitute a solution of sodium hydroxide. Attention may now be drawn to be explanation of these results. It is known from earlier in the chapter that the value of the electrode potential set up by dipping a metal rod into a solution containing ions of the metal depends on the concentration of the ions in the solution. The value of the electrode potential also depends on the concentration of the metal in the rod; for a pure metal, the concentration is constant and it is therefore disregarded. The concentration of the metal in the electrode may be decreased by dissolving it in mercury and using the amalgam as the electrode. If the concentration of the metal in the electrode is decreased, there will be correspondingly a reduced tendency for atoms of the metal to ionize and go into solution. The electrode potential set up between the metal and the solution of its ions therefore falls. Hence the electrode potential of sodium amalgam in a solution of sodium chloride is smaller than that of a sodium rod in the same solution. Let it be assumed that the electrode potential of sodium amalgam immersed in sodium chloride solution is –1 V. (The electrode potential of pure sodium dipped in a molar solution of Na^+ ions is –2.715 V.) The electrode potential of sodium amalgam in sodium chloride solution is equal to the discharge potential of Na^+ ions when the amalgam is used as the cathode. The discharge potential of Na^+ ions in the conditions described is thus –1 V. The discharge potential of H^+ in these conditions may be deduced as follows. The discharge potential of H^+ ions at a reversible hydrogen electrode dipped into a neutral aqueous solution is found to be about –0.4 V. When mercury is used as the cathode, this discharge potential goes up by the value of the overpotential of mercury, 0.798 V. The discharge potential of H^+ ions from a neutral solution at a mercury cathode is thus –0.47 – 0.798 = about –1.2 V. This is more than the value assumed for the electrode potential of sodium, and therefore no hydrogen discharge occurs during the electrolysis. If the sodium amalgam is made an electrode of a cell of which the other electrode is an iron rod, and the electrolyte is say, sodium chloride, the electrode potential of the sodium is the same as before, namely –1 V. The electrode potential of the hydrogen at the iron electrode, however, is only –0.4 V, since iron has a very low overpotential. The electrode potential which ensues from the tendency of sodium to leave the amalgam and enter the solution as ions is thus 0.6 V more than the potential necessary to generate hydrogen as gas at the surface of the iron. Hence the solution of sodium occurs spontaneously with the evolution of hydrogen. These considerations apply equally to a short-circuited cell in which an iron wire is brought into contact with mercury amalgam under the surface of an aqueous solution of an electrolyte.

6.5.5
Example of Electrolysis

The electrolysis of some typical solutions are now considered for the purpose of elaborating the nature of the products of the cathodic and the anodic reactions. A classification of cathodic and anodic reactions in a tabular form is shown in Table 6.15.

A solution containing the chlorides of copper, nickel, iron, and zinc is considered. In this case, two anodic reaction are possible

$$2\ Cl^- \rightleftharpoons Cl_2 + 2\ e^-; \qquad E^0_{Cl_2|Cl^-} = +1.39\ V$$

or

$$4\ OH^- \rightleftharpoons O_2 + 2\ H_2O + 4\ e^-; \qquad E^0_{O_2|OH^-} = +0.40\ V$$

Table 6.15 Classification of cathodic and anodic reactions.

Cathodic reactions	***Example***	***Anodic reactions***	***Example***
Metal discharge	$M^{n+} + n\,e^- \rightarrow M$ $Ni^{2+} + 2\,e^- \rightarrow Ni$	Metal dissolution	$M \rightarrow M^{n+} + n\,e^-$ $Cu \rightarrow Cu^{2+} + 2\,e^-$
Gas evolution	$2\,H^+ + 2\,e^- \rightarrow H_2$	Gas evolution	$4\,OH^- \rightarrow 2\,H_2O + O_2 + 4\,e^-$
Gas absorption	$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4(OH)^-$	Gas adsorption	$H_2 \rightarrow 2\,H^+ + 2\,e^-$
Reduction of an ion from a higher to lower valency	$M^{n+} + x\,e^- \rightarrow M^{(n-x)}$ $Fe^{3+} + e^- \rightarrow Fe^{2+}$	Oxidation of an ion from a lower to higher valency	$M^{(n-x)} \rightarrow M^{n+} + x\,e^-$ $Fe^{2+} \rightarrow Fe^{3+} + e^-$

The standard electrode potentials of $E^0_{Cl_2|Cl^-}$ and $E^0_{O_2|OH^-}$, are + 1.359 V and + 0.40 V, respectively, at 25 °C. Let it be assumed that the electrolyte in this case is neutral (which means $a_{OH^-} = 10^{-7}$); then the potential of the oxygen electrode can be calculated (at 25 °C) by using the Nernst equation:

$$E_{O_2|OH^-} = 0.40 + \frac{0.059}{4} \log_{10} \left(\frac{1}{10^{-7}} \right)^4$$

so that

$$E_{O_2|OH^-} = 0.40 + [0.059 \times (+7)] = +0.813$$

Since the oxygen overvoltage on a platinum electrode is equal to 0.45 V, the minimum potential required for oxygen evolution is (+ 0.813 + 0.45) V or 1.263 V. Since the voltage required to implement this reaction is lower than that for a normal chlorine electrode, it follows that oxygen will be evolved at the anode in preference to chlorine. In contrast to the two possible reactions at the anode, there are five reactions that are possible at the cathode as shown below:

$$Cu^{2+} + 2\,e^- \rightarrow Cu; \quad E^0_{Cu^{2+}|Cu} = +0.34\ V$$
$$Ni^{2+} + 2\,e^- \rightarrow Ni; \quad E_{Ni^{2+}|Ni} = -0.25\ V$$
$$Fe^{2+} + 2\,e^- \rightarrow Fe; \quad E^0_{Fe^{2+}|Fe} = -0.44\ V$$
$$Zn^{2+} + 2\,e^- \rightarrow Zn; \quad E_{Zn^{2+}|Zn} = -0.76\ V$$
$$2\,H^+ + 2\,e^- \rightarrow H_2; \quad E^0_{H^+|H_2} = 0\ V$$

Since the electrolyte solution is assumed to have a pH value of 7 (neutral),

$$E_{H^+|H_2} = 0 + \frac{0.059}{2} \log_{10} (a_{H^+})^2 = 0.059 \log_{10} (10^{-7})$$

which gives

$$E_{H^+|H_2} = -0.413\ V$$

It is seen from the above values of electrode potentials that copper is associated with the highest value, which signifies that it has the highest affinity for electrons; it will thus be electrodeposited in preference to the other metals. Finally, the reactions that take place at the anode and at the cathode are:

Anode: $4\,OH^- \rightarrow 2\,H_2O + O_2 + 4\,e^-$

Cathode: $Cu^{2+} + 2\,e^- \rightarrow Cu$

The voltage requirement for this cell will be

$$E_{cell} = 1.263\text{ V} - (+0.34)\text{ V} = +0.923\text{ V}$$

The value given above takes into account the oxygen overvoltage.

Let the electrolysis of dilute sulfuric acid (so-called electrolysis of water) with a platinum cathode and a platinum anode be considered next. Pure water is a very weak electrolyte and consequently a very poor conductor of electricity. It dissociates very slightly into H^+ ions (it may be recalled that in fact, H^+ ions does not remain as such but forms hydronium in H_3O^+ by combining with a molecule of water, $H^+ + H_2O \rightleftharpoons H_3O^+$) and OH^- ions. In the presence of little sulfuric acid (or for that matter any other strong electrolyte) the conductivity, i.e., ionization is greatly increased. The acidified water now contains H^+ ions, OH^- and SO_4^{2-} ions. During electrolysis with platinum electrodes, H^+ ions are attracted to the cathode, where each ion gains an electron and becomes a hydrogen atom:

$$H^+ + e^- \rightarrow H\ (g)$$

Hydrogen atoms combine in pairs to yield hydrogen molecules:

$$H\ (g) + H\ (g) \rightarrow H_2\ (g)$$

The SO_4^{2-} and the OH^- ions migrate towards the anode; however, the OH^- ions, residing lower in the electrochemical series, are discharged in the preference to the SO_4^{2-} ions, in spite of the high concentration of the latter. The anodic reaction can therefore be represented as:

$$OH^- \rightarrow e^- + OH$$

The OH radicals produced, having no independent existence, react with one another forming water and oxygen. Gaseous oxygen is thus evolved at the anode:

$$OH + OH \rightarrow H_2O\ (l) + O\ (g)$$

$$O\ (g) + O\ (g) \rightarrow O_2\ (g)$$

The discharge of OH^- ions disturbs the ionic equilibrium of water, and so more water ionizes to restore it:

$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$$

The occurrence of the excess H^+ ions so produced, along with the incoming SO_4^{2-} ions, is equivalent to an increased concentration of sulfuric acid at the anodic region. The total acidity at the anode and the cathode, taken together, remains constant. The final result namely, the evolution of 2 volumes of hydrogen at the cathode and of 1 volume of oxygen at the anode, is equivalent to the electrolysis of water. To see more clearly how the 2 : 1 volume ratio for the gases comes about, let the flow of four electrons through the solution be considered:

At the cathode: $4\ H^+\ (aq) + 4\ e^- \rightarrow 2\ H_2\ (g)$

At the anode: $4\ OH\ (aq) \rightarrow 2\ H_2O\ (l) + O_2\ (g) + 4\ e^-$

Thus, two moles of hydrogen molecules will be released for every mole of oxygen molecules produced.

The electrolysis of a copper(II) sulfate solution is now considered in two different situations. In the first, a copper cathode and a platinum or carbon anode are used. The second case involves the use of a copper cathode and a copper anode. The solution has Cu^{2+} (aq) and SO_4^{2-} (aq) ions from the copper(II) sulfate and H^+ (aq) and OH^- (aq) ions from water. Both Cu^{2+} (aq) and H^+ (aq) ions migrate to the copper cathode, and the Cu^{2+} ions, being lower in the electrochemical series, discharge in preference to the H^+ ions:

$Cu^{2+}\ (aq) + 2\ e^- \rightarrow Cu\ (s)$

Each of the Cu^{2+} ions take up two electrons and forms the neutral copper atom and the copper atoms thus formed are deposited as a brown layer on the cathode copper. H^+ remains in the solution. The negative OH^- and SO_4^{2-} ions (anions) migrate towards to the anode where OH^- ions, being less electronegative than SO_4^{2-} ions, are discharged by giving electrons to platinum or carbon anode used and furnish OH groups. The OH groups then interact to produce water and oxygen which evolves as a gas at the platinum or the carbon anode. The SO_4^{2-} ions are left in the solution. The residual solution is acidic as it contains H^+ and SO_4^{2-} ions, i.e., H_2SO_4, the concentration of which increases progressively as the electrolysis proceeds. With a copper anode, there are three possibilities: (i) discharge of SO_4^{2-} ions; (ii) discharge of OH^- ions; and (iii) conversion of copper atoms to Cu^{2+} ions. All of these involves loss of electrons. The third of these processes occurs the most readily: SO_4^{2-} and OH^- ions are not discharged and copper passes into the solution from the anode as Cu^{2+} ions:

$Cu\ (s) - 2\ e^- \rightarrow Cu^{2+}\ (aq)$

Besides copper passing into the solution as ions, the total concentration of the solution in respect of SO_4^{2-} ions (not discharged) and Cu^{2+} ions (copper is depositing on the cathode) remains constant. The electrolysis merely transfers copper from the anode to the cathode. With a platinum or a carbon anode, it is found that the color of the solution fades as copper is deposited, whereas with copper electrodes, the color does not change. The two situations, in fact, represent respectively the electrowinning and the electrorefining processes introduced later in the section on process classification.

6.5.6.1 **Electrochemical Separation and Co-deposition**

An important area of application of electrolysis is separation and co-deposition. If several ions exist together in an electrolytic solution in a cell, and the voltage is gradually raised from zero, the first metal to be plated is the lowest in the electrochemical series, provided that the ionic concentrations of the different metals are equivalent. As the voltage is increased, the metals which become plated move progressively towards the top of the series.

This explains why it is possible to plate metals below hydrogen in the electrochemical series, from acid solutions, without hydrogen evolution, whereas care must be exercised in plating metals that are above hydrogen in the electrochemical series, from such solutions.

The aforementioned fact is also the basis for the separation of co-occurring metals from each other. Whenever feasible, such electrochemical separation is an interesting and effective technique, in principle. In practice, however, such selective deposition is not considered very feasible, particularly for elements which are close neighbors in the electrochemical series. For example, the decomposition potentials of nickel and of cobalt are –0.25 V and –0.27 V, respectively. This small 0.02 V difference makes the selective deposition of nickel, leaving cobalt in the solution, or vice versa, rather difficult to achieve in practice. On the other hand, it is quite easy to co-deposit nickel and cobalt and to obtain an alloy.

While close neighbors in the electrochemical series can be co-deposited to form alloys relatively easily, the task becomes difficult when the desired alloy constituents are well separated in the series. A considerable degree of flexibility is available in the choice of alloy constituents in co-deposition, when the possibility of tailoring the deposition potential is taken advantage of by resorting to effecting activity/concentration changes in respect of the constituent ions. These manipulations may also be used to achieve separation when that is the objective. While the possibilities of electrochemical co-deposition or electrochemical separation are clear in terms of theoretical considerations, their use in practice still remains a subject of investigation. An example pertaining to these aspects is given below, with regard to silver and copper

$$E_{\mathrm{Ag^+|Ag}} = E^0_{\mathrm{Ag^+|Ag}} - \frac{RT}{F} \ln\left(\frac{a_{\mathrm{Ag}}}{a_{\mathrm{Ag^+}}}\right)$$

$$E_{\mathrm{Cu^+|Cu}} = E^0_{\mathrm{Cu^+|Cu}} - \frac{RT}{F} \ln\left(\frac{a_{\mathrm{Cu}}}{a_{\mathrm{Cu^{2+}}}}\right)$$

For co-deposition to occur, one must have

$$E_{\mathrm{Ag^+|Ag}} = E_{\mathrm{Cu^+|Cu}}$$

or

$$E^0_{\mathrm{Ag^+|Ag}} - \frac{RT}{F} \ln\left(\frac{a_{\mathrm{Ag}}}{a_{\mathrm{Ag^+}}}\right) = E^0_{\mathrm{Cu^{2+}|Cu}} - \frac{RT}{2F} \ln\left(\frac{a_{\mathrm{Cu}}}{a_{\mathrm{Cu^{2+}}}}\right)$$

If one considers the electrodeposit to be of pure silver and pure copper, then the activities of silver and copper can both be taken as unity. Therefore, the co-deposition condition can be expressed as

$$E_{\mathrm{Ag^+|Ag}} = E_{\mathrm{Cu^{2+}|Cu}} \quad \text{or} \quad 0.80\ \mathrm{V} - 0.34\ \mathrm{V} + \frac{RT}{F} \ln \frac{a^2_{\mathrm{Cu^{2+}}}}{a_{\mathrm{Ag^+}}}$$

(Taking $E^0_{\mathrm{Ag^+|Ag}} = 0.80\ \mathrm{V}$, $\mathrm{E}^0_{\mathrm{Cu^{2+}|Cu}} = 0.34\ \mathrm{V}$ and $a\mathrm{Ag} = a\mathrm{Cu} = 1$)

which yields

$$\ln \frac{a^2_{\mathrm{Cu}^{2+}}}{a_{\mathrm{Ag}^+}} = \frac{0.46\,F}{R\,T} = 7.81$$

So that

$$a^2_{\mathrm{Cu}^{2+}} = 65.3 \cdot 10^6\ a_{\mathrm{Ag}^+}$$

Thus, co-deposition of silver and copper can take place only when the silver concentration in the electrolyte falls to a very low level. This clearly indicates that the electrolytic process can, instead, be used for separating copper from silver. When both silver and copper ions are present, the initial deposition will mainly be of silver and the deposition of copper will take place only when the concentration of silver becomes very low. Another example worth considering here is the co-deposition of copper and zinc. Under normal conditions, the co-deposition of copper and zinc from an electrolyte containing copper and zinc sulfates is not feasible because of the large difference in the electrode potentials. If, however, an excess of alkali cyanides is added to the solution, both the metals form complex cyanides; the cuprocyanide complex is much more stable than the zinc cyanide complex and thus the concentration of the free copper ions available for deposition is considerably reduced. As a result of this, the deposition potentials for copper and zinc become very close and their co-deposition can take place to form alloys.

6.5.6.2 Molten Salt Electrolysis

It has been pointed out that metals residing below the position held by manganese (and, therefore, much below hydrogen) in the electrochemical series (Table 6.11) cannot be electrodeposited from aqueous solutions of their salts. These metals are called base metals or reactive metals and can be electrodeposited only from nonaqueous electrolytes such as solutions in organic solvents and molten salts. As with an aqueous electrolyte, there is a minimum voltage which is required to bring about the electrolysis of a molten salt.

Although the electrolysis of molten salts does not in principle differ from that of aqueous solutions, additional complications are encountered here owing to the problems related to the higher temperatures of operation, the resultant high reactivities of the components, the thermoelectric forces, and the stability of the deposited metals in the molten electrolyte. As a result of this, processes taking place in the melts and at the electrodes cannot be controlled to the same extent as in aqueous or other types of solutions. Considerations pertaining to Faraday's laws have indicated that it would be difficult to prove their applicability to the electrolysis of molten salts, since the current efficiencies obtained are generally too small in such cases.

The standard emf series based on hydrogen is obviously not applicable to molten salt electrolysis systems. No emf series similar to that for aqueous systems has been established for molten electrolytes; this is due to the nonavailability of accepted standard electrodes and the use of numerous molten electrolytes involving widely differing tamperers, consequent to the widely varying melting temperatures of the salts used. In spite of these, many emf series have been compiled, using a variety of molten salts with different stand-

Table 6.16 Electromotive force series in LiCl-KCl-eutectic, 723 K.

Couple	E^0 *m*	E^0	E^0x
Li(I)-Li(O)	–3.304	–3.320	–3.320
La(II)-La(O)	–2.877	–2.882	–2.912
Y(III)-Y(O)	–2.589	–2.864	–2.894
Nd(III)-Nd(O)	–2.819	–2.824	–2.854
Gd(III)-Gd(O)	–2.788	–2.793	–2.823
H_2 (g)-H(I)	–2.80	–2.98	–3.11
Mg(II)-Mg(O)	–2.580	–2.580	–2.580
Zr(IV)-Zr(II)	–1.864	–1.880	–1.970
Mn(II)-Mn(O)	–1.849	–1.849	–1.849
Hf(IV)-Hf(O)	–1.827	–1.835	–1.880
Zr(IV)-Zr(O)	–1.807	–1.815	–1.860
Al(III)-Al(O)	–1.762	–1.767	–1.797
Zr(II)-Zr(O)	–1.75	–1.75	–1.75
Ti(II)-Ti(O)	–1.74	–1.74	–1.74
Ti(III)-Ti(O)	–1.60	–1.61	–1.64
V(II)-V(O)	–1.533	–1.533	–1.533
Ti(III)-Ti(II)	–1.32	–1.34	–1.43

ard electrodes and with different concentration scales. Some of the commonly used emf series in respect of molten salts are based on the following: (i) the lithium chloride–potassium chloride eutectic composition at 450 °C; (ii) an equimolar mixture of sodium chloride and potassium chloride in the temperature range of 700–900 °C; (iii) the magnesium chloride–sodium chloride–potassium chloride eutectic composition at 475 °C; (iv) the aluminum chloride–sodium chloride–potassium chloride eutectic composition at 218 °C; (v) the lithium sulphate–potassium sulfate eutectic composition at 423 °C; and (vi) the sodium fluoride–potassium fluoride eutectic composition at 850 °C. One of these (in lithium chloride–potassium chloride) is shown in Table 6.16. In some of these series Pt^{2+}/Pt has been chosen as the reference electrode, while in others Ag^{+}/Ag has been used. The listing is then made, considering the potential of these electrodes to be zero under the standard conditions defined for the respective series. Such series, like the standard emf series, are useful in predicting the behaviors of various ionic species in electrolytic processes. With respect to any chosen ion/metal couple, all the other ionic species can be divided into two categories in any series, just as in the case of the electromotive (i.e., electrochemical) series. The first category comprises the group of nobler metals. The members of this group are less reactive with respect to the chosen metal and they are normally the first to electrodeposit cathodically. The baser metals are grouped in the second category. These metals are more reactive with respect to the chosen metal and, therefore, do not readily electrodeposit.

6.5.7
Process Classification

Irrespective of whether an aqueous or a molten salt medium is used, the main groups of electrolytic processes include electrowinning, electrorefining, electrosynthesis, electroextraction, electroplating, and electroforming. The main objective in electrowinning, electrorefining, and electroextraction is to achieve a high recovery of the metal in as pure a form as possible. Electrosynthesis, however, accomplishes the production of chemical compounds. Electroplating simply involves the deposition of a fine metallic covering layer on another material to improve the surface characteristics of the latter, from both aesthetic and technical viewpoints. Electroforming refers to the manufacture of metal articles entirely by electroplating. Besides these processes, there is also a process which can be called electroleaching, the main objective of which is to solubilize the metal values either from the anode feed or from the mineral particles which are circulated in the form of a slurry between the electrodes. The electrochemical process generates an adequate quantity of a suitable lixiviant to solubilize the metal values without much of side reactions. The occurrence of a simultaneous deposition of a product at the cathode, when feasible, could be an added incentive for the process.

6.6
Technological Aspects

6.6.1
Electrodes

In general, the physical state of the electrodes used in electrochemical processes is the solid state (monolithic or particulate). The material of which the electrode is composed may actually participate in the electrochemical reactions, being consumed by or deposited from the solution, or it may be inert and merely provide an interface at which the reactions may occur. There are three properties which all types of electrodes must possess if the power requirements of the process are to be minimized: (i) the electrodes should be able to conduct electricity well, i.e., they should be made of good conductors; (ii) the overpotentials at the electrodes should be low; and (iii) the electrodes should not become passivated, by which it is meant that they should not react to form on their surfaces any compound that inhibits the desired electrochemical reaction. Some additional desirable requirements for a satisfactory performance of the cell are that the electrodes should be amenable to being manufactured or prepared easily; that they should be resistant to corrosion by the elements within the cell; that they should be mechanically strong; and that they should be of low cost. Electrodes are usually mounted vertically, and in some cases horizontally; only in some rare special cases are they mounted in an inclined manner.

6.6.2
Electrolytes

The electrolytic cells in use in extractive metallurgy mostly operate with liquid electrolytes which may be either aqueous or nonaqueous. In some cases it is possible to use only nonaqueous electrolytes, while in others it is possible to use either aqueous or nonaqueous electrolytes. A nonaqueous electrolyte may be of the organic or of the molten salt varieties. In most metallurgical operations, either aqueous or molten salt electrolytes are used; only very rarely may an organic electrolyte be selected. The selection of the most suitable electrolyte is based on a variety of considerations. The choice of an electrolyte for lead, for example, is guided by the facts that lead forms an insoluble sulfate if sulfuric acid is used, and that a peroxide of lead is formed in solutions of other mineral acids. An electrolyte of lead fluorosilicate in hydrofluorosilicic acid (H_2SiF_6) is used in order to circumvent these problems.

An electrolyte can essentially be regarded as being composed of a functional component (which is essentially a compound of the metal to be electrodeposited) and an auxiliary electrolyte that acts as a solvent for the functional component. In the case of aqueous electrolysis, water is the solvent and the chosen salt is the functional electrolyte. The salt should preferably be ionic, or at least partially ionic, so that on dissolution in water it becomes ionized and the ionic species produced take part in the electrochemical reaction. Acids are added to aqueous electrolytes to lower their electrical resistance. They are preferred since they do not introduce extraneous ions which can discharge at the cathode. It must, however, be borne in mind that too high an acid concentration can lead to hydrogen discharge and thereby impair the electrodeposition process. Other additives are invariably added to achieve a desired form of the deposit (morphology and properties of the deposit) and for improving the process efficiency.

A difference between electrolytes in solution and in the molten state is that the latter, in general, do not need solvents to dissociate. When an electrolyte exists in the molten state as the only component present and not as a solution of one electrolyte in another molten electrolyte, all phenomena associated with the ionic concentration during electrolysis, such as concentration polarization, cease to be relevant.

In the case of molten salts, the functional electrolytes are generally oxides or halides. As examples of the use of oxides, mention may be made of the electrowinning processes for aluminum, tantalum, molybdenum, tungsten, and some of the rare earth metals. The appropriate oxides, dissolved in halide melts, act as the sources of the respective metals intended to be deposited cathodically. Halides are used as functional electrolytes for almost all other metals. In principle, all halides can be used, but in practice only fluorides and chlorides are used. Bromides and iodides are thermally unstable and are relatively expensive. Fluorides are ideally suited because of their stability and low volatility, their drawbacks pertain to the difficulty in obtaining them in forms free from oxygenated ions, and to their poor solubility in water. It is a truism that aqueous solubility makes the post-electrolysis separation of the electrodeposit from the electrolyte easy because the electrolyte can be leached away. The drawback associated with fluorides due to their poor solubility can, to a large extent, be overcome by using double fluorides instead of simple fluorides. Chlorides are widely used in electrodeposition because they are readily available in a pure form and have high solubilities in water. The main drawback of chlorides lies in their high hygroscopicity. Some of the chlorides and/or fluorides are partially covalent and partially ionic. In general, covalent halide compounds have low boiling/sublimation temperatures and are, therefore, difficult to retain in the bath. The retentivity of such halide compounds can be improved by changing the oxidation state and by complexing. Titanium tetrachloride, for instance, is a covalent compound and is extremely difficult to retain in the electrolyte; however, titanium trichloride and dichloride are partially ionic and can be easily retained in the electrolyte. As an example of complexing, mention may be made of Na_2ZrCl_6; it is in this form that zirconium chloride is retained in a molten salt bath.

The auxiliary electrolyte is generally an alkali metal or an alkaline earth metal halide or a mixture of these. Such halides have high decomposition potentials, relatively low vapor pressures at the operating bath temperatures, good electrolytic conductivities, and high solubilities for metal salts, or in other words, for the functional component of the electrolyte that acts as the source of the metal in the electrolytic process. Between the alkali metal halides and the alkaline earth metal halides, the former are preferred because the latter are difficult to obtain in a pure anhydrous state. In situations where a metal oxide is used as the functional electrolyte, fluorides are preferable as auxiliary electrolytes because they have high solubilities for oxide compounds. The physical properties of some of the salts used as electrolytes are given in Table 6.17.

Table 6.17 Physical properties of some salts.

Compound	*Melting point K*	*Boiling point K*	*Specific conductance Ohm^{-1} cm^{-1} at 1200 K*	*Decomposition potential E at 1073 K**
Nb_2O_5	1758	3200	360	–
MoO_3	1068	1428 (s)	1.700	–
NaCl	1073	1686	4.49	3.24
KCl	1063	1773	3.24	3.441
RbCl	988	1663	2.55	3.314
CsCl	918	1573	2.27	3.362
$CaCl_2$	1045	1873	2.79	3.323
$MgCl_2$	987	1691	2.58	2.46
NaF	1245	1977	5.493	3.781
KF	1130	1773	6.133	3.63
$TiCl_4$	250	409	–	1.784
$TiCl_3$	723 (d)	698 (s)	–	2.154
$ZrCl_4$	711	–	–	2.266
$HfCl_4$	707	592 (s)	–	2.537
VCl_2	1300	1650	–	2.103
$MoCl_5$	467	541	–	0.597
$CrCl_2$	1088 (s)	1573	–	1.370

d = disproportionates; *s* = sublimes, * = calculated from ΔG^0 values.

The composition of the electrolyte is quite important in controlling the electrolytic deposition of the pertinent metal, the chemical interaction of the deposit with the electrolyte, and the electrical conductivity of the electrolyte. In the case of molten salts, the solvent cations and the solvent anions influence the electrodeposition process through the formation of complexes. The stability of these complexes determines the extent of the reversibility of the overall electroreduction process and, hence, the type of the deposit formed. By selecting a suitable mixture of solvent cations to produce a chemically stable solution with strong solute cation–anion interactions, it is possible to optimize the stability of the complexes so as to obtain the best deposition kinetics. In the case of refractory and reactive metals, the presence of a reasonably stable complex is necessary in order to yield a coherent deposition rather than a dendritic type of deposition.

A special phenomenon which sometimes occurs during the electrolysis of molten electrolytes is the so called anode effect. As a consequence of this effect, the regular evolution of gas at the anode ceases, and the molten mass gets separated from the anode which is no longer wetted. A number of voltaic arcs are now formed between the molten mass and the anode; the ohmic resistance of the cell increases markedly and as a consequence the applied voltage rises and the current density falls. It can thus be said that the anode effect is characterized by the formation of a gaseous sheath around the electrode which prohibits it from having a physical contact with the electrolyte. This effect will be discussed in greater detail later in the text, in the context of aluminum electrolysis.

6.6.3
Current Efficiency

The current efficiency of an electrolytic process is a measure of the current or the charge actually used in carrying out the desired electrochemical reaction as compared to the theoretical requirement. It is, therefore, defined as the ratio of the theoretical current requirement to the actual current requirement for the desired reaction; alternatively, it may also be expressed as the ratio of amount of material actually deposited at the electrode to that which should have deposited on the basis of Faraday's law, by the passage of the same charge, assuming that no side reactions take place at the electrode. The current efficiency, can be expressed as

Current efficiency,

$$\begin{aligned}\eta &= \frac{\text{Theoretical current requirement}}{\text{Actual current requirement}}\\ &= \frac{\text{Material actually deposited on the electrode}}{\text{Material that should have deposited theoretically with the same charge}}\end{aligned}$$

The current efficiency may range from 25–30% to as high as 90–100%. The loss in efficiency may be due to several factors which influence the chemical and the electrochemical reactions at the electrodes. For example, factors such as the occurrence of side reactions, the passage of current by electronic conduction, and the dislodging of the deposited product from the electrode may substantially reduce the value of η. In general, the current efficiency depends on many factors such as the current density, the presence of additives and/or impurities in the electrolyte, the composition and the properties of the electrolyte, the electrolysis temperature, and the nature of the electrodes and of the electrodeposit. The current efficiency normally increases with increasing current density. In a fused salt electrolyte system, the current density and the current efficiency are empirically related as

$$\eta = 100 - k\,I^{-n}$$

where I is the current density and k and n are constants. This relationship indicates that the current efficiency is low at low current densities and that it increases with increasing current density. However, increasing the cathode current density beyond a certain value results in a decrease in the current efficiency, mainly due to the poor adherence of the cathode deposit. It is, therefore, necessary to experimentally determine the optimum current density required for obtaining the maximum current efficiency.

Electrolysis in molten salts obeys Faraday's laws, although the demonstration of their validity is sometimes very difficult, as mentioned earlier. In fact, often during the electrolysis of molten electrolytes there are considerable and not readily avoidable losses in the current efficiency. Some of the causes of such losses are: (i) evaporation or distillation of metal separated in the molten state; (ii) secondary reactions between the separated molten metal and the materials with which it comes into contact; and (iii) the solubility of the metal in the electrolyte. The latter cause appears to be the main one leading to a loss in current efficiency.

As mentioned earlier, the current efficiency also depends on the presence of additives and/or of impurities which may co-deposit or may influence the electrochemical reaction or may affect the overvoltages of the desirable and the undesirable reactions. The impurities which are more noble would be deposited; this would not only contaminate the metal but would also consume charge for undesirable reactions. Additives may be deliberately added when depositing alloys, so that the deposition potentials of the different metals involved could be brought closer; however, in most other cases these are considered as harmful impurities. The electrolyte, therefore, needs to be purified with respect to such impurities in order to improve the current efficiency.

The composition of the electrolyte affects the ionic and the electronic conductivities and the stability of chemical complexes for aqueous as well as for molten salt systems. The higher the electronic conductivity, the lower would be the current efficiency. In molten salt systems the composition also affects the melting temperature and the viscosity of the electrolyte. All these factors affect the nature of the deposit and also the current efficiency, particularly in molten salt electrolytic processes. Generally, a high concentration of the solute (functional electrolyte) brings down the melting temperature and increases the mass transfer rate, thus permitting the use of a high current density. In some cases, however, a high concentration of the solute increases the solubility of the electrodeposited metal and may also lead to polymerization, thus reducing the electrical conductivity of the electrolyte.

The electrolysis temperature affects the electrolyte conductivity, the overpotential, and the solubility of the electrodeposit in aqueous as well as in molten salt systems. The effect of temperature is particularly important in the latter case. The lower limit of the temperature of operation is set by the liquidus temperature of the bath and the solubility of the solute. Generally, the temperature chosen is at least 50 °C above the melting temperature of the bath, at which temperature the viscosity of the molten salt is almost the same as that of water at room temperature. The maximum temperature that can be used is limited by the stability of the bath, the volatilization of the functional electrolyte, the corrosion of the cell materials, the solubility of the electrodeposits in the electrolyte, and the degradation in the nature of the deposit. An increase in the electrolysis temperature normally results in an increase in the current efficiency, both in aqueous and in molten salt systems, due to increased electrical conductivity, reduced overpotential, enhanced mass transfer rates, and increased rates of crystal growth. However, a higher temperature also leads to an increased solubility of the electrodeposited metal, and this tends to bring about a reduction in the current efficiency.

The current efficiency also depends on the nature of the electrode and of the electrodeposit. Generally the current efficiency is high with electrodes which do not specifically polarize with respect to the desired reaction. The current efficiency is observed to be low when a powdery or a dendritic type of deposit is formed on the electrode. This is because of the relatively poor adherence of such deposits which results in mechanical loss and also because of the possibility of electrical short-circuiting between the electrodes, resulting in flow of an electrical current which does not contribute to the electrochemical reaction.

6.6.4
Energy Efficiency

The energy efficiency is defined as the amount of energy consumed in the production of unit quantity of the product. It can be expressed in terms of kWh per kg of the product, and also as the ratio of the minimum energy required theoretically to that actually used in producing a certain quantity of the product. The minimum energy required for forming a given quantity of the product can be theoretically obtained from the relevant data on the reversible potentials at the anode and at the cathode and from a knowledge of the fraction of the current which causes the electrochemical reaction. The actual energy consumed is the product of the cell voltage and the actual current used, and both these depend on the cell configuration and the general layout. Thus the energy efficiency can be expressed as:

$$\text{Energy efficiency} =$$

$$\frac{\text{Theoretical cell voltage} \cdot \text{Fraction of current required for desired reaction}}{\text{Actual cell voltage} \cdot \text{Actual current}}$$

Since the ratio of the fraction of the current used for the desired reaction to the actual current passed is the current efficiency, one obtains the following relationship:

$$\text{Energy efficiency} = \text{Current efficiency} \cdot \frac{\text{Theoretical cell voltage}}{\text{Actual cell voltage}}$$

In electrorefining and in electroplating, where the same metal is used as a soluble anode, the theoretical cell voltage is zero or almost zero; therefore, the energy efficiency, as per this definition, is expected to be zero or close to zero, whatever may be the current efficiency. The actual cell voltage depends on the current density, the temperature, the electrolyte composition, the overvoltages due to concentration polarization in the electrolyte and activation polarization at the electrode, and the ohmic losses within and outside the cell. The energy efficiency thus depends on all these factors. From this it would appear that all the factors which increase the actual cell voltage would reduce the energy efficiency; but this is not so because most of these factors also influence the current efficiency and it is the combined effect of all these that has a bearing on the energy efficiency. It is, therefore, necessary to determine experimentally the conditions which provide a high current efficiency with a low expenditure of energy.

6.6.5
Cell Features

Several factors are considered in the design of an electrolytic production cell. These include: (i) the nature of the product desired, the starting materials, and the level of production to be achieved; (ii) the current density, the current efficiency, the permissible recovery, and the electrolysis temperature; (iii) the compatibility of the container material with the electrolyte and of the electrodes with the electrolyte; and (iv) any specific requirements associated with the handling of the electrode products.

With a knowledge of the target of production and of the results of laboratory studies on the expected current density and the current efficiency, the minimum cathode area required can be determined by using the following relationship:

$$\text{Cathode area} = \frac{\text{Production rate}}{\text{Current density} \cdot \text{Current efficiency} \cdot \text{Electrochemical equivalent}}$$

It is then necessary to consider the electrode geometry to arrive at the number of cells needed, and also the cell layout to be used in order to match the available power supply in terms of current and voltage. The cell may be monopolar or bipolar, depending on the manner in which the electrodes are inserted into the circuit. This is carried out in two ways.

The insertion is monopolar when the electrode functions exclusively as either the anode or the cathode; and in this case it is connected with one of the poles of the electric source as shown in Figure 6.22 (a–f). Since the voltage for a single cell is very small (of the order of one to a few volts) several cells are usually connected in series and parallel combinations such that the overall potential drop corresponds to the available direct current power source. With bipolar insertions, however, there are a number of electrodes in each cell which function as anodes on one side and as cathodes on the other; apart from the end electrodes, these are not directly connected to the electric source.

Electrolytic cells are constructed of materials that can withstand the action of the electrolytes and of the electrode products. The cell may be of the open type or may be partially or fully closed, depending on the requirement of handling the electrode products. Some of these cells will be described while dealing with the production of specific metals. Very stringent requirements are imposed when considering the design of electrolytic cells for the deposition of refractory and reactive metals. Most of such metals are produced by using molten salt electrolytes. These metals are prone to atmospheric contamination at the electrolysis temperature, and it is thus necessary to operate the cell under an inert atmosphere.

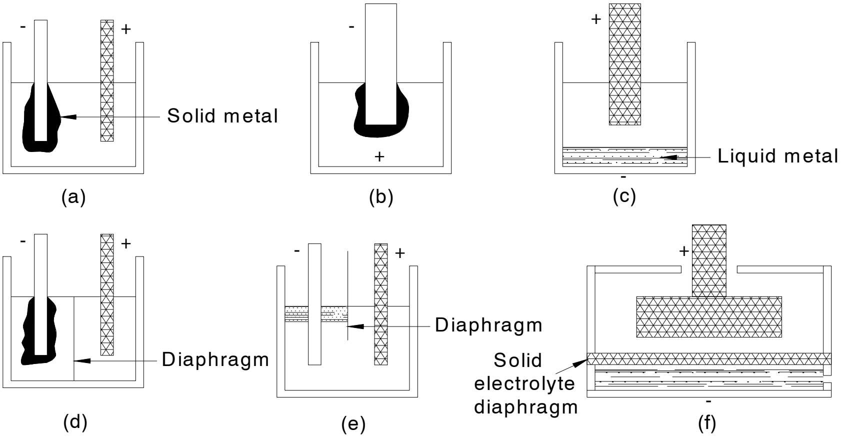

Figure 6.22 Schematic diagrams of electrolytic cells for metal extraction from moltent salts: (a–f) monopolar cells.

For continuous or semicontinuous operation, special care has to be taken in handling the hot electrodeposits without exposing the electrolyte to the atmosphere. Except in a very few cases, the metals are deposited in the solid state; the cell, therefore, should have a provision for cooling the deposits in a protective atmosphere. Generally, the cell is vacuum tight and has an arrangement for purging with an inert gas. In its simplest form, the electrolytic cell consists of an electrolyte chamber and a receiving chamber located above it, with a slide valve in between the two. The electrolytic chamber contains the molten electrolyte and has a provision for the insertion of the cathode and the anode. The receiving chamber is essentially meant for receiving the hot electrodeposits for cooling to room temperature before exposing them to the atmosphere and for inserting a new cathode for continuing the electrolysis. The slide valve essentially acts as a barrier to prevent the exposure of the molten electrolyte to atmospheric contamination during the changing of electrodes. A few cell configurations used for the electrodeposition of some of the refractory metals are shown in Figures 6.23 and 6.24.

Inert atmosphere laboratory-scale cells for carrying out molten salt electrolysis are usually of metallic construction and are electrically heated from outside. The construction material, therefore, has to withstand external oxidative corrosion and internal corrosion from the vapors of the molten salt and from the anode gases (if evolved). These cells are usually fabricated from inconel 600 or hastelloy C and have a liner of impervious graphite for containing the molten electrolyte. Larger electrolytic cells are constructed of a metallic shell lined inside with a refractory which may further have a graphite lining to contain the electrolyte. When a graphite lining cannot be used because of chemical interactions, a solid salt crust formed on the refractory surface serves to contain the molten electrolyte. In such cells, heating from an external source is not practicable due to the poor thermal conductivity of the refractory lining and these cells are generally internally heated. In some cases, however, premelted electrolyte is poured into the electrolytic cell and the electrolysis temperature is then maintained by the direct current itself by Joule heating. When the heat generated is large, some cooling may become necessary.

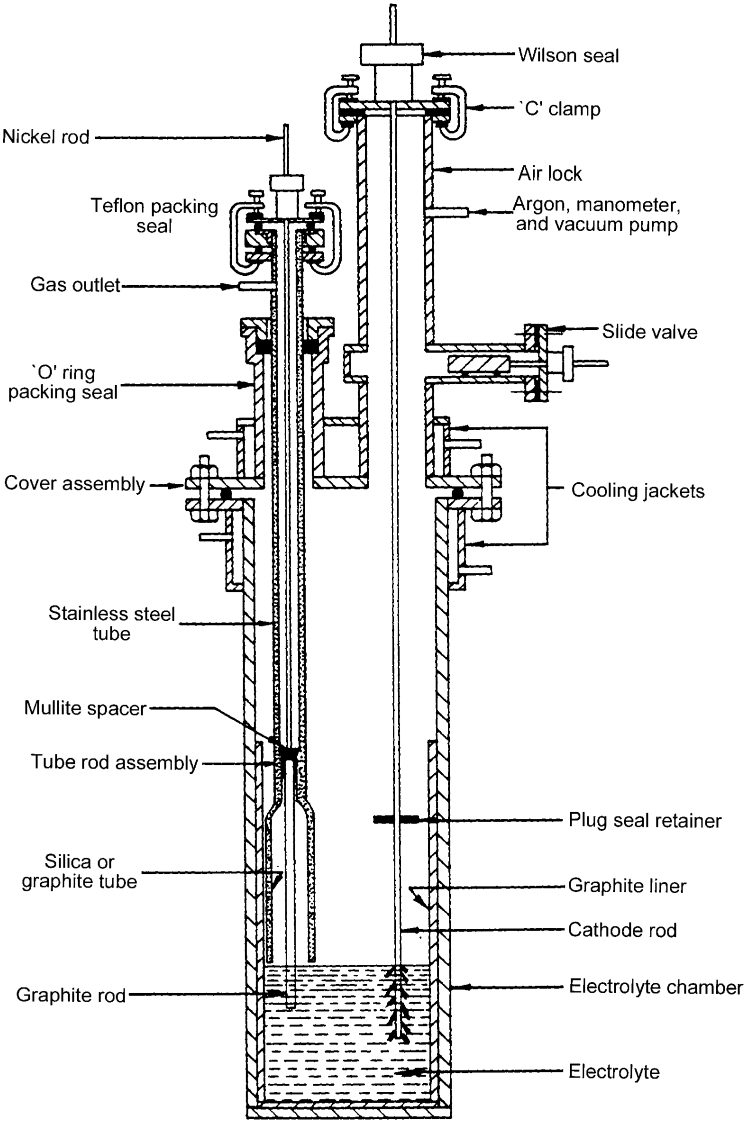

Figure 6.23 Electrowinning cell.

An account of cell features should make a reference to the diaphragm. The diaphragm used in some electrolytic processes is essentially constituted of a separator wall, though this allows the free passage of the electric current. It performs the important function of preventing the products of electrolysis formed at the anode from coming into contact with those formed at the cathode so as to avoid, as far as feasible, either secondary reactions which would lower the current efficiency, or contamination of the products which would diminish their value.

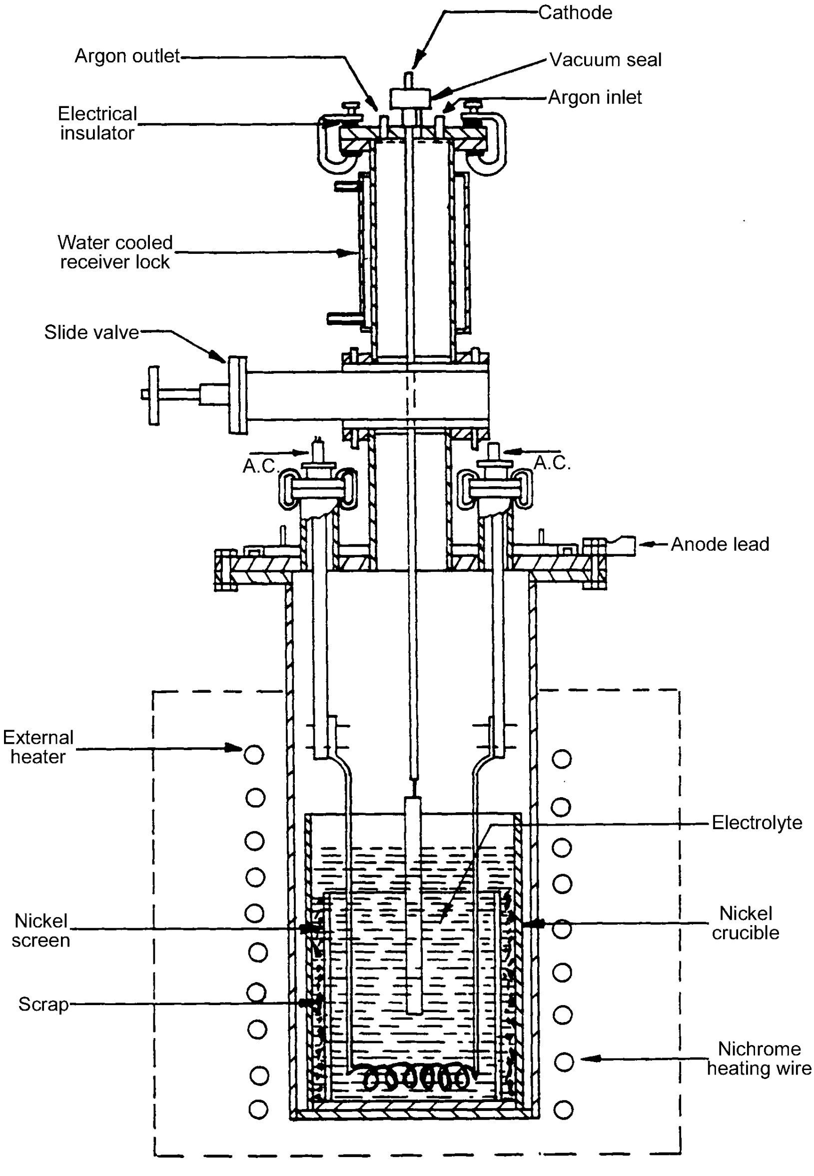

Figure 6.24 Internally-heated electrorefining cell.

When the products which have to be separated are gaseous or solid, the diaphragm assumes the function of a filter rather than that of a true diaphragm. For gases, the diaphragm often consists of a metallic division in the form of a plate or a mesh, with holes of a slightly smaller diameter than that of the gas bubbles. When such a metallic diaphragm is used, however, it is necessary that the electric potential between the two electrodes is less than twice the decomposition voltage of the electrolyte; otherwise, the metallic diaphragm might function as a bipolar electrode. Alternatively, the diaphragm may consist of a fabric which is compatible with the electrolyte. When the products which have to be separated are solid and it is essential for some reason that they do not reach the other electrode, the diaphragm may consist of a solid, porous divider; more frequently, however, it consists of a woollen sheath or a canvas of a fairly fine material, enclosing one of the two electrodes.

6.6.6
Cell Design Optimization

The design optimization of an electrolytic cell aims at a high throughput with a low energy consumption at the lowest feasible cost. The throughput of an electrochemical reactor is measured in terms of the space time yield, Y_t, defined as the volumetric quantity of the metal produced per unit time per unit volume of the process reactor. This quantity is expressed as:

$$Y_t = \frac{\text{Volume of product (in m}^3\text{)}}{\text{Electrolysis time (in h)} \cdot \text{Cell volume (in m}^3\text{)}}$$

The volume of the metal produced depends on the current density, the electrolysis time, the cathode area, and the electrochemical equivalent. Y_t is usually expressed as a function of the current density. The interrelationship among Y_t, the specific area of the cathode, A_s (m^2/m^3), i.e., the area of the cathode per unit volume of the reactor (cathode area/volume of the cell), the fractional current efficiency, η, and the current density, I, is given by:

$$Y_t = Q_E \cdot I \cdot A_s \cdot \eta$$

In the above relationship, Q_E is the volumetric quantity of the metal deposited per ampere hour at a current efficiency of 100% (i.e., when $\eta = 1$) as per Faraday's law, and can be obtained from the relationship:

$$Q_E = \frac{3600 \cdot \text{Atomic weight}}{n \cdot F \cdot \rho_m} = \frac{3600 \cdot \text{Electrochemical equivalent}}{F \cdot \rho_m}$$

where n is the number of moles of electrons transferred per mole of the product (i.e., the number of electrons taking part in the electrochemical reaction), the atomic weight divided by n is the electrochemical equivalent, F is Faraday's constant (96,500 coulombs per mole electrons) and $\grave{Q}_m$ is the density of the product in kg m^{-3}.

The space time yield, therefore, depends on the current density and the specific cathode area. In an electrolytic cell, the specific cathode area is generally very small; thus the space time yield is low as compared to most of the pyrometallurgical reactors. A good cell design should aim at obtaining a high value of the space time yield.

The other important factor in cell design optimization is the specific energy consumption, e_s, defined as:

$$e_s = \frac{I \cdot A_s \cdot E_{cell}}{Y_t \cdot \rho_m}$$

where E_{cell} is the cell voltage at the current density I. For a good cell design, e_s should have a low value. To achieve this it would be desirable to operate the cell at a low current density, with a low specific area of the cathode, at a low cell voltage. However, lowering the values of the cathode current density and the specific cathode area lowers the value of Y_t. Thus, it is necessary to maximize Y_t as a function of I and at the same time minimize the value of e_s as a function of I. These twin objectives can be realized by undertaking a dynamic analysis of the system or by actually carrying out the relevant experimental studies. The specific energy consumption also depends on the cell voltage, E_{cell}. Of the many components constituting the cell voltage, the ohmic losses can be readily controlled to reduce E_{cell}. This is achieved by optimizing the anode–cathode spacing and the electrode configuration. The narrower the gap between the anode and the cathode, the lower would be E_{cell} and correspondingly the lower would be the value of e_s. However, too narrow a gap between the anode and the cathode would lead to a low value of the current efficiency for certain types of electrolytic mass transport processes. An optimization of the cell design with respect to E_{cell} for a specified current density can be accomplished either through experimental studies or by using empirical relationships already established for similar types of cells.

The electrochemical method as such is highly capital intensive because of many factors. These include: (i) a relatively low space time yield due to physical limitations with regard to introducing large area electrodes in a given cell volume and also to feeding a very high power into a given cell; (ii) the conversion of the conventional ac power to dc and the passage of the dc power through massive bus bars of copper or aluminum which need expensive equipment; (iii) the requirement of a careful control of the air quality in the cell rooms to reduce the effects of noxious fumes and acid mists on operating personnel; (iv) the need to maintain a careful control on feed preparation because many of the impurities, if not removed initially, may find their way into the final product as contaminants; and (v) the expensive nature of electricity, which is needed in large quantities.

6.7
Cell Operation

The incorporation of desirable features by way of materials selection and design optimization with regard to the cell does not always ensure a successful electrodeposition of metals. The operational aspects of the cell are particularly important in molten salt electrolyte systems. The most important of these is the purity of the salts chosen in preparing the electrolyte; generally these should be as pure as possible, free from noble metal impurities and moisture. Moisture is a very deleterious impurity which may contribute to the contamination of the product. It is, therefore, necessary to ensure that all the salts used are made moisture-free by hot evacuation at high temperatures, either separately before charging into the electrolytic cell or within the electrolytic cell in the course of attaining the operating temperature. When the salts used for the preparation of the electrolyte are highly hygroscopic, it may be necessary to treat the molten salt with dry hydrogen chloride gas or with other chlorinating or halogenating agents for the removal of moisture and/or oxyhalide salts.

The preparation of molten salt electrolytes is relatively simple if all the chosen salts are nonvolatile at the operating temperature. The salts are weighed, mixed, and charged directly into the electrolytic cell. If the functional electrolyte is volatile, then it can be charged in two different ways. At first, the molten salt bath is formed by melting the components of the carrier electrolyte. The functional electrolyte (i.e., the volatile component) is then either formed in situ by a direct reaction of the constituent elements or is quickly immersed in the molten bath.

The salts used for preparing the electrolyte should be as pure as possible, but during the process of its formation the electrolyte may pick up certain impurities, or cost considerations may limit the selection of the salts to those with some amounts of impurities. If the salts contain noble metal impurities, it would be necessary to purify the electrolyte by pre-electrolysis at low operating voltages (in the range of 1.5–2.0 V) which should be less than the decomposition potential of the functional electrolyte so as to preferentially deposit the noble metals on a graphite or a steel cathode. Pre-electrolysis needs 10–40 amphere hours per kg of the electrolyte, and the required duration of this operation is judged by observing any sharp change in voltage. The preliminary stage is said to be over when the voltage reaches a value of 2.5–3.0 V. Pre-electrolysis also results in the removal of the last traces of oxygen which may be present in the electrolyte, either as moisture or as oxyhalides. After pre-electrolysis, the electrolyte is ready for the electrodeposition of the desired metal.

The electrolysis is started by connecting the electrodes to an external dc power source. While the liquid metals obtained in a molten salt process can be readily separated by draining out the metal, solid electrodeposits require careful handling. After the completion of an electrolytic cycle for a predetermined period, the deposits are separated from the electrolyte either by draining the molten salt or by lifting up the cathode. The nature of the cathode deposit depends on the operating conditions such as the cathode current density, the temperature, the concentration of the functional electrolyte, the type of the carrier electrolyte, and also on kinetic factors. The deposits may be coherent, dendritic, or powdery. Coherent deposits require cell operation under highly controlled conditions, with electrolytes containing ionic complexes of appropriate stability.

Polycrystalline deposits with rounded grains are obtained at high overvoltages. Long needles and dendritic types of deposits are usually obtained when the cell is operated at the limiting current density under the regime of diffusion-controlled mass transport and concentration polarization. Powdery types of deposits are obtained either as a result of the disproportionation of salts or as a result of secondary reactions occurring on a highly polarized cathode. The primary electrodeposition in such cases comprises the deposition of alkali metals from the carrier electrolyte which then chemically reduces the functional electrolyte to yield a loosely adherent powdery product at the cathode. The powdery and the dendritic types of deposits have been found to entrap substantial quantities of the electrolyte. Therefore, except in the case of coherent deposits and deposits in the form of liquids, the recovery of metals from the cathode deposit requires an elaborate scheme involving comminution, aqueous leaching, washing, drying, or sublimation to separate metal crystals from the accompanying salt. This is an involved process, requiring the expenditure of considerable amounts of energy; impurities may also be introduced during processing.

In general, the electrolysis of a molten salt at inert electrodes produces the metal at the cathode, e.g., calcium from calcium chloride (melting point 774 °C). The anion is often a halide ion which, on discharge, yields the halogen, e.g., chlorine from calcium chloride.

The metal may have a melting point below that of the salt, in which case it is in the molten state at the cathode. The molten metal will have little adhesion to a vertical cathode and, according to the relative densities of metal and salt, will sink to the bottom of the container or float to the melt surface. Since most metals yielded cathodically from melts are highly reactive at high temperatures, a layer of liberated metal on the surface of a melt may oxidize in the air or reunite with the product of the anodic process. If the cell is not designed properly the floating layer of metal may short circuit the electrodes. The same can take place when a dense metal accumulates to a sufficient depth beneath a melt so as to touch both the electrodes. In order to circumvent these problems the liberated metal itself can be made the cathode of the cell, and if the metal sinks in the melt, it may or may not be electrically connected to the containing vessel. The anode may itself be solid and vertical, the cathode being molten at the bottom of the container, or it may be liquid with the connections passing through the bottom of the container.

6.8
Electrowinning

A number of electrolytic processes are used for the industrial production of metals. Some metals such as zinc, copper, manganese, gallium, chromium, etc. are electrowon from aqueous baths. Another common electrolytic process used is molten salt electrolysis. The most important application of molten salt electrolysis till now has been in the electrowinning of metals. Today aluminum, magnesium, lithium, sodium, calcium, boron, cerium, tantalum, and mischmetal are produced in tonnage quantities by molten salt electrolysis. As a representative example, the electrowinning process for aluminum is taken up.

The first production of aluminum was by the chemical reduction of aluminum chloride with sodium. The electrolytic process, based on the fused salt electrolysis of alumina dissolved in cryolite, was independently developed in 1886 by C. M. Hall in America and P. L. Heroult in France. Soon afterwards a chemical process for producing pure alumina from bauxite, the commercial source of aluminum, was developed by Bayer and this led to the commercial production of aluminum by a combination of the Bayer and the Hall-Heroult processes. At present this is the main method which supplies all the world's needs in primary aluminum. However, a few other processes also have been developed for the production of the metal. On account of problems still waiting to be solved none of these alternative methods has seen commercial exploitation.

A consolidated picture of the different processes for the production of aluminum is shown in Figure 6.25. There are altogether four processes: (i) Alcan process; (ii) Toth process; (iii) Alcoa process; and (iv) Bayer process.

The Alcan (Aluminum Company of Canada) process is based on the direct reduction of the ore to form an aluminum alloy (by carbothermic reduction carried out in an electric arc furnace at about 2000 °C). The alloy is then reacted with aluminum trichloride at 1300 °C to form aluminum monochloride. The monochloride is next contacted with molten droplets of aluminum to form aluminum metal; the trichloride is regenerated for further reaction:

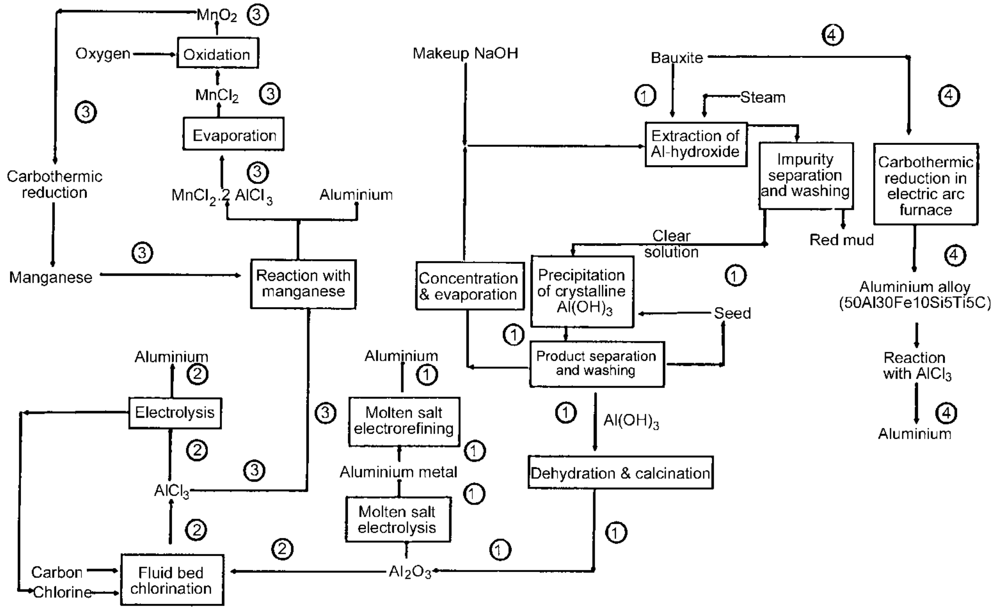

Figure 6.25 Flowsheets for Al extraction: stream
1 Bayer process, 2 Alcoa process, 3 Toth process, 4 Alcan process.

$$AlCl_3 + 2\ Al\ (alloy) \rightleftharpoons 3\ AlCl + 2\ Al + AlCl_3$$

$$8\ AlCl_3 + 3\ Mn = 2\ Al + 3\ (MnCl_2 \cdot 2\ AlCl_3)$$

$$Al_2O_3 + 3\ Cl_2 + 3\ C = 2\ AlCl_3 + 3\ CO$$

The Toth process is a pyrometallurgical process based on the formation of aluminum trichloride by chlorinating a mixture of alumina and carbon with chlorine at a temperature of 700–900 °C in a fluid bed reactor. The trichloride is then reduced with manganese at about 300 °C under 15 atm pressure. Aluminum trichloride is separated from the manganese chloride-aluminum trichloride melt by evaporation; chlorine gas is regenerated by the dechlorination of manganese chloride with oxygen at about 600 °C. The reductant manganese is obtained by the carbothermic reduction of manganese oxide. The chemical reactions occurring at the different stages are shown below:

$$MnCl_2 + O_2 \rightarrow MnO_2 \mid Mn_2O_3 + Cl_2$$

$$MnO_2 \mid Mn_2O_3 + 2\ C \rightarrow Mn + 2\ CO$$

The Alcoa (Aluminum Company of America) process involves the electrolysis of aluminum chloride which is carried out in a molten bath of the composition: 50% sodium chloride, 45% lithium chloride and 5% aluminum chloride, maintained at 700 °C. The Bayer process, which involves the production of pure alumina by the dissolution of bauxite with caustic soda and which has been described in the chapter on hydrometallurgy, must be taken into account while presenting a complete picture of the aluminum extraction flowsheet. It may, however, just be mentioned here that in the aluminum industry, the leaching of bauxite was usually conducted earlier in horizontal, mechanically-agitated autoclaves. Now most modern plants have adopted the continuous system in which 10 to 15 vertical autoclaves are connected in series. The pure alumina thus produced from bauxite forms the main source from which aluminum is produced by molten salt electrolysis.

Preparation of aluminum electrolytically from an aqueous solution is not possible because of the strongly negative potential of this metal. There are a number of reasons on account of which the metal cannot be prepared from a pure aluminum compound. The chloride possesses a very low conductance. It must be virtually considered to be a nonelectrolyte. Further, at ordinary pressures aluminum chloride sublimes (goes into the vapour state without melting). Other aluminum salts present various difficulties so that the focus is on aluminum oxide which is practically the only aluminum compound stable at high temperatures. Its melting temperature is above 2000 °C and so it cannot be electrolyzed in the pure molten state because the technical difficulties of constructing a furnace sufficiently large for an industrial process and operating at such a high temperature are very great. There would also be large losses of energy by radiation. The aluminum oxide must be dissolved in a suitable solvent which satisfies the following requirements: (i) it is required to be a good solvent for alumina; (ii) it should have a greater decomposition potential than alumina; (iii) it must be a good conductor; (iv) it should be free of impurities, particularly metallic ones, which would be deposited at a cathodic polarization less than that required to deposit aluminum; (v) it must have a low melting point, in order to minimise the loss of heat by radiation and to avoid the formation of aluminum carbide through the reaction of metallic aluminum with the carbon of the cathode; (vi) it must possess sufficient fluidity; (vii) it must have a density less than that of aluminum at the operating temperature; (viii) it must have a low vapour pressure; and (ix) it must not react with the electrodes or the products of electrolysis. The electrolyte whose properties best meet these requirements is cryolite: a double fluoride of sodium and aluminum, of the composition $3\,NaF \cdot AlF_3$, which should more strictly be considered as a complex fluoride, Na_3AlF_6.

The electrolysis of alumina is carried out in electrolyte cells made of mild steel which are lined inside with an insulating refractory and carbon (either carbon bricks or carbon and coal tar pitch). The cell bottom is connected to the cathode terminal and serves as the cathode. Carbon electrodes introduced from the top serve as anodes. A more detailed description is given below.

The aluminum industry, in its early days, used the so called pre-baked anodes. These were made in a separate plant, where they were pre-baked, and then transferred to the electrolytic plant, where they were consumed in the reduction process. Later the Norwegian engineer Soderberg introduced the large electrodes known by his name which were baked in place by the heat available at the top of the cell, thus not only eliminating electrode transportation but also saving in energy as compared to the pre-baking process. In the recent years, however, the pollution caused by the Soderberg electrodes, because of the emission of hydrocarbons during baking, has come to be regarded as unacceptable. The installation of ventilation and scrubbing systems renders the operation expensive. The industry is now switching back to pre-baked anodes. The anode connection is given through steel studs embedded in the carbon electrodes. The overvoltage of oxygen evolution on a pre-baked carbon electrode is lower than that on a Soderberg electrode. Therefore, the cell voltage and the energy consumption are lower when pre-baked electrodes are used; but a certain amount of energy is used up in making the electrodes. Figure 6.26 gives a diagrammatic view of a cell for aluminum production. Each cell usually has one or two rows of anodes, and a number of cells (also called pots) are connected to match the voltage available in the power supply. Cryolite, 3 NaF · AlF_3, melts at 1008 °C; the addition of alumina brings the melting point down to a lowest value of 958 °C which is attained when the melt contains 13.4% alumina. Beyond this eutectic composition of alumina the melting point rises and at 19.5% Al_2O_3 the melting point reaches 1050 °C. From the point of view of temperature it would appear best to operate the process at or near the eutectic composition, but working against this procedure are the facts that at such compositions the chemical conductivity of the melt is unacceptably low and its density is close to that of aluminum itself. The electrolyte is composed of cryolite (Na_3AlF_6) containing upto about 8% alumina; a higher alumina content is not preferred because it increases the electrolyte density. It is essential that the density of the electrolyte should always be less than that of molten aluminum which is 2.29 g/cm^3 at a temperature of 1000 °C; this is necessary to prevent aluminum from floating on the surface of the bath and reoxidizing with the oxygen evolved at the anode or with atmospheric oxygen. The electrolyte also contains some other additives for improving the cell performance. It has been observed that cryolite, with a slight excess of sodium fluoride, has a high electrical conductivity; but the use of such cryolite results in a reduced current efficiency. This may be due to the co-deposition of sodium at the cathode. An electrolyte with a slight excess of aluminum trifluoride (AlF_3), on the other hand, has a slightly reduced conductivity but yields a higher current efficiency. An improvement in the electrical conductivity can be brought about the addition of calcium difluoride (CaF_2) and/or magnesium difluoride (MgF_2). These additives also lower the melting temperature of the electrolyte, thereby permitting operation at lower temperatures. Generally the electrolysis is carried out at a temperature of 970 °C. An increase in the electrolysis temperature results in a decrease in the current efficiency, due presumably to the increased solubility of the electrodeposited metal in the molten bath. The electrolysis is carried out by melting the

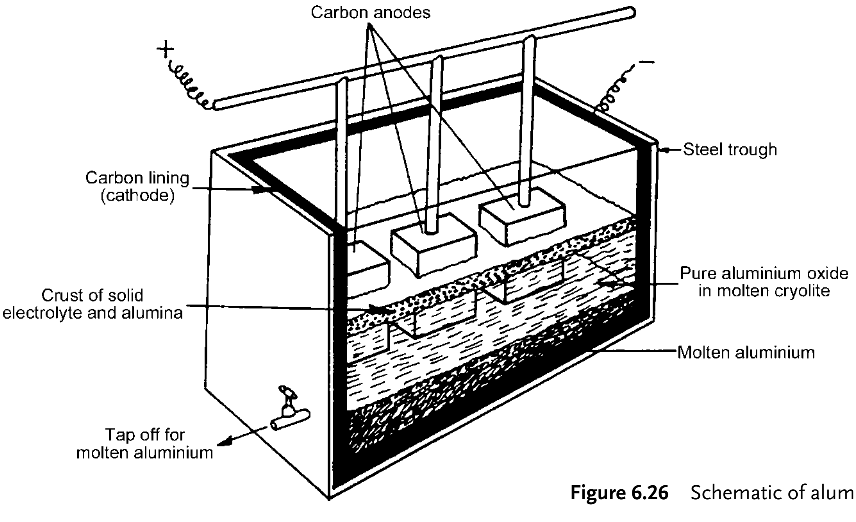

Figure 6.26 Schematic of aluminum cell.

cryolite in the cell by passing a current between the anodes and the cathode and then adding the requisite amounts of alumina and of fluoride salts of calcium, magnesium and lithium. On electrolysis, alumina decomposes to yield aluminum and oxygen. This oxygen combines with the carbon of the anode to form carbon dioxide and carbon monoxide. If the cell reaction were to comprise the following reaction:

$$Al_2O_3 = 2\ Al + 1.5\ O_2; \quad \Delta G^0_{970\,°C} = 305.5\ \text{kcal}$$

then one would have

$$E^0 = -2.21\ \text{V}$$

If the combination of oxygen and carbon at the anode is included in the electrochemical reaction then the free energy change is much smaller. For the reaction

$$Al_2O_3 + 1.5\ C = 2\ Al + 1.5\ CO_2; \quad \Delta G^0_{970\,°C} = 164\ \text{kcal}$$

so that

$$E^0 = -1.18\ \text{V}$$

In practice, the decomposition potential for this overall reaction is found to be about 1.5 V; this somewhat high value probably results from polarization and contact resistances. It could be seen that the electrochemical decomposition of alumina to deposit aluminum, using an inert anode, would require a theoretical cell voltage of 2.21 V as opposed to that of 1.18 V when carbon is used as the anode. Thus the participation of carbon in the cell reaction brings down the theoretically required cell voltage by almost 50%.

A comprehensive picture of the electrode processes occurring in aluminum electrolysis is shown in Figure 6.27. As indicated in this figure, alumina gets dissolved in cryolite with the formation of $AlOF_2^-$ and Na^+ ions. The former are dissociated into Al^{3+} and O^{2-} ions in the cathodic as well as in the anodic regions. The Al^{3+} ions are discharged at the cathode in several steps (not shown separately in the figure) and the oxygen ions are discharged at the anode with the evolution of carbon dioxide. The oxygen ions that are produced in the cathodic region combine with one-third of the Al^{3+} ions to form AlO_3^{3-} ions. These ions combine with AlF_3 molecules to regenerate the continuously dissociating $AlOF_2^-$ ions, which are consumed by the deposition of aluminum. The AlF_3 molecules involved in this recombination are obtained during the regeneration of cryolite from AlF_4^- and Na^+ ions. The AlF_4^- ions are generated in the reaction between the Al^{3+} and the F^- ions which are produced in the anodic region and which cannot be discharged there. The AlF_4^- ions are supplemented by the fluoride formed in the cathodic region. The processes occurring in the vicinity of the electrodes and in the bulk electrolyte constitute a closed chain, ensuring the dissolution of alumina, the recombination of cryolite and the deposition of aluminum at the cathode and of oxygen at the anode. The system is also in electrical equilibrium in that the same charge is transferred through the cathode and the anode in opposite directions.

In the aluminum electrowinning process a phenomenon called the “anode effect” is normally encountered when the alumina content in the electrolyte falls below 2%. The anode gets partially covered with a gas blanket and as a consequence, sparking occurs and the cell voltage fluctuates considerably due to frequent breaking and reestablishment of local contact between the anode and the electrolyte. A heavy current passes through the anode area

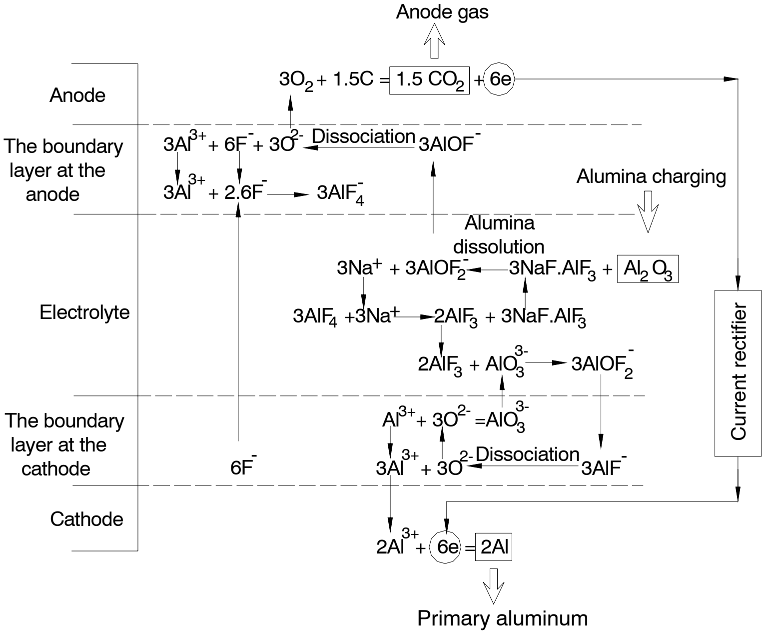

Figure 6.27 Anodic and cathodic processes involving aluminum.

which is in contact with the electrolyte, thereby causing localised superheating and vaporisation of the salt. As a result of the anode effect, the cell voltage may increase from 4–5 volts to 10–40 volts. It is generally assumed that this effect is mainly due to an insufficient wetting contact of the electrolyte with the anode. This situation is corrected by the addition of alumina to the electrolyte; this reduces the anode effect almost immediately and brings the cell back to its normal operation.

The Hall-Heroult process is a prodigious consumer of electrical energy. The energy required to produce 1 ton of aluminum from ore is more than twice that required to produce 1 ton of copper and ten times that for 1 ton of steel. More than 75% of this energy is consumed in the reduction of alumina to aluminum metal. The reasons for this high energy consumption have been presented in Table 6.18. The theoretical energy requirement for

Table 6.18 Reasons for high energy consumption in aluminum metal production.

1. High quality carbon anodes have to be prepared. These are consumed during the reduction of alumina by the oxygen generated. These consumables carbon anodes need frequent replacement. The changing of anodes is a labour intensive operation.
2. The anode and the cathode in the electrolytic cell have to be kept sufficiently apart to permit the formation of carbon monoxide and carbon dioxide and the smooth escape of these gases. This entails the use of a high voltage and thus involves a large energy consumption.
3. The collection and the processing of the effluent gases for minimising environmental pollution is difficult and expensive.

the production of aluminum is about 6.22 kWh per kg of the metal, whereas the best operating cells in the world today have an energy consumption of about 13.0 kWh per kg of aluminum and it is not practicable to reduce this energy consumption by any significant extent.

6.9
Electrorefining

The electrowinning processes essentially use anodes that do not dissolve anodically. In electrorefining, however, an impure metal is anodically dissolved as metal ions and subsequently these ions are reduced at the cathode to yield the pure metal; the cell reactions are:

Anode: $M_{\text{impure}} = M^{n+} + n\,\text{e}$

Cathode: $M^{n+} + n\,\text{e} = M_{\text{pure}}$

Anodic oxidation liberates some amount of energy whereas the cathode reaction consumes some energy. Thus, from the point of view of energy consumption, electrorefining is quite an efficient process which involves the overall reaction

$$M_{\text{impure}} \rightarrow M_{\text{pure}}$$

The standard free energy change (ΔG^0) for the above process is given by

$$\Delta G^0 = -R\,T \ln \frac{a_{\text{pure}}}{a_{\text{impure}}}$$

or

$$\Delta G^0 = -n\,F\,E^0$$

so that

$$E^0 = \frac{R\,T}{n\,F} \ln \frac{a_{\text{pure}}}{a_{\text{impure}}}$$

The quantities a_{pure} and a_{impure} denote the activities of the pure and the impure metals respectively. For a pure metal the activity a_{pure} is unity and thus $E^0 = -(R\,T/n\,F) \ln a_{\text{impure}}$. From this equation it can be noted that the potential requirement in electrorefining is quite small and that the process depends on the activity of the impure metal.

The purification obtained in electrorefining is based on the selectivity provided by the process itself. Electrorefining may, in principle, be carried out along two different paths, depending on the nature of the impurities to be removed. Either the impure metal forms the anode and the pure metal is concentrated in the cathode, or the impurities are selectively dissolved from the anode so that the purity of the metal constituting it increases. Although literature records electrorefining processes based on both these approaches, the former seems to dominate in commercial practice.

The metallic impurities present in an impure metal can be broadly divided into two groups: those nobler (less electronegative) and those less noble or baser (more electronegative) as compared to the metal to be purified. Purification with respect to these two classes of impurities occurs due to the chemical and the electrochemical reactions that take place at the anode and at the cathode. At the anode, the impurities which are baser than the metal to be purified would go into solution by chemical displacement and by electrochemical reactions whereas the nobler impurities would remain behind as sludges. At the cathode, the baser impurities would not get electrolytically deposited because of the unfavorable electrode potential and the concentration of these impurities would build up in the electrolyte. If, however, the baser impurities enter the cell via the electrolyte or from the construction materials of the cell, there would be no accumulation or build up because these would readily co-deposit at the cathode and contaminate the metal. It is for this reason that it is extremely important to select the electrolyte and the construction materials of the cell carefully. In actual practice, some of the baser impurities do get transferred to the cathode due to chemical reactions. As an example, let the case of the electrorefining of vanadium in a molten electrolyte composed of sodium chloride-potassium chloride-vanadium dichloride be considered. Aluminum and iron are typically considered as baser and nobler impurities in the metal. When the impure metal is brought into contact with the molten electrolyte, the following reaction occurs

$$2\ \mathrm{Al\ (metal)} + 3\ \mathrm{VCl_2\ (salt)} \leftrightarrow 2\ \mathrm{AlCl_3\ (salt)} + 3\ \mathrm{V\ (metal)}$$

whereas the reaction

$$\mathrm{Fe\ (metal)} + \mathrm{VCl_2\ (salt)} \rightarrow \mathrm{FeCl_2\ (salt)} + \mathrm{V\ (metal)}$$

does not occur (due to unfavorable thermodynamics). The amount of aluminum present in the cathode deposit can be calculated by considering equilibrium to have been established for the first displacement reaction. The equilibrium constant, K, is given by

$$K = \frac{(a_{\mathrm{AlCl_3}})^2 \cdot (a_{\mathrm{V}})^3}{(a_{\mathrm{Al}})^2 \cdot (a_{\mathrm{VCl_2}})^3}$$

With the progress of electrolysis the concentration of aluminum (and of other base impurities) increases; as a result of this the contamination of the cathode deposit also increases. A stage may be reached when the contamination exceeds acceptable limits, thereby calling for a premature termination of electrolysis. It is for this reason that it is desirable to purify and recycle the electrolyte wherever possible so that electrorefining could be conducted for extended periods, without having to contend with the problem of excessive contamination.

Electrorefining has been used for the purification of many common as well as reactive metals. It has been seen that the emf or the potential required for such a process is usually small because the energy needed for the reduction of the ionic species at the cathode is almost equal to that released by the oxidation of the crude metal at the anode. Some metals, such as copper, nickel, lead, silver, gold, etc., are refined by using aqueous electrolytes whereas molten salt electrolytes are necessary for the refining of reactive metals such as aluminum, zirconium, titanium, vanadium, etc. Brief accounts of the electrorefining processes adopted for two representative metals, one in aquatic medium and the other in fused medium are given in the following sections by way of examples.

6.9.1
Copper

In the copper electrorefining process, fire refined copper or blister copper is cast to form the anodes and the cathode is either a reusable stainless steel sheet or a thin sheet of electrodeposited copper which finally becomes a part of the refined cathode. The electrolyte is an acidified solution of copper sulfate.

The impurities in the crude copper consist of silver, gold, lead, bismuth, arsenic, antimony, iron, nickel, selenium, tellurium, oxygen, sulfur, zinc, cobalt, platinum, and traces of other elements. Of these, the more noble (Ag, Au, Pt) or the more electropositive are not anodically attacked and pass undissolved into the anodic sludge. Selenium and tellurium also remain undissolved as Ag_2Se and Ag_2Te; selenium and tellurium in excess of the silver combine with copper to form the equally insoluble CuSe and CuTe phases. Cuprous sulfide (Cu_2S) and, to some extent, cuprous oxide (Cu_2O) also remain undissolved. The processing of the slimes to recover the precious metals is a well recognized revenue earner in the copper industry. This represents a definite advantage of electrorefining over fire refining in which the precious metals, on account of their oxides being less stable as compared to those of copper, do not separate out. The more electronegative metals such as iron, nickel, cobalt, zinc, etc. readily pass into the solution electrolytically but, being much less noble, are not cathodically deposited. They accumulate in the solution unless they are precipitated chemically. For example, any lead in the anode is precipitated as lead sulfate and any tin will precipitates as an insoluble basic sulfate. Thus it is seen that some of the more electronegative metals may also be found in the anode slime. Arsenic, antimony and bismuth remain in the electrolyte; these are the most difficult to eliminate and also the most deleterious impurities. The standard electrode potentials for these three elements are very close to that for copper. It would thus be extremely difficult to separate copper from antimony, bismuth, and arsenic by purely electrolytic means. However, good results can be achieved by selecting a suitable electrolyte so that the greater part of these three elements passes into the anodic sludge as poorly soluble compounds. The most suitable electrolyte for this purpose is a solution of copper sulfate containing about 40 g/l of copper and 200 g/l of free sulfuric acid; this electrolyte also has other fundamental advantages. In this solution, antimony and bismuth, form poorly soluble compounds which collect in the anodic sludge. Arsenic also collects there particularly if some antimony is present. It is to be noted that a certain significant amount of arsenic oxidizes to arsenic acid; arsenic is deposited electrolytically from this acid only with difficulty, partly because the arsenic acid forms, with the bases present in the electrolyte, arsenates which tend to collect in the anodic sludge. The other two impurities which largely collect in the electrolyte are nickel and iron. The former increases the resistance of the electrolyte. The latter, on the other hand, lowers the current efficiency because it consumes electricity in oxidizing from the divalent to the trivalent state at the anode and in reducing from the trivalent- to the divalent state at the cathode. This is, in brief, the disposition of the impurities in the electrorefining of copper.

The other advantages which sulfuric acid has as an inert electrolyte are: (i) it increases the conductance of the bath; (ii) it is inexpensive; (iii) it strongly inhibits the hydrolysis of cuprous sulfate; (iv) it is nonvolatile and may be used at high concentrations and temperatures; and (v) it does not attack lead, so that it is possible to use this metal for plant construction. The only inconvenience of sulfuric acid is that copper dissolves in it essentially as the divalent ion; this means that the current consumption is double of that which would be consumed if the electrolysis were to be carried out in an electrolyte solution containing Cu^+ ions. Attempts to implement this alternative have not been very successful so that the use of sulfuric acid is yet to be challenged.

It is necessary to draw attention to two points in the context of the electrorefining of copper. First, as the electrolysis proceeds, the amount of free sulfuric acid gets depleted because it is fixed by all the less noble metals which remain in solution as well as by the Cu^+ ions which transform to Cu^{2+} ions by atmospheric oxygen. The fall in concentration of sulfuric acid promptly results in an increase in resistance. It may also cause hydrolysis of cuprous sulfate with the attendant precipitation of cuprous oxide. The insertion of an insoluble anode is often resorted to in order to circumvent this difficulty. The anodic process on this anode is the evolution of oxygen with a simultaneous regeneration of free sulfuric acid. Replacement of the acid is another option. Second, the concentration of Cu^{2+} ions must not be high in order that a good current efficiency may be obtained. During electrorefining some copper from the anode dissolves chemically also and as a consequence there is a build up of copper concentration in the electrolyte. It, therefore, becomes necessary to electrowin copper from the electrolyte so that the specified concentration level is maintained during the process of electrorefining. In general, it may be borne in mind that as electrolysis proceeds, the electrolyte becomes increasingly impure and also increasingly concentrated in copper sulfate. The periodic replacement of a part of the electrolyte with a fresh solution keeps the concentration of the impurities below the maximum acceptable level for a certain time. It follows that at more or less regular intervals the electrolyte must be completely renewed.

A cell used extensively for the refinement of copper uses the impure copper cast into slab-like anodes, 1 to 2 m long and a few centimeters thick. These anodes are suspended in an acid electrolyte between cathodes which start their life as thin starter sheets. The anodes are connected to the positive terminal of a dc power supply (via other cells placed in series), and the cathodes are connected to the negative terminal. The anodes are replaced when they become thin, and the cathodes are replaced by fresh starter sheets when they have grown in thickness by a few centimeters. This type of cell, as pointed out earlier, is known as a unipolar cell. An alternative design of the cell involves the use of bipolar electrodes. The flow of current in the cell is taken to occur from right to left. Only the end electrodes are connected to the external circuit; the other electrodes are insulated, apart from their contact with the electrolyte. Let any one of the insulated electrodes be considered. The inflow of current through the right hand side face would result in the deposition of copper on that face by the cathodic reaction. On the left hand side face, anodic dissolution of impure copper would occur. These bipolar electrodes would thus be progressively refined to pure copper. A brief comparison of the unipolar and the bipolar arrangements is presented in Table 6.19.

In comparison to electrorefining, the electrowinning process of copper, when using a copper sulfate-sulfuric acid electrolyte, presents an interesting situation. In the electro-

Table 6.19 Comparison between monopolar and bipolar electrolytic cells.

Monopolar cell	*Bipolar cell*
Advantages:	**Advantages:**
1. More impurities can be tolerated in the copper anode since the electrode distances are relatively large. 2. The fabrication of anodes and the operation of the electrolytic cell is relatively simple. 3. More suited for refining copper of varied impurity contents.	1. Energy losses are comparatively less because of small interelectrode distances and contacts are practically eliminated. 2. The refining cycle is shorter due to higher number of electrodes and the anodic residue is relatively small.
Disadvantages:	**Disadvantages:**
1. A large number of cathodes are needed. 2. There occurs a considerable loss of energy due to contact resistances. 3. The ohmic resistance of the cell is relatively more on account of electrode spacing being somewhat larger. 4. Due to impure anode there is a generation of larger amount of anodic residue. 5. The refining cycle is somewhat longer.	1. The starting copper must be fairly pure and the electrolyte must be kept at a relatively high level of purity. 2. The process is relatively more complex and requires careful control. 3. The fabrication of the anodes is generally by rolling which is more expensive than castings used for making anodes for monpolar cells. 4. There is a greater loss of precious metals. 5. More suited for refining copper having almost constant composition.

winning process, the cathodic reaction, $Cu^{2+} + 2\,e^- = Cu$ causes a depletion of Cu^{2+} ions, and the anodic reaction, $2\,OH^- = H_2O + 0.5\,O_2 + 2\,e^-$, causes a depletion of OH^- ions and consequently an increase in the number of H^+ ions because the dissociation $H_2O = H^+ + OH^-$ must take place in order to produce more OH^- ions. The SO_4^{2-} ions remain in solution so that the sulfuric acid concentration builds up. The spent electrolyte can, therefore, be used once again for leaching. It has thus been seen that while in electrorefining the concentration of copper in the electrolyte builds up, in electrowinning the sulfuric acid concentration builds up. The former is a consequence of a chemical reaction while the latter is a consequence of an electrochemical reaction.

Like that done in the case of zinc, a brief reference may be made here to a plant practice for copper. In James Bridge, U. K. an electrorefining tankhouse was completed in 1968. The initial designed plant capacity was 27,500 tons $year^{-1}$ at a current density of 175 Am^{-2}. The plant capacity was subsequently more than doubled to 56,000 tons $year^{-1}$ in five years by modifying the plant and operating the cells at a current density of 350 Am^{-2}. The plant uses impure copper anodes ($0.9\ m \times 1.04\ m$) and titanium sheets (area ~ m^{-2}) as starter cathodes. The starter cathode sheets are regularly pulled out after electrodeposition for a duration of 12 h. To meet the production target, ten thousand starter sheets are required to be replaced every week. There are two independent electrolyte circuits each serving one half of the tankhouse. Impurity build up is quite rapid because of the high current density used. To maintain the impurity level within a specified range, a high bleed off of the electrolyte is necessary. To depolarize the electrodes during electrolysis, the current is reduced to half its normal value and reversed for 2% of the cycle time. The current efficiency ranges from 85% to over 90% and most of the metallic impurities persisting in the refined copper are at a level of less than 10 ppm each. The anode slimes are periodically recovered from the cell bottom. The electrolyte is decanted just prior to slime recovery and held in a separate tank; it is then passed through a candle type clarifying filter, heated to the required temperature (72 °C) and pumped back into the electrolytic cells.

6.9.2
Vanadium

Vanadium metal production by calciothermy has been the mainstay until the emergence of an alternative process and that involves combination of aluminothermic reduction with fused salt electrorefining. Both the processes were capable of producing ductile grade vanadium. The aluminothermic way to making of vanadium seems to be gaining more grounds than the calciothermic preparation, which was in vogue and played a dominant and unchallenged role in the preparative metallurgy of vanadium. The aluminothermically reduced metal contains typically about 7% aluminum and 0.6% oxygen. The metal is crushed to chunks of 6 to 10 mm size and is used as the anode feed in an inert gas atmosphere electrolytic cell.

The electrolyte is made by in situ chlorination of vanadium to vanadium dichloride in a molten salt bath. Higher valent chlorides are difficult to retain in the bath and thus are not preferred. The molten bath, which is formed by sodium chloride or an equimolar mixture of potassium chloride-sodium chloride or of potassium chloride-lithium chloride or of sodium chloride-calcium chloride, is contained in a graphite crucible. The crucible also serves as an anode. Electrolysis is conducted at a temperature about 50 °C above the melting point of the salt bath, using an iron or a molybdenum cathode and a cathode current density of 25 to 75 $A\ \mathrm{dm}^{-2}$. The overall electrochemical deposition reaction involves the formation and the discharge of the divalent ionic species, V^{2+}:

Anode: $V_{\mathrm{impure}} \rightarrow V^{2+} + 2\ \mathrm{e}^-$

Cathode: $V^{2+} + 2\ \mathrm{e}^- \rightarrow V_{\mathrm{pure}}$

The quality of the refined metal, and the current efficiency strongly depend on the soluble vanadium in the bath and the quality of the anode feed. As the amount of vanadium in the anode decreases, the current efficiency and the purity of the refined product also decrease. A laboratory preparation of the metal with a purity of better than 99.5%, containing low levels of nitrogen (30–50 ppm) and of oxygen (400–1000 ppm) has been possible. The purity obtainable with potassium chloride-lithium chloride-vanadium dichloride and with sodium chloride-calcium chloride-vanadium dichloride mixtures is better than that obtainable with other molten salt mixtures. The major impurities are iron and chromium. Aluminum also gets dissolved in the melt due to chemical and electrochemical reactions but its concentrations in the electrolyte and in the final product have been found to be quite low. The average current efficiency of the process is about 70%, with a metal recovery of 80 to 85%.

6.10
Electroextraction

Electroextraction, in many respects, is similar to electrorefining. In this process an electrically conducting metal compound (instead of an impure metal) is used as a soluble anode and the electrolyte does not undergo decomposition.

Electroextraction processes have been utilized for the extraction of many metals from their compounds by using them as soluble anodes. Theoretically, the values of the emf required in these processes are smaller than the values of the decomposition potentials of the electrolytes but are larger than those generally required for the electrorefining of metals. The soluble anode should be chemically compatible with the electrolyte and should possess adequate electronic conductivity to permit the removal of the electrons generated due to the formation of the ionic species. Most of the carbides and a few sulfides are well suited to act as soluble anodes. Oxides and some sulfides may be compatible with the electrolyte but have poor electrical conductivity. Their conductivity can be improved by mixing them with graphite (or carbon) which provides conducting pathways to permit the removal of electrons from the various particles. A few examples of electroextraction processes have been presented in the sections that follow.

6.10.1
Molybdenum Compounds

The electroextraction process for molybdenum involves the use of its oxides, carbides or sulfides as soluble anodes in a potassium chloride-potassium hexachloromolybdate (K_3MoCl_6) molten electrolyte. An inert atmosphere electrolytic cell, with a provision for semicontinuous electrolysis, is used for this purpose. The process operation consists of the following steps. The salt mixture forming the carrier electrolyte is vacuum dried and melted. The functional electrolyte is then prepared by in situ chlorination of molybdenum, using a mixture of chlorine and nitrogen. The graphite crucible, placed inside the metallic chamber, is the container for the anode feed and the electrolyte. The anode feed is a pelletized charge which is made up of any one of the following: molybdenum carbide; molybdenum sesquisulfide; mixture of molybdenum dioxide with carbon; molybdic oxide with carbon; molybdenum disulfide with carbon. The incorporation of carbon is a mandatory requirement in the cases of molybdenum oxides and molysulfide for providing electrical conductivity to the anode charge. Carbon is introduced in the charge either by directly mixing these molybdenum compounds with carbon in the presence of a binder, or by mixing these molybdenum compounds with coal tar pitch, dissolved in benzene, and then drying the contents and compacting to form the required shapes. Molybdenum deposits on molybdenum cathodes. The operating conditions and the results pertaining to laboratory scale studies, with many different forms of molybdenum used as soluble anodes, have been presented in Table 6.20. In all the cases, the cathodic deposition is essentially the same whereas the anodic reactions differ because of the different compounds used. The cathodic deposition reactions can be represented as

$$Mo_2Cl_9^{3-} + 3\ Cl^- = 2\ (MoCl_6)^{3-}$$

$$(MoCl_6)^{3-} + 3\ Cl^- + 3\ e^- = Mo + 9\ Cl^-$$

Table 6.20 Operating data for electoextraction of molybdenum from various compounds in inert atmosphere laboratory cells.

Anode	***Mo_2C***	***MoS_2-C***	***Mo_2S_3***	***MoO_3-C***
Electrolyte	KCl-K_3MoCl_6	KCl-K_3MoCl_6	KCl-K_3MoCl_6	KCl-K_3MoCl_6
Electrolyte temperature, °C	930	900	900	950
Operating voltage, V	0.3–0.6	0.7–0.8	1.0–1.2	0.25–0.40
Cathode current density, A/dm^2	80	150	135	50
Cathode current density, %	60	50	85	97
Recovery, %	71	82	75	94
Hardness of melted metal, VHN	150–160	160–170	160–165	150
Purity (% metal)	99.9+	99.9+	99.9+	99.9+

The deposition of molybdenum occurs due to the discharge of the anionic species at the cathode and thus depends on the concentration and the diffusion of this species in the electrolyte.

It has been found that when molybdenum carbide (Mo_2C) is used as the soluble anode, a loose carbon crust forms on the surface of the pellets as the dissolution of molybdenum progresses. X-ray diffraction analysis of the spent anode has indicated a predominance of the Mo_2C phase. This suggests that the anodic reaction proceeds as

$$Mo_2C + 9\ Cl^- \rightarrow Mo_2Cl_9^{3-} + 6\ e^- + C$$

Similarly in the case of sulfides the reaction appears to proceed as follows:

$$Mo_2S_3 + 9\ Cl^- = Mo_2Cl_9^{3-} + 6\ e^- + 3\ S$$

and

$$2\ MoS_2 + 9\ Cl^- = Mo_2Cl_9^{3-} + 6\ e^- + 4\ S$$

In the case of oxide-carbon anodes, the operating potentials have been observed to be particularly low and the current efficiency and the metal recovery have been found to be high. These results suggest that the deposition may not be occurring as per the direct decomposition of the oxides (i.e., $MoO_2 \rightarrow Mo + O_2$ or $MoO_3 \rightarrow Mo + 1.5\ O_2$) but may be proceeding in a different way. The presence of carbon in the charge at the electrolysis temperature of 800 °C may result in the following chemical reactions:

$$MoO_2 + C = Mo + CO_2$$

$$MoO_3 + 1.5\ C = Mo + 1.5\ CO_2$$

These chemical reactions possibly precede the electrochemical reactions. Thus the electrochemical reactions in the case of molybdenum oxides may be taken to be similar to those which occur in electrorefining, i.e., electrochemical dissolution of molybdenum from the impure metallic molybdenum anode and subsequent deposition at the cathode. The combination of the chemical and the electrochemical reactions occurring at the anode can be represented in the following way:

$MoO_2 + C = Mo + CO_2$

$2\ Mo + 9\ Cl^- = Mo_2Cl_9^{3-} + 6\ e^-$

6.10.2
Nickel Sulfide

Nickel sulfide and nickel-copper matte, obtained by the pyrometallurgical processing of sulphidic nickel ores, have been used as soluble electrodes in the commercial extraction of nickel. There can be two strategies for carrying out electrolysis with the matte casting. In one, the matte can form the anode. In this case, the anodic dissolution of nickel causes deposition of elemental sulfur on the anode. With the progress of electrolysis the thickness of the sulfur product layer increases and this makes the dissolution of nickel increasingly more difficult. In order to maintain the current density in the cell, the potential applied to the cell must also increase as the electrochemical reaction proceeds. This leads to progressively increasing power requirements for the process. In the other strategy, the matte can form the cathode and electrolysis is carried out with an acidic solution. Sulfur from the cathode is dissolved in the ionic form and the electrochemical dissolution can be represented as:

$NiS\ (s) + 2\ e = Ni\ (s) + S^{2-}\ (aq)$

In the acid solution the sulfur ions react rapidly with hydrogen ions to form hydrogen sulfide according to the reaction:

$2\ H^+\ (aq) + S^{2-}\ (aq) = H_2S\ (g)$

This approach of using the sulfide as the cathode implies that while nickel metal is directly formed on the cathode, the sulfur is continuously removed as hydrogen sulfide gas. In the former case there is a build up of sulfur in the cell.

The process at the INCO Thompson Smelter, Manitoba, Canada, molten nickel sulfide matte is produced by the smelting and converting of a sulfide ore low in copper. The matte is cast directly into anodes from a holding furnace at about 1100 °C. When they have solidified, the anodes are placed in an insulated annealing box so that they cool slowly through the phase transformation, $\beta\ Ni_3S_2 \rightarrow \beta'\ Ni_3S_2$ which happens at 505 °C. This avoids the cracking and disintegration that would otherwise occur. The anodes corrode initially at a cell potential of about 2.6 V producing an anode slime containing over 90% elemental sulfur. The anode slime occupies about twice the volume of the original anode and is strongly adherent. The increasing thickness of anode slime during electrolysis increases the cell resistance, and the applied potential progressively climbs from about 2.6 to 4–5 V.

The anode potential is so positive, due principally to the activation overpotential, that the majority of the impurity metals (Fe, Cu, Co, etc.) in the anode dissolve with the nickel sulfide. In addition, some oxygen is evolved ($2\ H_2O = O_2 + 4\ H^+ + 4\ e^-$). The anodic current efficiency reduced to about 95% on account of this reaction. Small amounts of selenium and the precious metals remain undissolved in the anode slime along with sulfur. The anolyte contains impurities (Cu, Fe, Co) and, due to hydrogen ion (H^+) liberation, it has a low pH of 1.9. The electrolyte of this type is highly unfit for nickel electrowinning. It is required to be purified and pH raised to the range of 4–5 to maximize the cathode current efficiency.

In order to provide for purification of the electrolyte, diaphragm cells are used to form separate anode and cathode compartments, and the anodes are encased in loose-fitting, open-weave bags to facilitate the removal of slime with the anodes. The anolyte is continuously taken out, purified and fed into the cathode compartments where nickel electrodeposits on the cathodes. A small hydrostatic head of purified electrolyte in the cathode compartment is maintained in order to prevent the diffusion of anolyte with its impurities into the cathode compartments.

Anolyte purification process involves use of secondary cells in which aqueous sodium chloride is used. The electrode reactions in the cells are:

Anodic: $Ni_3S_2 = 3\ Ni^{2+} + 2\ S + 6\ e^-$

Cathodic: $2\ H_2O + 2\ e^- = H_2 + 2\ OH^-$

Mixing of the electrode products causes hydrolytic precipitation of the nickel and, after separation of the nickel hydroxide, the filtrate was returned to the cells. The sequence of the electrolytic purification steps is outlined in Figure 6.28. Nickel hydroxide slurry is first added to the anolyte for the purpose of raising the pH to 3.7 ($2\ H^+ + Ni(OH) = Ni^{2+} + 2\ H_2O$), and iron(II) is oxidized by introducing chlorine. This causes hydrolytic precipitation of the iron(III) and corrects the nickel ion deficiency by the low anodic current efficiency. The iron(III) hydroxide is removed by filteration. The clarified solution is then treated with nickel carbonate and further chlorine to oxidize the cobalt(II) and allow its separation as cobalt(III) hydroxide.

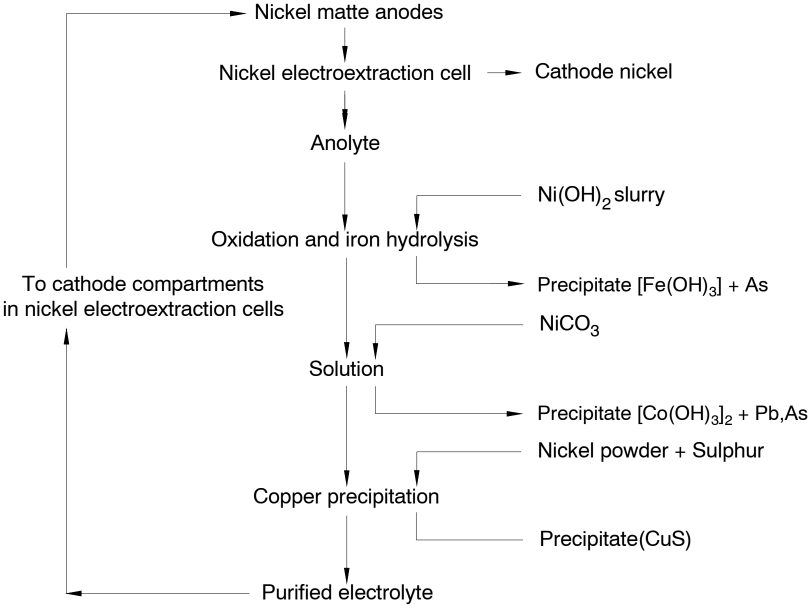

Figure 6.28 Electroextraction of nickel from nickel matte anodes (principally based on Thompson Refinery Plant practice).

$$2\,Co^{2+} + Cl_2 + 3\,H_2O + 3\,NiCO_3 = 2\,Co(OH)_2 + 3\,Ni^{2+} + 3\,CO_2 + 2\,Cl^-$$

Arsenic and lead are conveniently co-precipitated and removed with the cobalt precipitate. Finally, copper is separated from solution as copper(II) sulfide by stirring in nickel powder and elemental sulfur

$$Cu^{2+} + Ni + S = CuS + Ni^{2+}$$

followed by filtration. The nickel-bearing solution thus purified finally forms the feed for the cathodic compartments of the nickel electrowinning cells. The Thompson plant has since modified the purification scheme. In the modified procedure, copper is removed first. Copper(II) sulfide is precipitated with hydrogen sulfide, and lead and arsenic co-precipitate with it. Use of chlorine and nickel carbonate simultaneously implement oxidative hydrolysis of iron and cobalt.

When approximately 70% of each anode has dissolved away, the anode remains are removed in its bag and replaced by a new anode. The old anode remains are broken up and washed to remove the slime. Large pieces of sulfide scrap are returned to the converter for remelting.

The slime is recovered and heated in a brick-lined tank to melt the sulfur. The molten sulfur is filtered in a heated stainless-steel pressure filter to separate remaining nickel sulfide pieces and insoluble precious metals, and cast into moulds. The residue is remelted and cast into anodes, the resulting anode slime is now a relatively concentrated precious metal residue and is treated for the extraction of individual metals.

6.11
Electroleaching

6.11.1
Electrochemical Aspects

It is a truism that industrial electrochemistry had its origin in the large-scale electrolysis of alkali halides. The present text concentrates on sodium chloride, which is by far the most important and common among this class of salts. However, the reactions characterizing the electrolysis of all or anyone alkali halides take place in much the same way, irrespective of the alkali metal and the halogen that form the components of the salt. Since starting from the same compound, i.e., an alkali halide, it is possible to get a large variety of products, simply by changing the operating conditions, it is evident that the primary reactions must be accompanied by a good number of side reactions, any one of which maybe induced to occur by suitably adjusting the conditions used. In an aqueous solution of sodium chloride the ionic species Na^+, H^+, Cl^-, and OH^- are always present.

When the solution is electrolyzed between inert electrodes, Cl^- ions are discharged at the anode ($Cl^- - e^- \rightarrow Cl$) and H^+ ions at the cathode ($H^+ + e^- \rightarrow H$). This leaves Na^+ ions and OH^- ions in the solution to form sodium hydroxide. The chlorine liberated escapes almost immediately unless, of course, it is held in some chemical combination. If the objective is to produce chlorine and sodium hydroxide, the anodic and the cathodic products are kept separate so that they cannot react with each other. If on the other hand, the objective is to produce sodium hypochlorite (NaClO) or sodium chlorate ($NaClO_3$) or sodium perchlorate ($NaClO_4$), then the chlorine and sodium hydroxide are brought into intimate contact. The present description deals with hypochlorite and chlorate compounds. As far as the electroleaching process is concerned the main aim is to generate hypochlorite meant to be used as a leaching agent, and this will be considered first.

The combination process of the anodic chlorine and the cathodic OH^-, leading to the formation of the hypochlorite ions (ClO^-), can be represented by

$$Cl_2\ (aq) + 2\ OH^- = ClO^- + Cl^- + H_2O$$

The ClO^- is a strong oxidizing agent and it can readily oxidize several sulfides.

6.11.2
Process

The electroleaching process is basically a technique for producing an oxidizing environment in an ore slurry. In this process, the source material (such as ore, tailings, and mine waste) is sized by crushing, followed by grinding in a brine solution. For sulfide concentrates, however, crushing and grinding are generally not required. The resulting slurry is fed to agitated vessels, and electrooxidation cells are immersed in the pulp. A current is passed through the cells, generating an oxidizing environment. This step is followed by digestion to permit the residual oxidants to react. The digestion step is followed by solid–liquid separation. Finally, the clarified pregnant solutions are subjected to various treatments, depending on the level of metal content, for the recovery of the metal values. The barren solutions are recycled back to the grinding circuit.

The electroleaching process for molybdenite concentrate involves the generation of an oxidizing environment (mainly ClO^- ions) in the stirred brine-ore pulp. This is implemented by passing a direct current through the brine-ore pulp through immersed electrodes. The overall reaction can be expressed as

$$MoS_2 + 9\ OCl^- + 6\ OH^- \rightarrow MoO_4^{2-} + 2\ SO_4^{2-} + 3\ H_2O + 9\ Cl^-$$

For molybdenite concentrates hydroxy ions must be added to maintain a near neutral pH value. The pH value at which the electroleaching of other metal sulfides is conducted depends upon the amount of hydroxy ions added. For example, when a low grade cinnabar ore is treated, the pH remains almost neutral because of the calcite content of the ore. This is also true of carbonaceous gold ores.

The application of the electrochemical leaching process in the extraction and the recovery of molybdenum and rhenium from offgrade molybdenite concentrates, as practiced at the Reno Metallurgy Centre of the US Bureau of Mines, is worth a description here. The first step in this process involves the conditioning of the concentrate with recycled brine in a mixing tank. The slurry is then pumped to the bottom of a bipolar electrolytic cell (Figure 6.29). From the cell, the slurry passes under gravity to a stirred vessel and this continues till the completion of the dissolution process. Finally, the brine, containing molybdate ions, is subjected to liquid-solid separation by which the insolubles are discharged to the tailings.

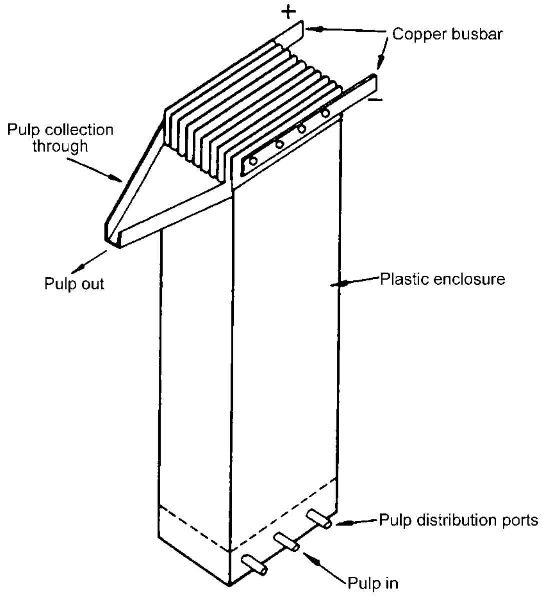

Figure 6.29
Isometric view of the bipolar cell.

The pregnant solution is then treated with sulfur dioxide gas by which the reduction of the chlorate ions contained in the solution takes place according to the reaction:

$$3\,H_2 + 2\,ClO_3^- + 3\,SO_2 \rightarrow 2\,Cl^- + 3\,H_2SO_4$$

The acid generated in the reaction causes a lowering of the solution pH. The removal of the chlorate ions is necessary since the organic extractant used in the subsequent extraction process tends to extract these ions. The solvent extraction process works well with the reduced pH resulting from the reduction of the chlorate ions by sulfur dioxide. The molybdenum-rhenium bearing aqueous feed is now chemically fit to go through the solvent extraction process which uses a tertiary amine as the extractant. The extractant, loaded with molybdenum and rhenium, is stripped with ammonium hydroxide. The solution laden with molybdenum as well as rhenium is subjected to carbon adsorption for obtaining a separation between the two. The carbon adsorbs rhenium while molybdenum remains in the effluent from the adsorption process. The effluent is treated with ammonia to obtain an ammoniacal solution of molybdenum. This solution is subjected either to crystallization for the recovery of molybdenum as ammonium paramolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$, or to neutralization for the recovery of molybdenum as ammonium polymolybdate, $(NH_4)_2Mo_4O_{13} \cdot 2\,H_2O$. The activated carbon with the rhenium value loaded into it is first washed with a 25% sodium chloride solution to remove any entrained molybdenum. It is then eluted with a methanol-water mixture. The activated carbon is regenerated with water. The eluate, containing rhenium, is subjected to a distillation process whereby methanol gets removed and is reused. The final rhenium-bearing solution is adjusted for its pH value; this value is brought down to about 1 and the solution is made to go through another round of solvent extraction wherein a tertiary amine is used as an organic extractant and ammonium hydroxide is used as a stripping reagent. The strip solution is crystallized to

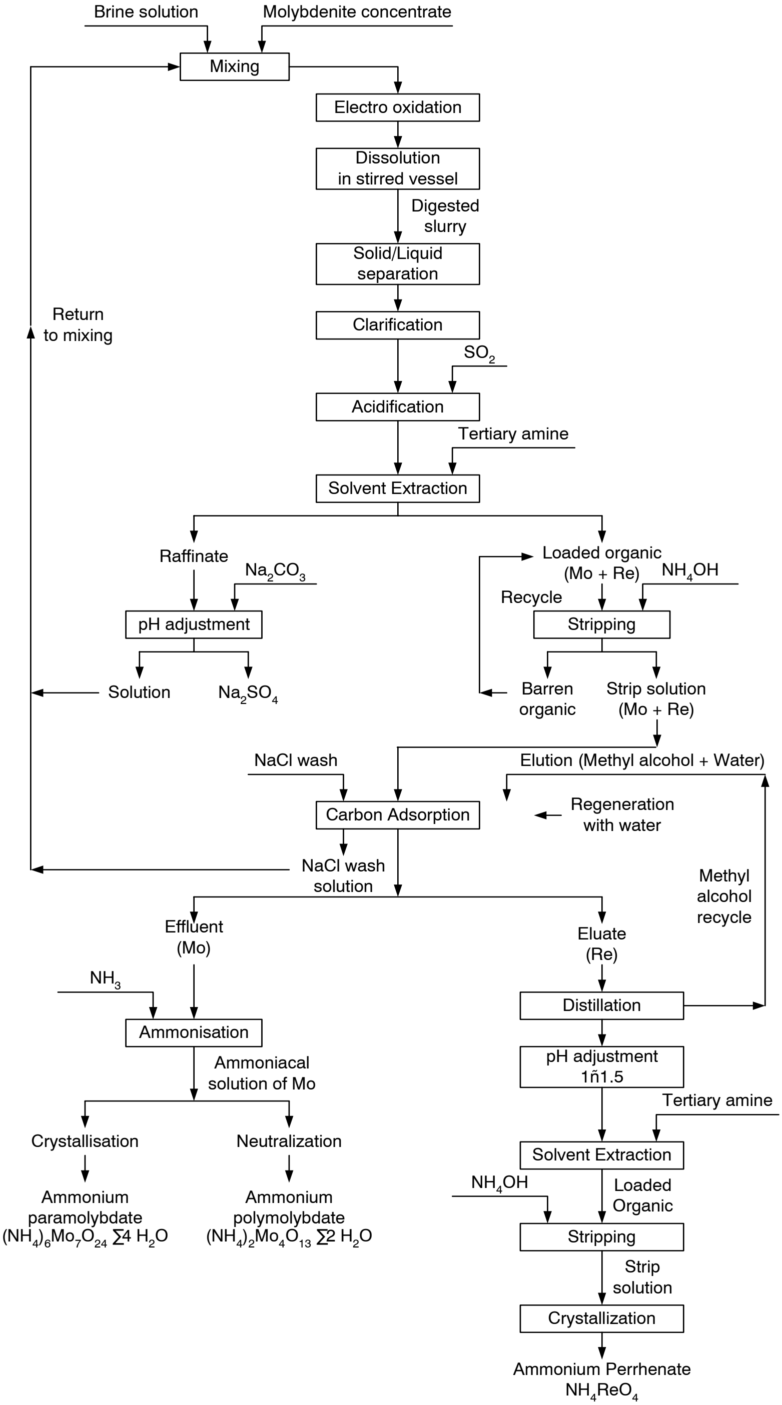

Figure 6.30 Outline of electroleaching process for molybdenite concentrate.

ammonium perrhenate (NH_4ReO_4). The complete picture of the process sequence described here for the electroleaching process for the molybdenite concentrate is depicted in Figure 6.30.

6.12
Electrosynthesis

The terminology electrosynthesis, it may be recounted here, refers to the preparation of chemical products by electrochemical means. As one of the major industries making use of this approach mention may be made of the chlor-alkali industry. It was pointed out in the earlier section dealing with electroleaching that for obtaining caustic soda from the electrolysis of brine or sodium chloride solution it is essential to keep the anodic chlorine and the cathodic sodium species separated. On the other hand, in order to steer the process to produce chlorated compounds of sodium, there should be no bar on the intermixing of the two species. Today the basic electrolytic chlor-alkali technologies are based on mercury cells, diaphragm cells and ion exchange membrane cells.

The mercury cell concept is shown in Figure 6.31 (A). Saturated brine is fed to the cell compartment and depleted brine overflows from the same compartment with about 15% salt depletion. Chlorine gas is liberated at the anode and sodium dissolves in the flowing mercury cathode. The sodium amalgam flows to the decomposer where water is added yielding caustic soda and liberating hydrogen gas ($2\ Na/Hg + 2\ H_2O \rightarrow 2\ NaOH + H_2 + Hg$). Two of the primary advantages of the mercury cell process are: (i) the caustic product contains low salt levels because the reaction leading to this product occurs outside the cell compartment and (ii) the caustic is produced at a 50% concentration directly from the decomposer process. The overall mercury cell process areas are shown in Figure 6.31 (B) and consist of brine purification, electrolysis, chlorine, cooling, drying, compression and liquefaction, if required, hydrogen cooling and compression for use as boiler fuel, and caustic filtration. The depleted brine from the cells is dechlorinated and recycled to the brine area for resaturation. Solid salt is required for the mercury cell process. This can be cited as a major disadvantage. Since brine depletion is only about 15% across the cell, the brine flow rate through the circuit is very high, thereby increasing the size and the cost of the brine area.

The principle of diaphragm cell is shown in Figure 6.32 (A). In this type of cell the anode and cathode are in adjacent compartments separated by a porous partition. The anode compartment contains strong brine while the cathode compartment contains dilute sodium hydroxide solution. The brine solution surface is maintained at a slightly higher level than that of the sodium hydroxide solution, and the hydrostatic pressure thus developed tends to force the brine through the porous diagram into the cathode compartment. When electrolysis is proceeding H^+ ions and Na^+ ions in both compartments migrate towards the cathode, and OH^- ions and Cl^- ions in the anode compartment, and OH^- ions in the cathode compartment, migrate towards the anode. The rate of flow of the brine from the anode compartment through the diagram is so controlled or regulated by adjustment of the hydrostatic pressure that it exactly equals the rate at which OH^- ions tend to pass from the cathode into the anode compartment. The diaphragm stops the mass-movement of the electrolytes

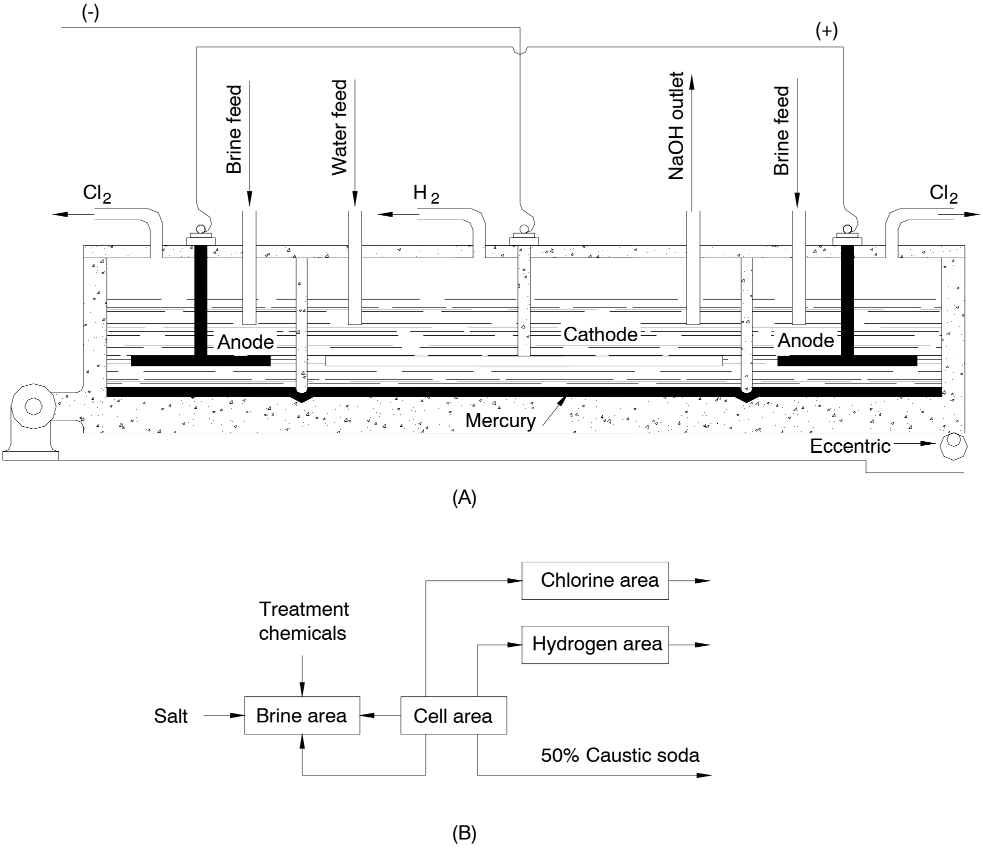

Figure 6.31 (A) Mercury cell concept; (B) overall mercury cell process areas.

from one compartment to the other by diffusion and convection. The effect of the diaphragm and the pressure of the anode solution is to retain the sodium hydroxide in the cathode compartment, to stop contact between the sodium hydroxide and chlorine, and to ensure that only very small quantities of sodium chloride contaminate the sodium hydroxide solution. The overall diaphragm cell process is shown in Figure 6.32 (B). The brine area is a one-pass system. The chlorine and hydrogen areas are similar to those in the mercury cell process. The cell liquor produced, however, must be further processed in an evaporation and salt separation system. The quality of the caustic is degraded by the presence of salt in the final product. A high quality salt is recovered, however, which is redissolved to produce the feed brine. The Townsend cell (Figure 6.32 C) operated by the Hooker Electrochemical Co. at Niagara may be described as a typical example. A carbon anode fits into the central compartment, and it holds purified brine which continuously flows through the cell. Chlorine exits through an opening provided at the top. The sides of the anode compartment form the porous diaphragm, and are made of asbestos fibre pained with a mixture of asbestos fibre, ferric oxide, and colloidal ferric hydroxide. The cathodes are iron

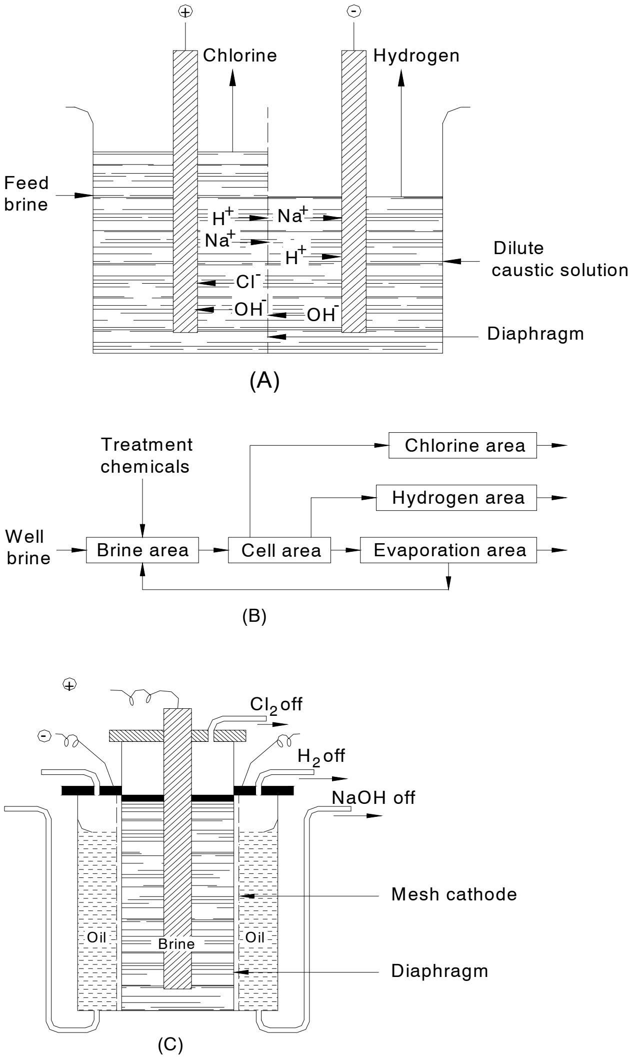

Figure 6.32
(A) Diagram cell concept.
(B) Overall diaphragm cell process.
(C) Townsend cell.

grids which press against the outside of the diaphragm. The cathode compartment is filled with kerosene. It may be seen from the figure that the surface of the brine is made somewhat higher than that of the kerosene so that requisite hydrostatic pressure is developed. When the electrolysis is proceeding Cl^- ions are discharged at the anode and the chlorine gas is led away and collected. H^+ ions are discharged at the cathode where simultaneously Na^+ ions and OH^- ions accumulate in the water which diffuses through the diaphragm from the anode compartment. The evolution of hydrogen brushes away the drops of sodium hydroxide solution into the main bulk of the kerosene and they fall to the bottom of the cathode compartment where they coalesce. The sodium hydroxide solution is siphoned out of the cell and concentrated. The process yields a 15% solution of sodium hydroxide.

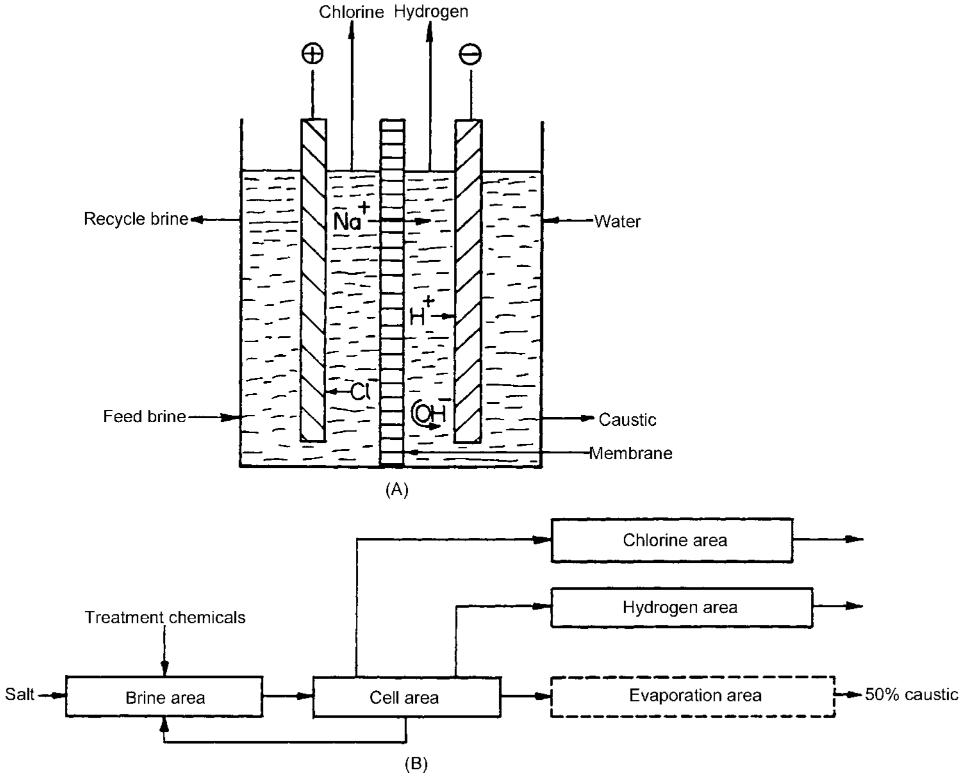

Figure 6.33 (A) Membrane electrolyer; (B) typical membrane process.

A simplified diagram of the membrane electrolyzer is shown in Figure 6.33 (A). The operating mode is quite similar to that of the mercury cell. Saturated brine is fed to the anolyte compartment, is partially decomposed, and is then recycled to the brine area for reconcentration following a dechlorination step. Chlorine gas is liberated at the anode. Sodium ions diffuse through the membrane and react with hydroxy ions in the catholyte compartment. Hydrogen gas is generated at the cathode. Purified water is continuously added to the catholyte compartment for the caustic soda reaction. Just as in the mercury cell concept, there is no direct contact between the brine and the caustic so that a low chloride caustic is produced directly from the electrolyzer. The caustic concentration is between 25% and 35%. Figure 6.33 (B) presents the typical membrane process where, like in the mercury cell process, depleted brine is dechlorinated and recycled back to the brine area for resaturation and reuse. The membrane cell process requires solid salt for brine reconcentration. In addition, evaporation is necessary as in the diaphragm process to produce 50% caustic; but a much smaller evaporation system is required and the need for salt separation equipment is eliminated.

A comparison of the advantages and the disadvantages of membrane cells and of mercury cells is given in Table 6.21. A similar comparison between membrane cells and diaphragm cells is given in Table 6.22.

Table 6.21 Comparison between membrane cells and mercury cells.

Advantages	*Disadvantages*
Eliminate mercury handling	Very pure brine required
No hydrogen in chlorine	Some evaporation required to produce 50% caustic
More adaptable to small installations	
Smaller brine area system	

Table 6.22 Comparison between membrane cells and diaphragm cells.

Advantages	*Disadvantages*
Eliminate asbestos handling	Requires solid salt
No hydrogen in chlorine	Very pure brine required
No chlorates and sulfates in caustic	
Low chloride grade caustic	
Small evaporation required 50% caustic	
No need for salt separation equipment	
Lower total energy consumption	

6.13
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7
Energy and Environment

7.1
Introduction

7.1.1
General

Energy- and environmental-related issues are currently of paramount importance and are now attracting more attention and emphasis worldwide than ever before. At present, in fact, concerns are overwhelming with regard to excessive and wasteful energy consumption, conservation ethics, and savings aspects. In the case of the environment, the sermon is protection, and threats from the degradation of environs should be avoided as far as is practicable or feasible. Activities, industrial, or otherwise, must be benign environmentally, and should meet environmentally acceptable specifications. Indeed, many countries of the world have already imposed legislations, debarring, for example, industries from any inadvertent, free, or untreated plant discharges to the three environs of land, air, and water. An environment from which any unwelcoming load that is harmful to all who matter in the ecosystem is removed is held in high esteem. Today, signs of propensity dispel and shun the smoking chimneys and tall stacks that once were welcoming and prestigious indicators of the industrial development and growth of a country. Those days are gone, and such areas are now regarded as highly disastrous.

On the energy front, it is relevant to address matters pertaining to the correlation between energy use and development; the correlation between energy use and national income; the correlation between energy use and standard of living; the fundamental law of energy use; the role of renewable energy sources; and benefits of renewable energy not considered in the standard economic accounts book. This chapter should be treated as only an illustrative and not as an exhaustive narration. To summarize, it may be worthwhile placing on record that the present materialistic age faces many challenges, including the development of production processes and technologies that are compatible with available raw materials and increasingly efficient, and the eradication of smokestacks and waste material heaps, to change the manufacture and processing of materials into environmentally friendly schemes.

It is understandable that the main focus of this chapter is on chemical metallurgy, and accordingly the chapter's design and organization may be limited in scope and orientation. It is, however, hoped that the text fulfils the objective of conveying the due importance and

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laying the corresponding emphasis on energy and environment – the two parameters of great significance in the context of present-day science and technology. A concise picture of the sources of pollution in the processing and production of metals is given here to provide readers with an initial flavor of the range and diversity of the problems involved and confronted.

- The first stage – mining – incorporates two facets from the point of view of pollution. One facet is the waste rock that is raised from its undisturbed position underground to the surface; the other facet is the overburden created as a result of open-pit mining. As these solids accumulate, a dump encompassing a huge area is produced; moreover, as the dump surface dries, high winds may produce unwelcome dust storms. Although the prevention of such storms can be made possible by keeping the dumps continually wet, the practice of planting and cultivating shrubs and trees to serve as windbreaks deserves more attention. Another problem involves the explosives used in mining, which generate nitrogenous gases (NO_x). An explosive which, chemically, is ammonium nitrate duly decomposes to yield nitrous oxide, and this undergoes oxidation in air to nitrogen dioxide (NO_2) – one of the main contributors to the problem of acid rain.
- Mineral beneficiation involves the removal of as much as possible of any undesirable associates (known as gangue minerals), and tailings from these beneficiation processes represent a major disposal problem.
- Extractive metallurgy is represented by the trio of pyrometallurgy, hydrometallurgy, and electrometallurgy. Major pollution problems in metallurgical plants ensue from the largest metal industry producing iron and steel; from aluminum production; from processing of sulfide ores; from some hydro-based metallurgical processes; from the treatment of sources containing radioactive materials; from the preparative metallurgy of certain industrial minerals; and from the electroplating industry installations.

Pyrometallurgy generates dust, slag, and gases. *Dust* emitted in this way may involve a considerable cost to the plant itself, especially when the lost particles are of high value. The introduction of devices such as cyclones, scrubbers, and electrostatic precipitators has been largely instrumental ino solving the dust problem. The production of *slags* in pyrometallurgy occurs widely, and at present, only a minimal proportion is utilized in processes such as road construction and cement manufacture. The construction of tall stacks has recently been in vogue to raise emission heights and curb the effects of bothersome or harmful *gases* at ground level; however, this does not provide an adequate solution to the pollution problem since in due course they are brought back to ground level by the action of the rain and so the very purpose of these stacks is defeated. Whilst on the present topic, it is important that attention be given to acid rain, which, in recent years, has been the center of much concern. The damaging issues of acid rain have attracted considerable media attention and have been disseminated strongly to the public domain in regard to forests that are on the verge or extinction, lakes that can no longer support aquatic life, and stone buildings that are literally dissolving away with each rainfall. This is a worldwide problem of major concern. The causes are well understood, but the answers to the problem are either costly or produce further problems. Rain water as such is normally slightly acidic because CO_2 from the atmosphere reacts to form carbonic acid. However, in many parts of the world, acids other than carbonic acid are found in the rain. This greater acidity of rain is caused mainly by oxides of nitrogen and sulfur, which are present in the atmosphere from a variety of sources. The formation of NO in the atmosphere occurs by electrical storms, but contributions also come from combustion processes, especially automobile engines. A rather simple chemistry involving the reaction of NO with O_2 in the atmosphere to NO_2, followed by its reaction with more O_2 and water in clouds and rain leads ultimately to a solution of nitric acid. The sulfur oxides that are major contributors to acid rain have a variety of sources. Volcanoes, when active, discharge vast amounts of SO_2 into the atmosphere, whilst additional sources include forest fires and the bacterial degradation of organic matter. In addition to these natural sources, human activities produce large amounts of SO_2, including the combustion of sulfur-bearing coals and other fossil fuels, and the roasting of sulfidic sources of metals such as copper, nickel, lead, zinc, and molybdenum. The simple chemical reaction then follows, whereby SO_2 is converted to SO_3, which then dissolves in water to form sulfuric acid solution. The effects of acid rain are painful; damage occurs to stone buildings and monuments, and acid rain is extremely harmful to plant, forest, and animal life. Lakes in some regions of the world are known to have been exposed to as much as four metric tons of H_2SO_4 per square kilometer. As the acid concentration increases, marine life dies, and the end result is a crystal-clear, unwelcoming and completely sterile lake. A solution to the problem of acid lakes is to pump pulverized limestone or lime to neutralize the acid, and some lakes in Sweden, Canada, and the United States have been treated in this way. One shortcoming with this procedure is that, in addition to being costly, it must be repeated annually and is impractical for large bodies of water. The procedure, in essence, touches the consequences of acid rain while the causes remain untouched. In an attempt to to combat acid rain, the initial suggestion is to exercise extreme control over the release of nitrogen and sulfur oxides into the atmosphere. The main target is automobile emissions, as these are the major contributors of nitrogen oxides. Some countries have imposed tough emission control standards for cars sold and operated within their territory, though the automobile manufacturers have warned against tougher standards, stating that the cost to the consumer would be high and that standards would not be easy to meet. A reduction in sulfur oxides also introduces difficult choices for the public, as the elimination of sulfur from fossil fuels is not only very costly but also technically difficult. A cheaper but less efficient procedure would be to expel the SO_2 after its formation by fuel combustion. The technology for this process is fairly simple, but the installation costs and the disposal of the solid waste produced leads to other problems. Alternative energy sources such as solar, geothermal, and nuclear might help solve the problem, but these alternatives have a high price tag and are generally not popular. To conclude, it is perhaps correct to suggest that the public will encounter difficult choices in order to reduce acid rain production. However, the problem is not simply going to disappear, as hydrometallurgy generates both residues and waste solutions. Slags are normally stable when stored outside, but solid residues resulting from the filtration of aqueous solutions are less stable in that they mostly carry soluble components. This prohibits their disposal in ponds as it may lead to the contamination of surface waters unless suitable procedures are utilized. Liquid effluents arising from hydrobased operations often carry toxic reagents, and it is mandatory that such effluents be treated before being released to join general streams. The aluminum industry represents a major electrometallurgical operation which produces gases and dust, and this industry is currently witnessing intense improvement. Problems of pollution are also associated with copper electrorefining, though at present these are of relatively manageable status. Fortunately, human endeavour has led to great successes in dealing with pollution problems.

Further information on some of the diverse areas and examples as described above, and also for other related matters, will be outlined as the chapter advances from this introduction.

7.1.2
Extraction and Process Metallurgy

For a very long time, the prime objective of process metallurgy has been to devise and implement processes for the economic and large-scale extraction of metals from the available ores. An abundant supply of fairly rich and pure ores, relatively uncomplicated flowsheets, an easy and adequate availability of electricity and of fossil fuels, and, above all, a considerable latitude with regard to the location and the operation of metal production plants, were the characteristic features of the metallurgical industry during the period between 1860 and the early 1970s. The energy crisis and the rapid escalations in the energy prices since 1973, together with the realization that world supplies of oil and natural gas are limited, have brought into focus considerations pertaining to economy in energy consumption in the processes utilized for metal extraction. The need to seek new processes that are less energy-intensive has been strongly felt, and the advisability or desirability to modify existing processes so that energy conservation practices can be incorporated within them has also been both extensive and well understood. In addition, it has been realized that energy economy in metal extraction is not an isolated issue but is interlinked with two other major problems. One of these issues is the concern over the rapid depletion and exhaustion of the rich and pure (or high-grade) ores and the concomitant need to make processing leaner, more complex, and to use unconventional ores and resources. The other issue pertains to the rapidly growing awareness and concern with regard to the environmental impact of the metallurgical industries. Indeed, environmental considerations may now overshadow all other technical advantages associated with the setting up and running of some metallurgical plants. Thus, the current status and the future evolution of the process metallurgical industry are set to be guided to a large extent by energy- and environment-related considerations. In response to, and in anticipation of, these new and challenging constraints, there have been many new and significant developments in process metallurgy. Modifications of the existing processes, of the technologies, and of the engineering must also be counted in the present scenario.

7.2
Energy Economy

It is useful first to make a general presentation on energy itself before dealing with its economy. This given objective is fulfilled and best served by comparing production from the three main energy sources: fossil fuel energy; nuclear energy; and solar energy.

The dominant source of energy in the world is *fossil fuels*. There are several advantages associated with energy extraction from fossil fuels, including accessibility, ease of transportation, and ease of use. Most of the energy is obtained from combustion of the fuel with air, which is abundantly available and generally free. There are three major problems connected with the combustion of fossil fuels: fossil fuels are nonrenewable resources; they are complex substances; and they contain elements other than just hydrogen and carbon. The combustion of fossil fuels, therefore, quite understably generates more than just CO_2 and water, and hence both impurities in the fuels and complications in the burning process lead to air pollution. Even if pollution problems were eliminated, the generation of huge amounts CO_2 is grievously injurious to the environment. Several facts are worth mentioning here as regards fossil fuel resources. The earlier scenario of the continued discovery of fossil fuels surpassing their consumption no longer holds, as consumption now surpasses new finds of deposits. The Earth's oil supply will run out if the current consumption trends continue, and the position on natural gas is in no way any better. The most plentiful fossil fuel is coal, amounting to about 90% of the world's fossil fuels. Many important processes, such as the production of electricity, can be powered by coal or petroleum, but other processes – especially transportation – involve petroleum liquids almost exclusively. Those countries having large coal reserves but no cash reserves for oil importing, have begun to build coal liquefaction plants; the gasification of coal renders its energy available in gaseous form, and such plants are being built in several sites. As the supply of petroleum worsens, it will be deployed more as a source of plastics, fibers, and industrial feedstocks than be combusted as a source of energy. A cryptic remark was once made that "putting petroleum into flames makes as much sense as similar doings with bank notes", implying therein that it has more value than as a fuel.

While nuclear energy has been dealt with elsewhere in the text, reference may at present be drawn to *solar energy*. This represents a potential replacement for the combustion of fossil fuels, and appears to be free and also free of pollution. It is, however, clear that certain associated problems exist, or solar-powered facilities would have been a far more common sight. In fact, there are several problems. Solar energy is characterized by not being constant – it is available only on clear days, and never at night, and even on clear days the sudden appearance of occasional clouds can be obscuring. Solar energy is low in intensity, and collection devices must be huge in order to gather useful quanta of energy. In fact, the most practical solar energy conversion devices are water heaters. As yet, solar energy cannot be used for the generation of electricity in an economical way, though a promising large-scale application of solar energy might be to coerce an endothermic reaction to form products – a very interesting proposition to the chemical and metallurgical industries.

Large energy inputs in the form of fuels, electrical energy, and reagents, which have themselves been prepared by energy-intensive processes, are required in the production of primary metals through the stages of mining, ore beneficiation, smelting, and refining. The overall energy intensity of a metal may result from high levels of energy intensity in one or more of these stages. For example, metals such as gold, copper, and molybdenum are energy-intensive because they are recovered from low-grade ores: many tons of the ores must be processed to recover one ton of the metal. Metals such as aluminum and magnesium are energy-intensive because large energy inputs are required to reduce their compounds to the metallic state. In this context, it is interesting to note that, as of now, steel is one of the least energy-intensive “metals” because it is obtained from a high-grade ore and is also easy to process. At the other extreme is titanium, which has the reputation of being the most energy-intensive of the metals produced in large quantities. Titanium is produced from relatively low-grade ores, and its extraction flowsheet involves the use of complex reduction chemistry and energy-intensive reagents.

7.2.1
Fuel Equivalents

The energy consumed in a process or the energy intensity of a process is expressed by the term “process fuel equivalent” (PFE) which is defined as

$$\mathrm{PFE} = \mathrm{F} + \mathrm{E} + \mathrm{S} - \mathrm{B}$$

In the expression given above, all the terms have units of Joules per ton ($\mathrm{J\ t^{-1}}$) of the product. F is the gross heating value of all the fuels used, E is the fuel equivalent of the electrical energy used, S is the fuel equivalent of all the major supplies and reagents used, and B is the fuel equivalent of the useful by-products and the surplus steam produced in the process. The term “material fuel equivalent” (MFE) is used to express the energy requirement for the production of a primary metal in the unfabricated form. Like the PFE, the MFE is expressed in units of $\mathrm{J\ t^{-1}}$, and is evaluated as the sum of all the process energies (or PFEs) leading to the product. Typically, the PFEs associated with mining of raw materials, ore beneficiation, smelting, or any other means of metal extraction and refining are all added up. In recent times – as will be described in a later section – the energy required for ensuring the abatement of pollution, normally associated with each step, is also taken into consideration to obtain the MFE value. It should be noted that in the evaluation of the term E in the expression for the PFE, the inefficiency of electrical energy generation from the primary fuel is charged against the process in question. The conversion of electrical energy to thermal energy units is usually based on a thermal conversion efficiency of 33% for electric power obtained from non-hydro power sources. This highlights the fact that electricity can be regarded as a premium form of energy. In the case of metals such as aluminum and magnesium, which require large amounts of electrical energy for their production, nearly half of the MFE corresponds to the energy loss in the production of electrical energy.

The estimated values of the MFE for several common and less common metals are listed in Table 7.1. The MFE values range from $28 \cdot 10^9\ \mathrm{J\ t^{-1}}$ for steel slabs to $68400 \cdot 10^9\ \mathrm{J\ t^{-1}}$ for refined gold bars. This wide range, indicating that the MFE values can differ by a factor of 2400, is a reflection of the widely different ore grades and the widely different processing technologies that are employed in the production of various metals.

Before leaving the present topic it is important that a general account be given on electricity. This bears the reputation of being the cleanest form of energy, but it is, of course, not a source. It is generated from any of primary energy sources, transmitted and distributed with relative ease, and converted into useful work, heat, or light, at any end-use location. Although it can be stored in small quantities by electrochemical reconversions, as yet there has not been any advance to store electricity in any appreciable amounts. Apart from this characteristic, which is a very significant one indeed, it is the perfect energy go-between. It cannot be substituted in a number of specific applications which are too well-known to

Table 7.1 Material feed equivalent (MFE) for selected primary metals.

Metal	*Product form*	*MFE (10^9 J t^{-1}*
Iron	Steel slabs	28
Lead	Refined ingot	31
Manganese	Ferromanganese	58
Zinc	Slab (electrolytic)	70
Chromium	Ferrochrome (high C)	71
Silicon	Ferrosilicon (50%)	89
Sodium	Metal	107
Copper	Wire bar, refined	128
Cobalt	Electrolytic	144
Nickel	Electrolytic (from sulfide ore)	167
Molybdenum	Molybdic oxide (crude)	168
Cadmium	Electrolytic	178
Niobium	Ferroniobium	220
Tin	Refined ingot	221
Aluminum	Ingot	284
Tantalum	Metal powder	289
Tungsten	Metal powder	402
Magnesium	Electrolytic ingot	416
Mercury	Refined metal	459
Titanium	Sponge metal	474
Hafnium	Sponge metal	768
Uranium	Yellow cake (U_3O_8)	902
Zirconium	Sponge metal	1390
Silver	Refined bars	1710
Beryllium	Cast metal	6100
Gold	Refined bars	68400

warrant mention. One of most important advantages of electricity is that it possesses the greatest potential for allowing efficient conversion of energy resources into end application work. In space and water heating, the direct use of fossil fuels and solar energy may be competitive, but even here, because of its ease of control and flexible location, electricity is often the favorite. The literature records argument that electrification is a result, not a cause, of national affluence. Electricity in the national energy consumption is a measure of living standards, supported by energy surpluses derived from fossil fuels.

7.2.2
Mining and Ore Preparation

The location and the nature of the ore strongly determine the energy requirements for its mining and primary processing. Typical data for some major ore types and processing methods are summarized in Table 7.2. An alluvial ore, which consists of unconsolidated sand and gravel lying near the Earth's surface, requires the least energy. It needs only to be excavated by shovels or dredges and to be processed for the separation of the heavy minerals. Examples include titanium, zirconium, and also tin minerals. For these, the dredging of the alluvial ore followed by a physical concentration of the heavy minerals on board the dredge requires 0.023 to 0.07 · 10^9 joules for every ton of ore excavated and processed. Next come the typical hard rock ores that can be mined from the surface by open-pit methods and processed by crushing and grinding (to about 100 μm particle size), followed by concentration by flotation. The energy requirement for such ores is in the range of 0.35 to 0.45 · 10^9 joules for every ton of ore mined and processed. For treating a hard rock ore that is deeply buried, the sequence of operations consists of underground mining, crushing, fine grinding, and flotation. These require about 1.0 · 10^9 joules of energy per ton of the ore. In mining, the energy needed for the drilling, blasting, ventilation, and dewatering of underground mines is relatively small. The operations of loading the ore, lifting it out of the pit or the mine, and its haulage are the most energy-intensive. In primary physical beneficiation, fine grinding of the ore is the most energy-intensive operation and the energy requirement for this may range from 0.11 to 0.28 · 10^9 J t^{-1}, depending on the hardness of the rock and the fineness to which it has to be ground. In contrast, for a coarse grinding of rock and for mineral separation by flotation, magnetic separation, or gravity concentration, the total energy requirement is only about 0.07 to 0.10 · 10^9 J t^{-1} of ore. Milling and concentration are usually performed near the mine site in order to minimize the energy consumed in transporting large quantities of ore. Crushing in gyratory and cone crushers involves less energy consumption as compared to grinding in rod and ball mills. The latter consume a considerable amount of steel, which indirectly amounts to energy consumption.

When ores are mineralized in such a way that discrete grains of valuable minerals are contained in a matrix of gangue minerals, physical concentration methods such as flotation, gravity separation, and magnetic separation can yield valuable mineral concentrates with recoveries in the range of 80 to 95% of the value in the ore. However, there are important ore types in which the nature of mineralization is not amenable to physical concentration, and so primary processing by chemical means is necessary.

Primary chemical treatments of the ore can be of two types. If the metal values in the ore are selectively soluble in a relatively dilute acidic or alkaline solution, leaving the gangue unaffected, and if the metal values in the ore can be removed from the solution by a simple process such as precipitation, ion exchange, or solvent extraction, the treatment turns out to be the least energy-intensive among the chemical beneficiation techniques. In such cases, mining and selective leaching to the stage of a concentrate containing the metal together require about 0.35 to 1.4 · 10^9 joules of energy per ton of ore. Selective leaching of gold and uranium ores respectively are examples where the energy requirement corresponds to the lower and the higher limits of this range. When the ore is so mineralized that the entire rock matrix has to be attacked either by chemical digestion in hot, concentrated, aqueous solutions, or by smelting to yield molten phases, the treatment turns out to be the most

Table 7.2 Unit energy for mining and primary processing.

Ore type and processing method	***Unit energy (10^9 J t^{-1} g ore)***
Alluvial ore, physical concentration	0.023 – 0.07
Hard rock ore, physical concentration	0.35 – 1.0
Hard rock ore, selective leaching	0.35 – 1.4
Hard rock ore, chemical digestion, or smelting	4.5 – 14.0

energy-intensive among the chemical beneficiation techniques. The energy requirement in such cases is about 4.5 to 14 · 10^9 joules of energy per ton of ore for mining and primary processing. About 8.5 to 10 · 10^9 joules are required for the smelting of one ton of nickel laterite ores to produce molten ferronickel and slag. The production of pure aluminum oxide from bauxite ores by strong alkali digestion at elevated temperatures and pressures (Bayer process) requires about 8.5 · 10^9 joules of energy per ton of ore. Aluminum refining by the Bayer process consumes about 16% of the total energy needed for the production of one ton of primary aluminum.

Metallic ores can vary widely in grade (% metal content). The grade of the ore, G, determines the number of tons of the ore, T, that must be processed to recover one ton of the metal. If the recovery (% metal recovered) during processing is represented by R, the terms G, T, and R are related as follows:

$$T = 10{,}000/(G\ R)$$

According to this relationship, if the desired recovery is fixed at 90%, only about 1.7 tons of high-grade direct shipping iron ore (~ 65% iron) need be processed to produce 1 ton of iron. To produce 1 ton of gold from an ore containing 0.001% gold, about 111,000 tons of the ore will have to be processed. If U is the energy required for mining and primary processing of 1 ton of the ore, the energy requirement, E, for the recovery of 1 ton of the metal, corresponding to the stages of mining and primary processing only, will be

$$E = U\ T = 10{,}000\ U\ /\ (G\ R)$$

This relationship is illustrated in Figure 7.1, where E is plotted against G for a recovery level (R) of 80%. The pronounced influence of ore type and ore grade on energy requirements is clearly brought out in this figure. Each of the bands in the figure represents an ore type, with the width of the band indicating the typical range of energy required for the mining and primary processing of 1 ton of ore. The upward slope of the band from right to left highlights the effect of ore grade on the energy required for the recovery of 1 ton of metal. This has been called by Kellogg "the tyranny of ore grade". No band is shown for the selective leaching of ores because this is almost identical to that for the concentration of hard rock ores. Two specific situations in the same band may be considered which amply illustrate the tyranny of the ore grade. According to the figure, the recovery of 1 ton of copper from a hard-rock ore of 0.6% grade involves 73 · 10^9 J of energy expenditure for mining and concentration. On the other hand, the recovery of 1 ton of gold from an ore of 0.001% grade involves a much higher energy expenditure of 44,000 · 10^9 J for mining and selective leaching. Apart from the tyranny of the ore grade, one has to contend with the tyranny of the ore type. If the amounts of energy required for mining and primary processing for the recovery of 1 ton of nickel as ferronickel from two different types of nickel ores of the same grade are compared, it is seen that the energy required in the case of nickel laterites is more than ten times greater than that required in the case of sulfide nickel ores. Examples such as these bring into focus the pattern of energy demands in the future when ores other than those which are presently being mined and processed will have to be exploited.

With the passage of time, the average grade of the ores mined for metal production has become progressively leaner, and this trend will continue in the future because metallic

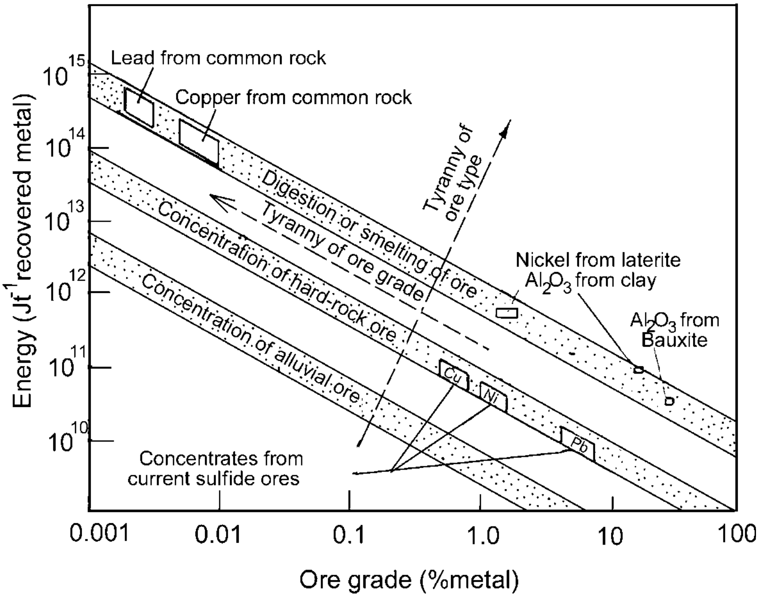

Figure 7.1 The relationship between energy requirement versus ore grade energy conservation.

ores are nonrenewable resources. For example, fifty years ago the average grades of the iron and the copper ores mined in USA were about 55% and 1%, respectively. At present, these grades are about 34% and 0.6%. As illustrated in Figure 7.1, a decrease in the grade of the ore of a given type results in an increase in the energy requirement for producing 1 ton of the metal. Such an increase in the energy needed may be offset by technological advances leading to energy savings in presently energy-intensive processes. In mining and primary processing, for instance, the use of belt conveyors (in the place of the current practice of truck haulage) for transporting the ore from open-pit mines can result in energy savings. Improvements in grinding circuits, as for example, by the use of computers for control purposes, can also result in energy savings. The relief brought about by the energy saving measures known at present can support the economics of mining and primary processing upto a certain decrease in ore grade, but not beyond that. Many of the suggested future sources of metals, of which common rock (which contains metals such as copper, lead, and zinc in ppm levels) is an example, are very low in grade and also are mineralogically complex. Their processing will involve digestion with strong reagents or smelting of the rock. As a result, the energy consumption for metal recovery from these sources will place them at the top left-hand corner of Figure 7.1. The energy requirement in such a situation will be about 1000 times higher compared to the present level. The escalation in energy intensity attendant to the processing of the possible future sources of metals can again be illustrated by taking the example of deep-sea manganese nodules. These constitute a unique type of mineral resource, which, by virtue of its extensive availability, may very well prove to be a major commercial source for some nonferrous metals in the future. This resource is also remarkable on account of its complexity. A special feature of these nodules, which has a bearing on the energy requirement for their processing, is their water content, which is tenaciously held even at high temperatures, due to capillary condensation in extremely fine (nanometer size) pores. This strongly held water content renders such standard extraction processes as roasting and smelting prohibitively energy-intensive. The energy intensity for the processing of manganese nodules is also excessively high because of the fact that the nodules are indifferent to physical concentration processes such as flotation or magnetic separation. As a consequence, processes designed to treat concentrates have to be applied to the ore itself, making the entire operation energetically unviable, unlike the situation obtained with most of the land-based metal resources.

7.2.2.1 **Energy Conservation**

No summary of energy and its applications can be concluded and completed without discussing energy conservation measures. Historically, energy has been an inexpensive commodity, and humans have become used to spending energy on a huge scale. The future depends on a well-designed energy policy that involves fossil fuels, nuclear fuels, and solar energy and that does not lose the right of concerns over environs.

It is ironic to note that, when energy costs are low, squandering energy is often more economical than making constructions to conserve it, and it is perhaps for this reason that procedures which wasted energy were common sights for many years. Producers of oil were unhappy when they stumbled on pockets of natural gas, since the gas posed an explosion hazard, and so huge amounts of gas were simply burned off. Likewise, the construction of buildings and housings with an absence of insulation was in vogue as heating them was cheaper than buying effective thermal insulation. Similarly, very little attention was given to the fuel efficiency of automobiles, as gasoline constituted a minor expense in the cost of running a car.

Now, there has been a turn around in the status. Much of the low-cost domestic petroleum has already been pumped from the ground, and as oil wells have been drilled deeper and deeper the cost of oil concomitantly has gone higher and higher.

Much effort has gone into conserving energy as industries have begun to realize that energy is not the cheap commodity that it once was, that automobile efficiencies have risen many fold, and that most communities need insulation in all new buildings. There is, however, no room for complacency, as the end is not in sight and there is still scope for additional improvement. In this respect the current activities of car manufacturing industries, with an emphasis on producing fuel-efficient cars and engines, barely needs any elaboration.

It is superfluous to address here the needs for registering even further improvement of energy conservation. While research in relevant fields will continue to focus attention on energy issues, the societal habits of the population must undergo change. An estimate has been made that about 50% reduction in energy consumption is a realistic goal for dwellings and industries within the next few decades.

It is important to understand that great amounts of energy can easily be saved without the need for high-technology devices. For example, increasing the seating capacity of a car from two to four would amount to reduced energy consumption and emissions of a few percent. Even greater gains would ensue from a wider use of public transportation. Changes in practices are significant, but a global policy that covers economic evolution and progress, efficiency, and conservation must also be executed.

The integration of entirely new technologies to a greater degree than in the past (because of their previous doubtful status) may be highly rewarding. An example of this is the fuel cell (FC), which was mentioned earlier. The story of the FC goes back to 1839 when Sir William Grove forecast that it should be possible to reverse the process of electrolysis of water (thereby reacting H_2 and O_2 to produce electricity), although the FC in working form first appeared at a much later time.

It may be recalled that the FC is an electrochemical engine that generates power without recombustion or rotating machinery. It generates electricity by uniting hydrogen ions, pulled from a hydrogen-bearing fuel, with oxygen. It may also be recalled that some FCs need pure hydrogen as a fuel source; others can work on methane (natural gas) or other hydrocarbons. The efficiency of FCs can be as much as 80–90%; this implies that instead of the massive power plants of today, new power plants could be created anywhere, anytime by the stacking of several FCs. These localized power generators will have no transmission and distribution losses, and no pollution will be caused, as an inspiring bonus of this technology is that it produces water as a by-product. The first use of FCs was conceived in vehicles, in a project conducted by the Electric Fuel Corporation in the USA to manufacture a FC-driven bus in Las Vegas. Indeed, a fleet of FC-powered double-decker buses will soon be made operational in London. India will also be recipient of this simple technology. FC-powered buses are also being introduced in Brazil, Mexico, Egypt, and China, where pollution levels will be correspondingly reduced as a result. All told, it is perhaps not a total dream to recognize the great potential of the FC to change our lives, homes, and cities. The view from our homes will no longer be high-voltage transmission lines, or electric poles. No longer will the vehicles passing be emitting unsightly black smoke from their exhaust pipes. The world around will be cleaner, and liberated from pollution. With good fortune, these changes will arrive sooner than expected, and much will be owed to FC technology which is rapidly evolving.

7.2.3
Reduction and Refining

The processes of reduction and refining convert the metal concentrate, obtained as the result of mining and primary processing, to the primary metal in some unfabricated form (ingot, sponge, slab, cathode, etc.). Reduction may be effected by pyrometallurgical processes (as in the cases of iron, copper, and lead) or by electrowinning (as in the cases of zinc, aluminum, and magnesium). The reduced metal is often refined by pyrometallurgical processes (e.g., steel, lead and tin) or by electrorefining (e.g., copper, silver, and gold). Since the starting material for reduction is a concentrate or an interprocess intermediate that is rich in metal content, the energy requirements for these stages are independent of the ore grade. However, the grade (% metal content) of the concentrate does influence the energy requirements.

The process energy required for the reduction and the refining of interprocess intermediates to primary unfabricated metals is basically composed of two parts. One part corresponds to the theoretical minimum free energy requirement for the decomposition of the pure metal compound yielding the metal. The other part comprises the extra energy required due to the inefficiency of the actual reduction processes. This component would be

Table 7.3 Process energy for metal production from concentrates.

Metal (process)	***Process energy***	***Free energy***	***Free energy/ Process energy ratio***
	· 10^9 J t^{-1} metal		
Titanium sponge (no reduction)	417	19	0.045
Magnesium (electrolytic)	394	23	0.058
Aluminum (Hall process)	229	29	0.13
Sodium (electrolytic)	106	8.1	0.077
Nickel (sulfide smelt)	103	3.6	0.035
Ferrochrome, high C (arc furnace)	64	10	0.16
Ferromanganese (arc furnace)	56	8.5	0.15
Copper (smelt, electrorefine)	56	2.1	0.038
Zinc (electrolytic)	56	4.9	0.087
Steel (blast furnace, BOF)	26	6.6	0.25
Lead (smelt, fire refine)	21	0.93	0.044

absent if the process could be carried out under reversible (maximum efficiency) conditions, and would assume progressively larger values as the efficiency of the reduction processes decreases. The process energies required for metal production from concentrates for a number of metals are listed in Table 7.3.

There are differences, which are sometimes very large, when the process energies pertinent to different metals are considered. One inherent reason for this is that the theoretical minimum energy required for the reduction of a compound to the metallic state differs from metal to metal. For example, assuming that the processes are carried out under reversible (ideal) conditions, the reduction of alumina to aluminum will always require more than four times the energy needed for the reduction of ferric oxide to iron. The value of the energy needed per ton of the metal is higher for a metal which forms a more stable metal oxide and has a lower atomic weight and a larger valency in the stable metal oxide. Thus, the production of aluminum, magnesium, and titanium would always be far more energy-intensive than the production of lead, copper, and nickel.

The values given in the second column of Table 7.3 are the estimates of the energy needed in actual processes for the production of metals. The values of the ratio of the process energy to the free energy vary from 28.5 for nickel to 4.0 for steels. These values roughly indicate the energy efficiency of the reduction processes as practiced. The nickel reduction process consumes about 28 times the theoretical minimum energy needed for the reduction. The corresponding value for steels is about 4. Thus, steel production processes are far more efficient than the nickel production processes. Besides nickel, the metals copper, lead, and titanium are also produced at very low efficiencies. There are many process features which interact to determine the overall energy efficiency. The most important among these are: (i) the need for large amounts of electrical energy; (ii) the necessity of using a complex flowsheet and energy-intensive reagents; (iii) the requirement of handling low-grade interprocess intermediates (feed material); (iv) the necessity of adopting energy-intensive measures against pollution; and (v) batch production and small batch sizes.

The electrowinning of aluminum, magnesium, sodium, and zinc and the electric furnace processing of ferrochrome and ferromanganese require large amounts of electrical energy. It is to be noted that this electrical energy is produced at a low efficiency from fuels, and that this is reflected in the lower energy efficiencies of electrolytic and electric furnace processes.

When the flowsheet is complex and involves numerous process steps, a low-energy efficiency will result. The metals titanium and magnesium are difficult to reduce, and their production involves chloride intermediates which are produced from the oxide raw materials. Titanium requires magnesium or sodium as the reducing agent, and these metals are themselves obtained by electrolytic processes which are energy-intensive. Another feature which may add to the complexity of the process flowsheet is the need to separate impurities and by-products using special processes; this is the case with copper, lead, and nickel.

Just as a low grade of an ore is associated with increased energy requirements in mining and primary processing, a low grade of the feed material can increase the energy needed for metal reduction. The reason is the same: more energy is required to process larger amounts of a low-grade material to produce a ton of the metal. For example, the sulfide concentrates of nickel and copper contain ~8% nickel and ~25% copper, respectively. The energy requirements pertinent to the processing of these concentrates are higher than those corresponding to most of the other metals cited in Table 7.3, for which the feed materials contain 50–70% of the metal.

Mandatory pollution control measures, which are usually energy-intensive, add substantially to the process energies of certain metals. Copper, nickel, zinc, and lead are produced from sulfide concentrates, and sulfur dioxide emission occurs during their processing. Pollution control regulations do not permit the release of sulfur dioxide into the atmosphere. The installation and operation of gas-handling circuits consume energy which is added to the metal production energy requirement. The total process energy required for the production of 1 ton of copper includes about $8 \cdot 10^9$ joules for the relevant pollution control measures. In the electrolytic production of aluminum metal, the energy needed for the abatement of pollution from fluorine and fluorides is added to the process energy. The process energy for iron and steel-making includes the energy required for containing air pollution from coke ovens and from steel-making dusts.

Batch-type production processes, particularly those with small batch sizes, have less energy efficiency as compared to continuous processes. A typical example of a batch operation on a relatively small scale is the production of titanium in 1-ton batches of the metal. The energy efficiency of the process is much less than that of continuous methods such as iron being produced in a blast furnace, or even of large-scale batch methods such as basic oxygen steel-making. The heat losses per unit of production are much less in continuous and large-batch processes, and this also enables the waste heat from process streams to be used.

7.2.3.1 **Improved Process Design**

As in the case of mining and primary processing, increases in the process energy levels can be arrested and even reduced to a considerable extent in the reduction step also by correct process design to conserve energy. For example, an increase in the size of the furnace/reactor results in a relatively reduced energy loss due to radiation and thereby may improve the energy efficiency of the process. This has been practiced for iron making in blast furnaces and smelting in reverberatory furnaces. Occasionally, the form of energy also results in improved efficiency; for example, electrical energy is more efficient than energy derived from the combustion of fossil fuels. One of the main reasons for this is that a large amount of nitrogen has to be unnecessarily heated during the fuel combustion. Improvements in processes can also be obtained by using correctly graded charge components, as this prevents channeling and ensures a proper gas/solid reaction. The use of high pressures or of sub-atmospheric pressures can also improve a process by altering the process thermodynamics in a desired direction. Yet another approach to process improvement involves the preheating of either the fuel or the air used or of the charge, or of all of these.

Many of these measures (and some others, such as oxygen enrichment) have been implemented for a number of metals and are likely to be extended to many more. In pyrometallurgy, in particular, the use of commercial-purity oxygen with reactor designs capable of high-intensity reactions has resulted in improved energy efficiencies. For example, in steel-making, the energy-efficient basic oxygen steel-making process has largely replaced the old method of open-hearth steel-making. In basic oxygen steel-making oxygen is blown at supersonic velocities into a bath of molten pig iron through a lance positioned above the metal bath. A rapid oxidation of carbon, silicon, and the other impurities present in the bath occurs due to an intimate mixing of the metal, the slag, and the gas phases. Compared to the open-hearth process, which needs a processing time of 8–12 h, a batch of 200 tons of steel can be produced in about 0.67 h by basic oxygen steel-making. The specific capacity, which is defined as the number of tons of product produced per day per cubic meter of reactor volume, is ~65 for a basic oxygen converter as compared to ~2 for the open-hearth process. The energy requirement of the basic oxygen process stems mainly from the need for producing oxygen from air which itself corresponds to $\sim 2.6 \cdot 10^9$ joules per ton of steel, whereas for the open-hearth process it is $\sim 5.8 \cdot 10^9$ joules per ton. In the open-hearth process, fuel is needed to maintain the furnace at the required temperature for many hours. A further decrease in the net energy requirement of the basic oxygen process can be brought about if the energy associated with the carbon monoxide that emerges from the mouth of the vessel can be captured and utilized.

Another major example of improved process design to conserve energy pertains to the flash smelting of the sulfide concentrates of copper or nickel with oxygen-enriched air or with undiluted oxygen. The oxygen flash smelting furnace has a specific capacity which is about four times greater than that of the conventional reverberatory furnace. Besides, the PFE in flash smelting is 35–50% lower than the PFE in reverberatory smelting. Flash smelting also offers the possibility of computerization and automated process control. As regards continuous copper smelting and converting processes, although such schemes have lower capital costs because several processes are combined in one vessel, a further upgrading with regard to copper by treatment in a converter is necessary and this involves a large amount of energy consumption.

Primary aluminum production by the Hall–Heroult process is quite energy consuming. In aluminum production, electricity represents 70% of the total energy requirement, while about 90% of this electricity is used for the electrolysis of alumina. However, many minor design improvements have resulted in a decrease in the energy requirement which was ~22 kWh kg^{-1} of aluminum in the 1940s to ~14 kWh kg^{-1} in the 1980s. A further decrease in the energy requirement could result from the adoption of the new fused chloride process for the electrolytic production of aluminum.

The electrolytic production of magnesium consumes between 12 MWh and 18 MWh per ton of the metal, depending on the cell design. The cell power consumption could possibly be reduced to 9.94 MWh per ton by improved cell technology, through the use of electrolytes of high conductivity, enabling high current densities to be obtained, and the exploitation of small density differences to control the separation of magnesium from the electrolyte. An additional energy of ~15 MWh per ton is required for the preparation of the anhydrous magnesium chloride feed for the cell. The power requirements of conventional electrolysis are comparable to those of the thermal process of silicothermic reduction under vacuum, where the preparation of the ferrosilicon reductant is rather energy-intensive, needing ~11.7 MWh per ton.

7.2.3.2 Waste Heat Recovery

The waste heat may in general be defined as the heat in the products of combustion discharged from an installation after having the primary functions fulfilled. A fundamental consideration is that waste heat is not wastage or surplus on account of any inefficiency of the primary plant, but it is no longer usable for its primary purpose. The heat content of products of combustion rises with temperature and so, clearly, the hotter the waste gases the greater is the quantity of heat available for recovery. Waste heat recovery in any metallurgical operation is very important because it not only improves the heat economy of the furnace but may also improve the process efficiency. Usually, a compromise must be worked out between the cost of the heat recovery systems used and the value of the heat recovered. Waste heat recovery can be accomplished either by direct or by indirect systems.

- In a *direct system*, the heat recovered is directly returned to the process stream. For instance, incoming air for combustion and/or incoming fuel can be preheated by the hot waste gases flowing out of a process furnace. This recycling system has many advantages, one of which is that the system is never generating waste heat which cannot be used.

- In an *indirect system*, the heat recovered is not directly returned to the process stream but is used to heat water or generate steam for use in other general purpose applications in a plant practice. Flue gases from industrial process heating are now regarded as a secondary source of heat though, only the sensible heat from the flue gases can be recovered to some extent. Complete recovery of waste heat is neither theoretically possible nor economically feasible, and hence only the optimum quantity of heat is advisable to be recovered. The principal techniques for waste recovery are: (i) recovery as steam through waste heat boilers; (ii) as sensible heat through recuperators and regenerators; (iii) preheating of solid stocks approaching the hot zone; and (iv) superheating steam, preheating boiler feed water, and combustion air in boiler. In confining the present scope to the metallurgical industry, it is clear that there exists a very large variety of systems for waste heat recovery. To illustrate the variety and diversity of these systems, reference may be drawn to recuperators, regenerators, stoves, waste heat boilers, and rotary kilns.

- *Recuperators* are heat exchangers which are mainly used for the recovery of heat from waste gases to preheat the gaseous fuel or the air used for combustion. The two streams – the hot fluid stream and the colder stream – are not allowed to mix with each other as

Table 7.4 Comparison between metallic and ceramic recuperators.

1. Metallic recuperators are 10 to 20 times lighter compared to an equivalent ceramic recuperator.
2. Metallic recuperators occupy less space than ceramic ones.
3. Metallic recuperators are practically leak-proof and so are also capable of handling toxic fuel gases. The ceramic recuperators leak to the extent of about 50% of the volume gases and air handled.
4. Metallic recuperators are favorably disposed economically when applied for preheating air below 650 °C. Ceramic recuperators are only economic when applied for preheating air above 650 °C.
5. Metallic recuperators can operate with higher pressure differentials between flue gas and air side than ceramic recuperators.
6. Metallic recuperators are easier to maintain and install than ceramic ones, they also involve less initial cost.

they are separated by metallic membranes. Because of limitations of the operating temperatures for the metals, refractory tubes/channels are constructed for operation at higher temperature. Metallic recuperators are more efficient because of their low resistance to heat flow and their more compact and sound construction. Depending on the mode of heat transfer, the metallic recuperators are of three types: radiation; convection; and combined radiation and convection type. The recuperators can be parallel or cocurrent, countercurrent, and crossflow types; counterflow recuperators are most efficient. A comparison between metallic cuperators and ceramic recuperators is provided in Table 7.4.

- *Regenerators*, on the other hand, are heat exchangers constructed of refractory bricks, operated in pairs and which work in a cyclic manner (intermittently), unlike recuperators which are continuous in operation. These generally comprise larger chambers made of ceramic bricks which alternately absorb heat from the hot gases in one cycle and then transfer it to the ambient air passing through them in the next cycle. Comparison between regenerators with the recuperators is shown in Table 7.5. A simplified depiction of the principles of heat recovery systems involving regenerators and recuperators are shown in Figure 7.2. A stove is essentially a combination of a furnace and a regenerator. A fuel with a relatively low calorific value (e.g., blast furnace gas) is burnt in the combustion chamber and the hot gases are used to heat the regenerator brickwork which in turn imparts its heat to the ambient air introduced into the regenerator.

Table 7.5 Comparison between regenerators and recuperators.

1. Use of regenerators is limited to large steel-melting furnaces; for example, an open-hearth furnace, and by-product coke ovens with fuel combustion systems only.
2. Regenerators require larger capital outlay and more involved civil works as compared with recuperators.
3. The overall size and space requirement of a regenerator is very high compared to an equivalent recuperator.
4. A higher initial and maintenance cost is involved with regenerators as compared with recuperators.

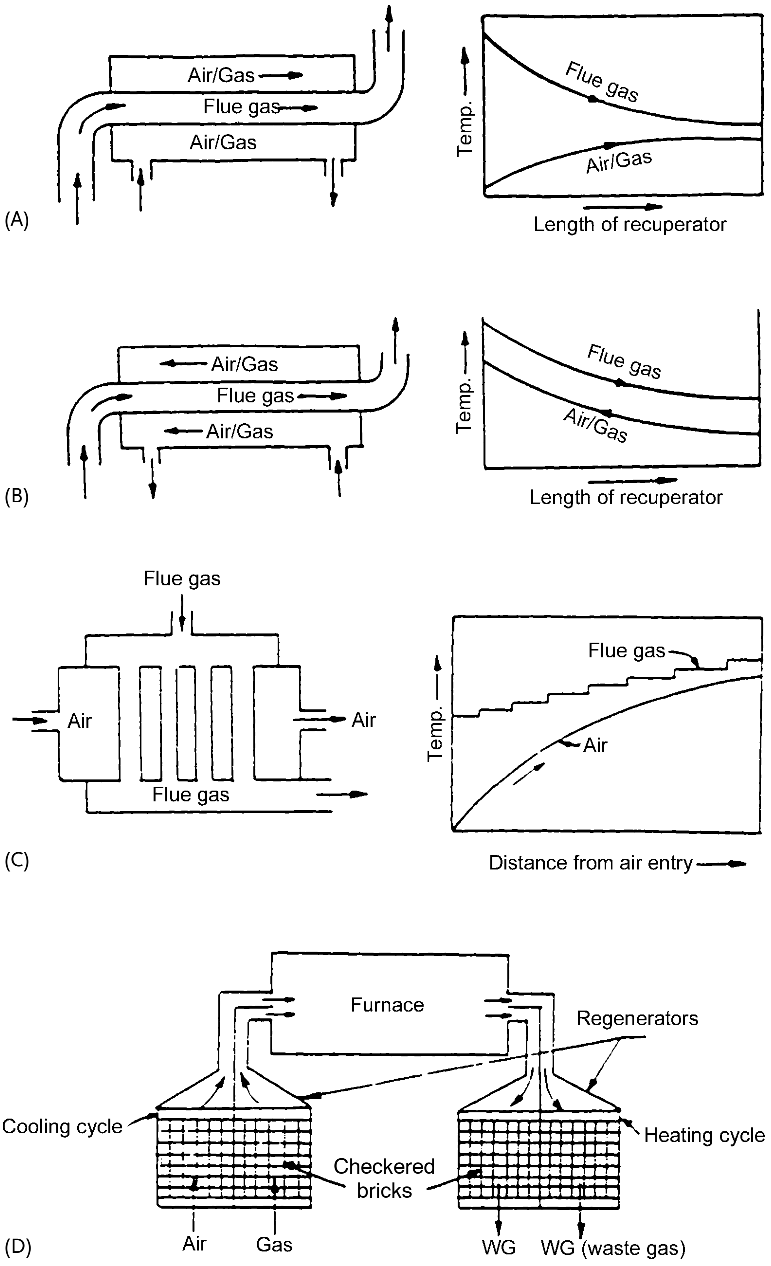

Figure 7.2 Simplified depiction of principles of heat-recovery systems involving recuperators and regenerators.
(A) Parallel-flow recuperator type and its temperature distribution.
(B) Countercurrent flow recuperator type and its temperature distribution.
(C) Cross-flow recuperator and its temperature distribution.
(D) Regenerator.

- *Waste heat boilers* are used to generate steam using hot waste gases. In the reverberatory furnace used for copper smelting, much of the heat of combustion is carried away by the waste gases, which leave the furnace at a very high temperature. Waste heat boilers, therefore, constitute an integral part of the furnace. The quantity of heat that will be recovered in a waste heat boiler depends on the temperature of the gases. Waste heat boilers suffer from the following limitations: (i) when the flue gas temperatures are higher than 650–750 °C, the waste heat boilers are not considered; (ii) since the heat is recovered in the form of steam, it is applicable to those installations where steam thus raised can be used totally in the immediate vicinity; (iii) there is difficulty in using this system in small and medium furnace installations; and (iv) when the flue gas temperatures are of the higher order, these can be used in combination with recuperators permitting higher overall heat recovery.
- In a *rotary kiln*, a countercurrent movement of the charge and the gases results in utilization of the heat carried by the hot gases to preheat the charge.

The iron smelting process in the blast furnace is a classic example worth mentioning in order to illustrate some general features of waste heat recovery. With respect to the combustion of its fuel and the resultant formation of gases, the iron blast furnace is like a huge gas producer. There is always an excess of carbon in the combustion zone, and the product formed in it is carbon monoxide. There is, of course, no steam blown in as such, but whatever moisture is present in the blast is decomposed by carbon, as in creating producer gas:

$$H_2O + C = CO + H_2$$

Added to this hydrogen are any hydrogen and other volatile matter expelled from coke, and these two sources account for the small percentage of hydrogen and methane found in the blast furnace gas. It must be noted that the furnace charge enters at the top and is subjected to a gradual heating as it slowly descends the furnace, while the blast enters directly in the hottest part. Moisture in the ore, flux, and coke is evaporated in the upper part of the furnace and enters the furnace gas as water vapor. Blast furnace gas is accordingly combustible, though of a much lower heating value than producer gas. The high temperatures needed in the blast furnace necessitate the use of a preheated blast. Burning a portion of the blast furnace gas in “hot blast stoves” constitutes a convenient and cheap method of heating the blast. To prevent the escape of the blast furnace gas during charging, two conical bells are fitted to the top of the blast furnace. The charge in the skip is delivered to the upper bell, which is then lowered to allow the charge to fall onto the lower bell; the latter meanwhile is held against its hopper, thus preventing the escape of gas. The upper bell is then raised and the lower bell lowered so as to permit entrance of the charge to the furnace and to preclude the escape of gas, all of which passes along the downtake. Heat recovery is implemented by Cowper stoves installed with a blast furnace. These stoves consist of tall iron cylinders lined with firebricks and packed with checker brickwork (so as to provide a large surface area) with a circular gas flue on one side. A part of the gas from the blast furnace, together with sufficient air to burn it, passes through until the bricks are red hot. The combustion products escape through a chimney. The gas is then passed through a second stove, and the air blast to the tuyeres is sent through the first stove until the brickwork has cooled. The two stoves thus alternately work as absorbers and emitters of heat, or as heat regenerators. It may be added that the blast furnace gas, besides its use in heating of the Cowper stoves in which the gas is burnt with sufficient air for combustion, is well known for a number of other applications. It is used for steam raising in boilers fitted with gas burners instead of the usual grate, as fuel for gas engines driving blowers to supply the large volume of air needed in the blast furnace, for mixing with coke oven gas as a fuel in open-hearth steel furnaces and reheating furnaces, and to a certain extent for illuminating purposes. Figure 7.2 (B) shows a regenerator installed with an open-hearth steel-making furnace. The furnace is heated by producer gas, and the air and gas are supplied through separate regenerators of chequer brick works; these are used in pairs and are traversed alternately by the hot products of combustion, and the gas and air, as in Cowper stoves.

7.2.4
Materials Conservation

Materials, like all resources, are limited in supply. Consequently, materials conservation is a very important issue. Before discussing the ways by which materials conservation can be accomplished, it will be useful to refer to the total materials cycle, shown in a simplified form in Figure 7.3. In this global scenario, natural resources extracted from the earth are first converted into basic materials and then further processed into engineering materials. These, in turn, are manufactured into products which society requires. At the end of their useful life period, these products are either put back in to the earth as waste, or are recycled. Not only does every operation in the cycle require energy, but there is also the involvement of the environment. There is a strong interaction among the three elements – materials, energy, and environment – that occurs at virtually every point in this materials cycle. At every stage in the cycle, materials and energy losses are encountered which, for common

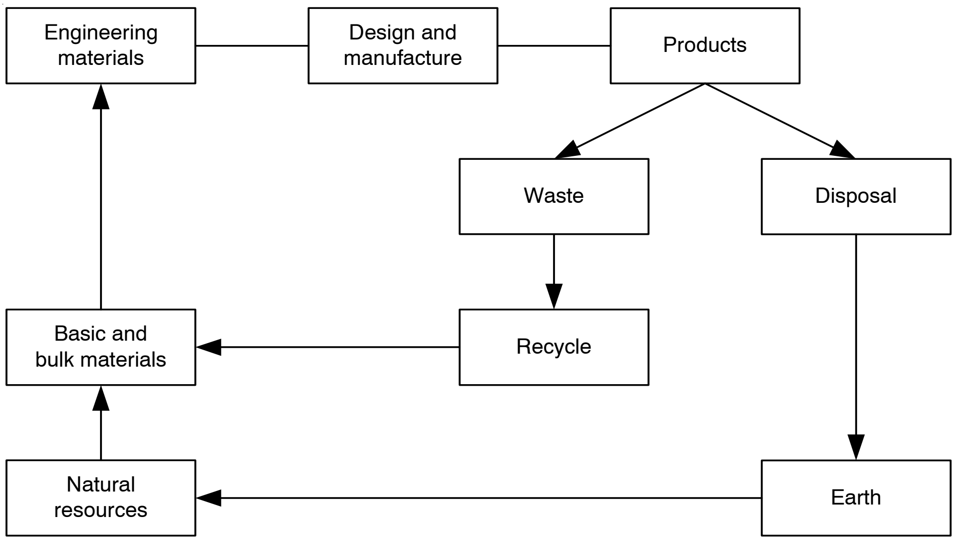

Figure 7.3 Simplified diagram of the total material cycle.

metals, account for about 50–70% of the total amount that enters the cycle. A reduction in these losses in the materials cycle can be a defined as materials conservation.

There are three ways of accomplishing materials conservation: (i) effective materials utilization; (ii) materials substitution; and (iii) materials recycling.

Effective materials utilization covers a very broad range of activities as it encompasses not only product design, development, and deployment, but also manufacturing and processing. Materials substitution is probably the most important of the three approaches listed with regard to materials conservation. Substitution directly alters the usage of materials, but can be employed advantageously only if the substitute material possesses properties that permit a given function to be achieved at a lower cost. One can identify several types of substitution which can contribute to the overall objective of materials conservation. As some representative examples, reference may be drawn to the substitution of:

a) abundant materials for more scarce ones; thus aluminum can be used in place of copper in electrical applications, or ceramics in place of high-temperature alloys in turbine engines;
b) nonmetals for metals; thus, plastics can be used in place of zinc or aluminum in some structural applications, or glass for metals in containers;
c) renewable materials for nonrenewable materials; thus, wood can be used instead of metallic materials for constructional purposes;
d) synthetic materials for natural materials; thus, quartz crystals can be used in electronic applications, and synthetic diamond in cutting and polishing applications;
e) composite materials for monolithic materials.

There are several factors which should be borne in mind while considering materials substitution as a means of materials conservation. The time required to effectively implement such a substitution may be substantial because of the requirements of examining alternative materials, of developing design and reliability data, and of evaluating the substitute in a manufacturing environment. In addition, the proposed substitute material may require new processing methods or may influence related technologies that interact with it in its intended use. All these factors can make the substitution process slower than desired. There are specific situations where substitution does not work at all, generally because the scale of use or the cost requirements cannot be met by any other material. For example, no material could replace steel in structural applications or lead in its application in batteries. The materials flows are altered by substitution, and this may create other problems in various parts of the materials cycle, particularly in basic materials supply and in recycling. Recycling has long been a part and parcel of the materials industry. It adds to materials supply and helps to slow down resource depletion, and it also scores over the other two ways of materials conservation, namely, effective use and substitution, in that no product or manufacturing alterations are required, though such alterations can be used for enhancement of recyclability.

Materials recycling or resource recycling is essentially resource recovery, which is the means by which waste resources usually destined for disposal are used as secondary resources or secondary raw materials to serve as valued inputs to the economy, fulfilling both producer and consumer needs. Resource recycling, as has been pointed out, increases the supply of available material, and thereby offers a potentially attractive means of reducing the demand on both renewable and nonrenewable resources. A basic objective should be to make better use of the resources already taken from nature and, to the extent possible and feasible, not to dispose of these in landfills or subject these to combustion or incineration for no useful purpose other than achieving a reduction in the volume of the waste. Resource recovery has environmental, conservational, public health-related, and aesthetic overtones.

Although the term *recycling* is applied most often to municipal wastes, it also applies to industrial or any other wastes. Municipal solid wastes come from: (i) construction and demolition; (ii) industry; and (iii) domestic sources. There are also special categories such as radioactive wastes which can sometimes be recycled (as in the case of nuclear waste reprocessing in the back end of the nuclear fuel cycle). Owing to the large volume and the generally low specific value of demolition materials (classified basically into two groups – one involving use in pavements and the other in residential and nonresidential structures), the degree to which they are recycled depends not only on where and in what condition and quantity they are produced, but also on the materials themselves. For example, ready availability of wood in the USA acts as a disincentive to process demolition wood there. Industrial waste streams, including most sources of industrial metal scraps, are never earmarked for disposal, but for recycling.

Interest in recycling has grown phenomenally during recent years, and this can largely be attributed to the increased use of metals in the present industrialized society and to the widespread use of several metals and other elements that were little more than laboratory curiosities some twenty or thirty years ago. In the latter category, mention may be made of such typical elements as gallium, indium, and germanium in electronics, and cadmium and mercury in batteries. The metallic contents of the wastes arising from the processing of these elements present the possibility of contamination of ground water from landfill, and of air pollution from incineration. A second reason for the increased emphasis on recycling stems from the knowledge that recycling is very energy-efficient. In a world that is greatly concerned about the consumption of energy, and particularly of fossil-fuel energy, this is a very important consideration. Thirdly, the new uses of some elements in large quantities may overwhelm the known primary sources; for example, the expansion of platinum consumption in the catalytic converters of automobile exhaust systems.

There are a number of factors which must be taken into account when considering recycled materials as possible sources of supply, including: (i) the physical and the chemical state of the material; (ii) the chemical composition of the material, including the presence or otherwise of unwanted materials or contaminants; (iii) the reliability of the source of supply; and (iv) the cost of this source material.

7.2.5
Reclamation and Recycling of Metals

When nonrenewable mineral resources are processed for metal extraction and the metals extracted are utilized in various ways and in diverse forms, they become potentially available for reclamation and recycling. Recycled metals produced by the extraction and refining of metallic wastes are known as *secondary metals*, whereas metals produced from primary ores are termed *primary metals*. A classification of recyclable metalliferous resources such

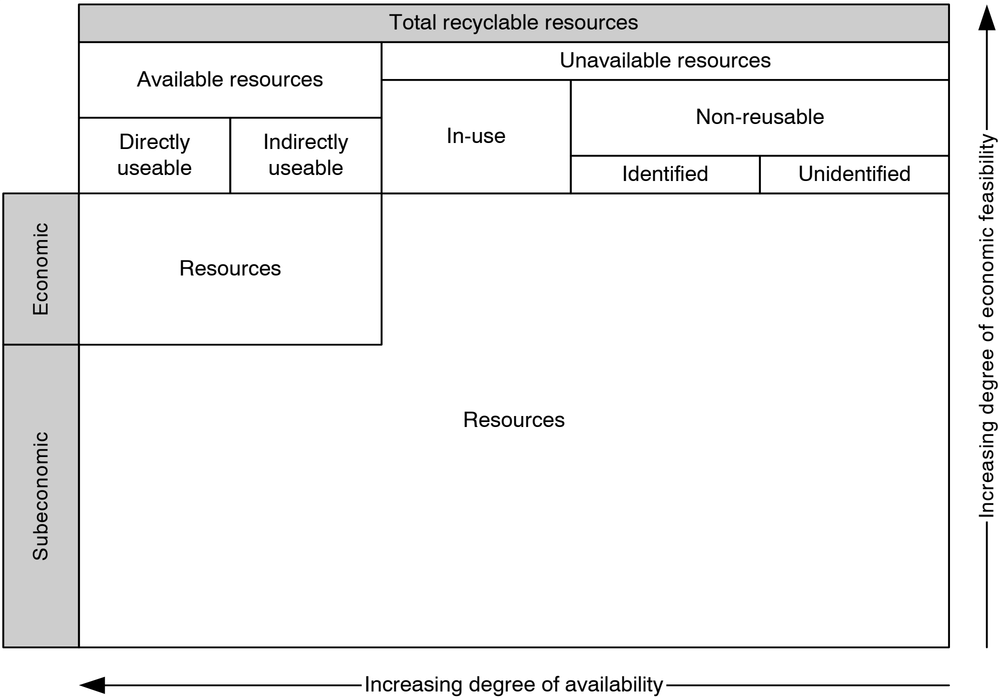

Figure 7.4 Classification of recyclable metalliferous resources.

as scrap and wastes is depicted in Figure 7.4. The parameters on which such a classification is based are economic feasibility of extraction and extent of availability.

Until now, the entire volume of primary materials produced may be considered to constitute the totality of the recyclable resources. It follows, from this point of view, that the sum of the remaining nonrenewable metalliferous mineral resources and the existing recyclable metalliferous resources at any point of time is constant, and equals the total metal resources of the world. Though the total resources potentially available for metal extraction remain unchanged, the relative proportion of the resources belonging to the two categories change continuously: with the passage of time, the recyclable resources grow at the expense of the nonrenewable resources and progressively become increasingly important. The relationship between nonrenewable and recyclable resources is illustrated schematically in Figure 7.5. That portion of the available recyclable resources that can be economically recovered and re-used at present has been designated as recyclable reserves in this figure.

Secondary raw materials recovered from scrap are more concentrated and more pure than primary raw materials. Scrap is already in the metallic form, and requires only purification which, in the most favorable or desirable cases, involves only melting. The recovery of secondary metals can, therefore, be carried out with fewer and simpler operations, consuming a smaller amount of energy and causing less pollution, than primary metals production. For example, the production of 1 ton of copper from ore consumes about 116 GJ of energy, while the consumption is only about 19 GJ when the production is from scrap.

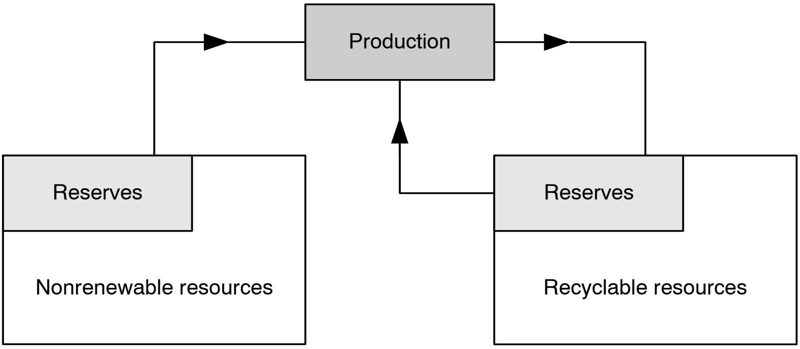

Figure 7.5 Relationship between nonrenewable and recyclable resources.

The degree of availability of recyclable resources such as scrap and wastes is a widely varying parameter. By way of illustration, scrap can be classified as new scrap (or in-process scrap) and old scrap (or post-consumer scrap). The former, which constitutes the majority of scrap processed at present, is derived mainly from the wastes generated during metal production and fabrication, and can be reclaimed and recycled with relative ease.

New scrap can be further subdivided into home scrap (generated during the production of either primary or secondary metal) and prompt industrial scrap (generated during the manufacture of metal articles). Home scrap, since it originates within the metal production plant, is recycled in-house. The amounts of home scrap and prompt industrial scrap are directly related to the level of manufacturing, and plentiful supplies ensue from these two sources in times of economic expansion. Almost all home scrap, as well as a sizeable part of prompt industrial scrap, are recycled and that also occurs within relatively short time periods. The recycling of home scrap and prompt industrial scrap does not really add to supply, though these are both very important components of recycling. The incentive is to minimize material losses and to lessen the burden on materials inventories. Thus, the recycling of scrap from these sources generally appears to be insensitive to the market prices for scrap as it would be recycled whatever the prevailing market conditions at any point in time.

Old scrap is derived from discarded or obsolete components which may have had quite an extensive and useful life span before becoming redundant and available for recycling. It is derived from many sources (discarded automobiles, outdated electronic gear, railroad cars, ships, etc.), and is dependent on the lifetime of the sources of generation. This varies greatly from source to source (the lifetime of a car can be 10–12 years, lead batteries last 2–4 years, metallic cans used as containers for soft drinks become scrap within months of manufacture). One can achieve a substantial increase in metal recycling from obsolete scrap. Unlike the other two sources – namely, home scrap and prompt industrial scrap – obsolete scrap does add to materials supply and is not insensitive to the market price. In fact, the prices go up at times of shortages in metals. This is one of the problems in recovering metals from obsolete scrap as the fluctuation in price can clearly affect the viability of any scrap recovery process.

New scrap is generally of high grade, is generated in large amounts at few locations, and can thus be easily collected and sorted. Old scrap, on the other hand, is generally of a lower grade and is often contaminated by paint, paper, grease, food, glas and other metals and alloys that cannot be completely separated. However, in the future, old scrap dumps may be important sources of secondary metals. The production of a saleable secondary metal from old scrap is far more energy-intensive than its production from new scrap, but is far less energy-intensive when compared with primary metal production.

7.2.5.1 **Secondary Metal Production**

Secondary metals production may refer to secondary metal extraction or to secondary alloy production. Secondary metal extraction normally extracts one metal from the waste and sells any valuable by-products to other metal extractors or chemical processors. In secondary alloy production, the scrap is blended and refined so as to yield an alloy of the desired chemistry. In both cases it is necessary to deal with various sizes, shapes, and compositions of waste materials and the processing route adopted; moreover, the plant where the process is implemented should have sufficient flexibility to handle such widely varying input material.

Solid metal scrap is generally recycled by adopting a pyrometallurgical route, whereas scrap in liquid form (e.g., spent electrolytes from electrochemical processing of metals) is usually subjected to a hydrometallurgical recycling route. There are basically two methods of processing liquid effluents for recovering the associated metal values:

1. Precipitation of a group of metals as a sludge followed by the recovery of the individual metals by a pyrometallurgical or hydrometallurgical route.
2. Extraction of a selected metal by applying solvent extraction, ion exchange, electrolysis, or gaseous reduction.

Event though there is a considerable overlap of the pyrometallurgical and the hydrometallurgical routes adopted, the industrial recovery techniques are generally based on pyrometallurgical extraction.

The MFE for the production of secondary metals comprises the energy required for the collection, sorting, and transportation of scrap, and that required for the preparation of and the processing to saleable secondary metals, as well as the energy equivalent of the supplies of major consumables and reagents. The most significant point is that the MFE for secondary metals is only a small fraction of the energy required to produce the primary metals from ores. This is so because most scrap metals are very high-grade raw materials and already exist in the metallic state. The MFE values pertaining to the production of many secondary metals and primary metals are listed in Table 7.6.

The energy requirement for the production of a given quality of a secondary metal is determined by the purity of the scrap processed. This dependence resembles the effect of ore grade on the energy required for producing a primary metal. The MFE values for processing three types of copper scrap are given in Table 7.6. A low-grade copper scrap (No. 3 scrap) consists of skimmings, grindings, ashes, residues, slags, brass, electric motors, switch boards, etc. The copper content averages ~30%, but some of these items may contain as little as only 5% copper. Processing of the scrap involves smelting in a cupola furnace to black copper, converting, anode refining, electrolytic refining, melting, and casting. The scrap designated as No. 2 scrap consists mainly of burnt wire, and of copper contaminated with solder, iron, oil, etc. The average copper content is about 96% and processing involves

Table 7.6 Material fuel equivalent (MFE) for production of secondary metals.

Secondary metal	*Type of scrap used*	*MFE (10^9 J t^{-1})*	*MFE (% of processing)*
Aluminum (alloy 380)	Various	17.5	6.2
Aluminum (can stock)	Scrap cans	10.1	3.6
Copper (refined)	No. 1 scrap	4.4	3.4
Copper (refined	No. 2 scrap	20.1	16
Copper (refined)	Low-grade (No. 3 scrap)	49.3	39
Brass, bronze	New scrap	8.2	6.4
Steel billets	Various	9.7	35
Lead (soft)	Batteries, etc.	9.4	30
Lead (hard)	Batteries, etc.	11.2	36
Nickel alloy	Alloy scrap	12.9	7.7
Tin (refined)	Tinned steel, new	201	91
Zinc (cast alloy)	New scrap	3.8	5.4
Zinc (slab)	Various	22.0	31

only anode refining, electrolytic refining, melting, and casting. Clean uninsulated copper scrap is called No. 1 scrap. This requires only melting and casting.

Among all the metals listed in Table 7.6, the MFE for the production of secondary tin is as much as 91% of the MFE for the production of primary tin. This unusual situation arises from the fact that tinned steel contains only 0.2–0.3% tin, and the processing of this source involves dissolution of the tin in a caustic solution, followed by an energy-intensive electrowinning operation to obtain metallic tin. An advantage is that the detinned steel scrap is suitable for steel manufacture.

The production of secondary zinc requires only 20–25% of the energy required for primary zinc production. Only one-fourth of the total zinc produced is the secondary metal. The reason for such limited recycling is that the major application of zinc is in castings rather than in parts.

A brief description is given of typical recycling routes for a few metals by way of illustration. In the case of iron and steel, both cast iron scrap and steel scrap are used extensively in the production of cast irons using cupola and electric melting; very often, steel scrap forms a part of the charge in the steel-making processes. The main problems associated with the use of steel scrap in steel-making concern the residual copper and tin, the concentrations of which must be kept low in order to prevent an unacceptable depletion in mechanical properties. Somewhat higher levels can be tolerated in cast irons, however.

A significant proportion of zinc scrap is blended and melted to product zinc–copper alloys of different compositions, while a relatively small proportion is recycled as the refined metal. A large volume of zinc wastes ise also recycled as zinc compounds such as the oxide, chloride, and sulfate. Among the zinc compounds, zinc oxide is the most important and is produced from zinc wastes by: (i) electrothermically reducing galvanizer's ash in a rotary kiln, where oxidation of zinc vapor occurs at a lower end of the kiln to yield zinc oxide; (ii) melting metallic zinc scrap in a horizontal retort with the resulting zinc vapor being oxidized to zinc oxide on contact with air; or (iii) acid dissolution of impure zinc oxide wastes followed by solution purification, precipitation of zinc carbonate and calcination to zinc oxide.

High-grade lead scrap is generally melted and refined to the required composition in kettle furnaces, while middle- and low-grade lead residues, lead-rich slurries, etc. are generally smelted in reverberatory furnaces, blast furnaces, or rotary-hearth furnaces. A large proportion of lead is used in the manufacture of storage batteries. For the reclamation of lead, the lead scrap obtained from the batteries is smelted with coke and fluxes in a rotary, reverberatory, or blast furnace. The major sources from which precious metals can be recovered include solution and electrochemical wastes, smeltable materials and slags, printed circuits and electronic scrap, and photographic film and paper. In general, the solid wastes are subjected to a pyrometallurgical recovery route, while liquids are subjected to a hydrometallurgical or an electrometallurgical route with adoption of a final electrowinning step. The cleaner solid scrap sources are normally smelted in a blast furnace with litherage, coke and pyrites. While coke provides the necessary reduction conditions and thermal energy, pyrites provides a sulfide matte. The precious metals are collected in a lead bullion created due to the presence of litherage; they also occur to a smaller extent in the sulfide matte. The three liquids, namely, slag, matte, and bullion, are tapped at different levels from the furnace hearth. Fines containing the precious metals are pelletized before charging to the blast furnace, and the larger items are crushed to aid charging. Scrap which is more rich in precious metals is melted with coke and litherage in a reverberatory furnace, again yielding slag, matte, and lead bullion. Silver is recovered from the bullion by preferential oxidation of impurities, and gold is recovered by chlorination. Each is subjected to a final electrorefining treatment.

To conclude this section, reference may be drawn to what is called the “Placid process” for recycling lead from batteries. Placid denotes the leaching of lead in warm, slightly acidic, hydrochloric acid brine to form soluble lead chloride. Lead is won from the lead chloride on the cathode of an electrowinning cell and is collected. Chloride anions are released simultaneously, but then react immediately with hydrogen ions that have been produced stoichiometrically from electrolysis of water in the anolyte and passed into the catholyte through a membrane. The hydrochloric acid that is formed is returned as a make-up content to the leaching bath.

7.3
Environmental Impact

It is generally well accepted that the principal causes of ecological degradation in industralized countries, particularly curing the post World War II era, are drastic changes in the technology of agricultural and industrial production, and transportation. In most cases, although the new and more polluting technologies have been more energy-inefficient than those they replaced, they have also been more profitable because they have utilized cheap energy. The ecological crisis has been blamed on a variety of factors, and in this context it is relevant to record some quotes pertaining to different points of references such as on exploding population: “Freedom to breed will bring ruin to all”; on affluence and wastefulness: “The affluent society has become an effluent society”; on man’s innate aggressiveness: “The first problem is people. The second problem, a most fundamental one, lies within us – our basic aggressions”; on profits: “Environmental rape is a fact of our national life only because it is more profitable than responsible stewardship of the earth’s limited resources”;

on technology: “A runaway technology, whose only law is profit, has for years poisoned our air, ravaged our soil, stripped our forests bare, and corrupted our water resources”. The very survival of human beings on the Earth depends on having a stable and continuing existence of an adequate environment, which encompasses a thin skin of air, water, and soil. It is important to point out the four laws of ecology that highlight the essentials of this science of planetary housekeeping.

- The *first law* states that everything is connected to everything else. The ecosystem comprises multiple interconnected parts, which interact with each other. The feedback features of ecosystems become useful in order to amplify and intensify several processes.
- The *second law* states that everything must go somewhere. In nature, there is no such thing as “waste”. In every natural system, what ensues from one organism as waste is used by another. Nothing can be expected to “go away”.
- The *third law* states that nature knows best. Modern technology aims to achieve improvement on nature. This law holds, however, that any major change created by man in a natural system is likely to be harmful to that system.
- The *fourth law* states that there is no such thing as a free lunch. In ecology, as in economics, the law emphasizes that every gain is achieved at some cost. In a way, this law integrates the former three laws. Since the global system is connected in a total manner, anything gathered from it by human endeavors must be paid back; the payment of the cost involved cannot be by-passed – it can only be delayed.

Environmental pollution is now a matter of considerable concern because the extent of pollution has been growing over the years. The major types of pollution and some of their origins are listed in Table 7.7. It should be noted that this list does not include noise pollution, which is becoming increasingly prominent in present times. To cite some representatively sources of pollution in different spheres of operations, mention may first be made of ore mining. In underground mining there is a generation of waste rock that comes to surface, while in open-pit mining there is removal of what is called “overburden”. Explosives uses in mining produce nitrogenous gases which, when oxidized in air, leads to the generation of acid. The beneficiation process that normally follows is usually not without the production of tailings. The metallurgical processes that follow generate different pollutants. Pyrometallurgy gives rise to gases, dusts, slags; electrometallurgy to gases and dusts; and hydrometallurgy to residues and waste solutions. This in essence is an extremely brief and perhaps an oversimplified description of the picture of emissions ensuing from mining and metal industries; further in-depth studies would produce a much longer list.

Metal extraction processes generate solid, liquid, and gaseous pollutants, and currently the control of the emission of these is one of the prime concerns of the process metallurgical industry. Airborne emissions are believed to be responsible for global warming, acid rain, and ozone depletion. Rising levels of carbon dioxide, oxides of nitrogen, and carbon fluorides are believed to contribute to climatic warming through the greenhouse effect. The oxides of nitrogen and sulfur are converted into acids that form acid rain, while nitrogen oxides are decomposed by ultraviolet radiation to form atomic nitrogen which plays a significant role in the depletion of ozone. All of these gases are generated in considerable quantities in the metal manufacturing industry.

Table 7.7 Types of environmental pollution.

Type of pollution	*Air pollution*	*Water pollution*	*Land pollution*
Generated from	Gases (SO_2, SO_3, H_2S, nitrogen oxides, CO, CO_2, O_3, HF, aerosols, photochemical oxidants, etc.); particulates (dust, smoke, smog, lead dust, etc.); Deforestatiod; radioactive gases.	Domestic sewage; industrial wastes; run-off from land and fields; suspended particles; oil from oil spills; wash waters; radioactive contaminants; clays, ores, and fine particle-laden waters.	Improperly disposed biological wastes; dumping of wastes from diverse industrial operations; chemicals; radioactive wastes; pollutants precipitated from air and water.

Another group of pollutants that may escape into the atmosphere in uncontrolled processing includes toxic metal vapors, dust, and gases. Many metallurgical processes are electricity-intensive, and the generation of electricity from fossil fuels is accompanied by the generation of significant quantities of pollutants. In metal processing, the emission of pollutants can be encountered at every step: in mining, in ore preparation, in metal production and processing, and even in secondary metal production.

7.3.1
Mining

In modern extractive metallurgy practice, it is important that one gains an appreciation of environmental constraints on mineral resource development. Although metals are widely recycled, this is normally not sufficient to meet demand, and mining has traditionally provided a continuous supply of essential industrial raw materials. Society does, however, now rightfully expect mining to be undertaken with minimum or practically zero lasting impact on the environment. Although this is technically perfectly feasible, and extensive rehabilitation of a mine site can be achieved, very significant additional expenses are incurred when undertaking tasks such as reclamation, controlling the quality of water discharged from a mining operation, suppressing dust and noise, and reducing the visual impact of the operation. This can not only adversely influence the financial viability of an existing operation; it may also prevent the development of an economically marginal project.

Society, of course, is in need of metals such as titanium to produce jet engines for aircraft, as much as it needs petroleum products as a source of fuel for their running. Like oil, mineral deposits do not regenerate themselves when they are exhausted. While there exists no threat from any immediate scarcity of mineral sources, if these are to be recovered with minimum or practically no impact on the environment, then it is required that society pays more for these products in order to meet the additional costs incurred when implementing an environmentally benign mining operation.

As an alternative to the situation of confronting higher price structures for minerals, extraction needs to be undertaken from locations where they occur in greater concentrations than is the case for many known deposits. Such prized grade deposits are geologically exotic, usually quite small, and certainly difficult to locate.

Ore deposits are removed for processing by a variety of mining methods, depending on the type and extent of the ore bodies. Wherever geological, geotechnical, mining, economical, and environmental conditions have been suitable, surface mining has been widely adopted. However, large open-pit mines require large areas of land for mining and spoil heaps, and this land is lost – albeit temporarily – for other uses such as agriculture. Environmental constraints and increased public concern are moving in the direction of a reduction or elimination of surface mining operations in many parts of the world. Scars left from strip mining, open-pits, quarries, and sand and gravel pits, accumulation of rejected waste, pollution of streams and ground water by acids and solids and of the atmosphere by dust are among the main complaints of the public. As a result, in future, access to mineral deposits in areas of natural beauty, national parks and urban settlements will probably be by underground mining methods. The latter are, of course, the exclusive choice for working deposits that lie deep within the earth and cannot be maneuvered or approached by any other means.

7.3.2
Ore Preparation

A considerable amount of dust is generated in the crushing, grinding, and concentration operations usually associated with ore preparation. Tailings generated during ore preparation require disposal, for example, by impoundment. Copper tailings can give rise to acid generation, and measures are needed to control such complications.

One major environmental problem is associated with the Bayer process for alumina production from bauxite. The residue (called “red mud”) which is obtained in the process contains unextracted oxides (e.g., alumina, ferric oxide, titanium dioxide, silicon dioxide, calcium oxide) and various insoluble materials. This solid waste is washed and discharged into impoundment ponds or into the marine environment.

7.3.3
Metal Production and Processing

Although in reduction and smelting processes the effluents generated are mainly in the gaseous and the solid forms, it may be recalled that dusts and fine particulate solids are also generated during the mining and ore preparation stages. However, the descriptions of effluents and some of the methods of their treatment that are presented here are mostly confined to the metallurgically based processes. For the sake of brevity, references to other industries have been avoided.

7.3.3.1 Gaseous Effluents

During metals processing, in particular during reduction, carbon dioxide is perhaps the most preponderant gaseous effluent, in terms of volume. Significant carbon dioxide emissions are also associated (see above) with the generation of electric power used for metal reduction purposes. In electrolytic aluminum production, carbon fluoride gas and its oxygenated forms (e.g., COF_2 and CO_2) are produced due to anode effects. If the carbon dioxide produced during electricity generation is not considered when assessing carbon dioxide emission during the reduction process, the environmental impacts of the carbon dioxide effluent are comparable for steel, copper, and titanium production, and are somewhat higher for aluminum and magnesium, on a weight of product basis.

Carbon monoxide emission is significant in aluminum electrolysis. In the iron blast furnace, the carbon monoxide produced in the furnace is recovered for its fuel value or is burnt to carbon dioxide. The carbon monoxide produced in the chlorinator in titanium processing is burnt to carbon dioxide. In zinc production in horizontal/vertical retorts, the gas leaving the retort contains 45% zinc, 50% carbon dioxide (428 kg per ton of zinc), and 1% carbon monoxide. Blast furnace reduction generates a gas containing 12% carbon dioxide. Among the various instances of carbon dioxide emission mentioned, that associated with the steel industry has the most significant global impact because the annual production of steels is many orders of magnitude greater than those of the other metals. In fact, the iron and steel industry is the source of a wide variety of pollutants, the effects of which cannot be overlooked not only because of their nature but also because of their sheer volume.

In the manufacture of iron in the blast furnace, coke is an essential raw material, and for every ton of pig iron produced, 0.6 ton of coke is needed. Coke is made by heating coal in gas-tight ovens, whereby the volatile constituents are driven off and a hard and porous carbonaceous material is obtained. The process of coke manufacture leads to the generation of several pollutants. In addition, the emission of dust and of hazardous gases such as carbon monoxide, hydrogen sulfide, and hydrocarbons occurs during the charging and discharging of coke ovens, and also during the quenching of red-hot coke. The sulfur present in the coal gives rise to organic sulfur compounds (in addition to hydrogen sulfide), which escape along with the noncondensible gases leaving the oven. The burning of these gases as fuel, without treatment to remove the sulfur compounds, results in the formation of sulfur dioxide.

The best-known methods for the removal of hydrogen sulfide from gaseous fuels include: (i) passing the gas over ferric oxide which reacts to form a mixture of iron sulfides ($Fe_2O_3 + 3\ H_2S \rightarrow FeS + FeS_2 + 3\ H_2O$); (ii) absorbing the gas in an organic solvent (triethanolamine) and subsequently deabsorbing by thermally heating the organic and oxidizing it (i.e., H_2S) on a heated alumina catalyst to yield elemental sulfur ($H_2S + 0.5\ O_2 \rightarrow S + H_2O$); and (iii) absorbing the gas in sodium carbonate solution followed by oxidation using sodium vanadate as a catalyst, liberating elemental sulfur which is separated by flotation with air bubbles (the catalyst in the reduced form which is left behind is regenerated by oxidation with anthraquinone disulfonic acid, ADA). The first process is used when the hydrogen sulfide content in the gas is low; the second process (the Claus Process, named after its inventor) is used to remove appreciable amounts of hydrogen sulfide. The third process is called the Stretford process.

In the blast furnace, the reaction of the nitrogen in the blast with coke leads to the formation of poisonous chemicals such as hydrogen cyanide and cyanogens, and each cubic meter of the blast furnace gas contains from 200 to 2000 mg of these compounds. The blast furnace gas is scrubbed with water in the dust collection system; the cyanide compounds dissolve in the water, which is then discharged after the compounds have been destroyed. Another poisonous emission in blast furnace operations is hydrogen sulfide. The sulfur present in the coke is converted into calcium sulfide in the slag, the water-quenching of which reads to the generation of hydrogen sulfide through the reaction of calcium sulfide with water.

Emission of pollutants also occurs in steel-making. The calcium fluoride used as a flux in the manufacture of steels in the open-hearth process decomposes on contact with water present in the combustion gases of the furnace. This causes hydrogen fluoride and carbon monoxide to be formed; thus, the stack gas contains hydrogen fluoride at a concentration of about 3000 ppm. Removal of hydrogen fluoride from the stack gas is essential because this concentration is about 1000 times the permitted value; fluorosis in cattle or damage to vegetation can occur in the event of such uncontrolled emission. This is a major disadvantage of the open-hearth process.

Attendant to the manufacture of steels by an oxygen top-blowing process (LD process) is the formation of thick, brown fumes of particulate iron oxide; these are extremely fine and difficult to remove from the stack gases. This is a disadvantage of the LD process from which the bottom oxygen-blowing process does not suffer. Ferroalloys such as ferromanganese and ferrosilicon are used to introduce manganese and silicon into steels, and these alloys usually contain phosphorus and arsenic as impurities derived from the raw materials. During the crushing and storage of these alloys, poisonous gases such as phosphine (PH_3) and arsine (AsH_3) form due to the reaction between iron phosphide or iron arsenide and moisture. These reactions occur slowly, producing the noxious gases over an extended period of time. The gas formation is accompanied by the formation of hydrogen, and as a result the gas mixture represents an explosive hazard when it comes into contact with air.

Next to iron and steel-making, major pollution problems are encountered in the treatment of nonferrous sulfide ores or, in general, in the treatment of sulfur-containing resources, which yield a variety of gaseous, solid, and liquid wastes for disposal. The smelting method produces sulfur-bearing gases which present onerous air pollution problems. The issue of controlling the production of sulfur-containing off gases has assumed major significance. Solid residue disposal techniques are undergoing close scruting on the basis that apart from sulfidic origins all metallurgical industries generate such waste. The issue of liquid waste is similar. Hence, vigorous controls over liquid effluents arising from various process plants have attracted close attention in the establishment of new plants. In credence to all these it is perhaps not right to single out sulfidic sources as contributing to pollution.

In general, the flue gases from pyro processes contain appreciable quantities of sulfur dioxide. There are two possible strategies to achieve desired levels of smelter emission control: (i) the upgrading of existing smelter operations and (ii) the installation of a new smelter based on nonpolluting technology. It is not difficult to provide a general outline of these possibilities. Where little or no new capacity is anticipated, resources should be concentrated on technology to upgrade existing smelters. Where upgrading could be realized with less capital outlay than by replacement with an extra smelting furnace, new technology furnaces offer vast benefits with regard to operating costs through increased productivity, energy preservation, and pollution restraint. Recent years have witnessed to the development of several processes that, fundamentally, are direct smelting routes. For base metals such as lead, the blast furnace in tandem with a sintering/roasting device has been the mainstay of the lead smelting industry. Conventionally, the sulfur dioxide contents of off-gases are rather low, whereas the off-gases of various recent direct smelting processes contain higher percentages of sulfur dioxide which can be conveniently handled. New technology direct-smelting furnaces which function semicontinuously offer substantial gains in terms of capital and energy costs. Different smelting operations give rise to different sulfur contents. Likewise, various alternative smelting approaches have led to the formulation of sulfur dioxide treatment related strategies, including either conventional/strong or weak sulfur dioxide stream control. It may be added that technology exists to produce all marketable forms of sulfur: liquid sulfur dioxide, sulfuric acid, and elemental sulfur.

With regard to the conventional/strong sulfur dioxide stream, single-absorption sulfuric acid plants function optimally at 7–9% sulfur dioxide in the feed, with the outgoing gas level varying from 500 to 2500 ppm. However, double-absorption processes have a higher absorption efficiency, with traditional plants running at about 4–8% sulfur dioxide feed gas and a minimum oxygen to sulfur dioxide ratio of 1: 1. A normal method to handle sulfur dioxide rich effluent from the new smelting processes would be to dilute the gas to about 10% sulfur dioxide, from where conventional plants take over the process. It may be noted, however, that there is a direct relationship between the gas volume and capital and operating costs. A design which substantially reduces the gas volume will have great effect on efficiency. In one of the known procedures, in order to prevent overheating and loss of the vanadium catalyst, part of the incoming sulfur dioxide is diluted and the reaction is implemented in two stages by suitably mixing the product gas from first stage and feed gas. With regard to the variants of the sulfuric acid process, the conversion efficiency is inversely related to the amount of sulfur dioxide emitted. Plants that operate on the single-absorption process principle are required to reduce the emission of sulfur dioxide, for example by absorption into sodium sulfate/bisulfate solution. Current technology for sulfur production from sulfur dioxide requires a reducing agent and is energy-intensive, and in its present form it may not be economically attractive unless natural gas is available at negligible cost. With regard to the production of liquid sulfur dioxide, the drying of sulfur dioxide bearing gases may require concentrated sulfuric acid, and it is desirable that the sulfur dioxide content of the tail gas of the liquid sulfur dioxide plant is not negligible and must be processed further, for example, in an acid plant. In situations where there is no possible use for the sulfuric acid or liquid sulfur dioxide, the associated sulfur can be fixed as gypsum, a solid waste product which can (in theory) be stored directly. However, almost three tons of limestone are needed to scrub one ton of flue gas sulfur, yielding over four tons of waste. The stability of dumped gypsum over long periods remains an open question, although in particular cases (e.g., in Japan) the gypsum produced may be sold commercially.

As the name implies, weak stream control technology is concerned with the weak sulfur dioxide streams emitted during smelting. A well-known example of uncontrolled emissions of sulfur dioxide from primary smelters is the reverberatory furnace yielding weak sulfur dioxide emissions. Enrichment of oxygen and use of concentration/neutralization may be cited as among the different approaches to sulfur dioxide stream control. As a specific example, reference may be drawn to desulfurization systems on the off-gases from reverberatories. One method involves the use of a magnesium oxide concentration system which absorbs sulfur dioxide from the weak stream and regenerates it as a suitable processible concentration in the 10–13% sulfur dioxide level. The second method involves use of a nonregenerative lime/limestone system which yields gypsum as a saleable product.

In view of the concern about air quality, the recovery and disposal of sulfur dioxide has been the subject of many investigations, though none has yet been really successful (see Table 7.8). It should be mentioned that the options giving rise to highly concentrated sulfur dioxide suitable for liquefaction, or a gas stream sufficiently rich in sulfur dioxide to manufacture sulfuric acid, presuppose the existence of available markets for either liquid sulfur dioxide or sulfuric acid.

The environmental problem of sulfur dioxide emission, as has been pointed out, is very much associated with sulfidic sources of metals, among which a peer example is copper production. In this context, it would be beneficial to describe the past and present approaches to copper smelting. In the past, copper metallurgy was dominated by reverberatory furnaces for smelting sulfidic copper concentrate to matte, followed by the use of Pierce–Smith converters to convert the matte into blister copper. The sulfur dioxide stream from the reverberatory furnaces is continuous but not rich in sulfur dioxide (about 1%) because it contains carbon dioxide and water vapor (products of fuel combustion), nitrogen from the air (used in the combustion of that fuel), and excess air. The gas is quite dilute and unworthy of economical conversion of its sulfur content into sulfuric acid. In the past, the course chosen was to construct stacks to disperse the gas into the atmosphere in order to minimize its adverse effects on the immediate surroundings. However, this is not an en-

Table 7.8 Options for handling sulfur dioxide pollution.

S.No.	*Approach*	*Details*
1.	Improvement of current methods	a) Improving sulfuric acid production technique to use a dilute (~ 1% sulfur dioxide) gas stream as the input in place of the presently used concentrated (~ 10% sulfur dioxide) gas stream. b) Improving the pyrometallurgical processes to minimize sulfur dioxide emission; for example, by use of electric furnaces or by efficient collection of the emitted gas during the conversion of white metal. c) Improving the sulfur dioxide concentration in the exit gas by use of tonnage oxygen.
2.	Disposal of sulfur dioxide	Trapping sulfur dioxide in lime or limestone to yield calcium sulphate.
3.	Utilization of sulfur dioxide	a) Conversion of dilute sulfuric acid through catalytic oxidation in aqueous phase. b) Absorption in ammonia to yield ammonium sulfate fertilizer. c) Absorption in phosphate rock to yield superphosphate fertilizer. d) Concentration to levels suitable for liquefaction or sulfuric acid manufacture by the absorption–desorption process. Suitable absorbents may include water, dimethylaniline, tributylphosphate, activated charcoal, and synthetic zeolites. e) Chemical reaction with a solid or a liquid reagent followed by conversion to hydrogen sulfide which is readily convertible to elemental sulfur. The reagents include solid sodium aluminate, aqueous solution of sodium citrate, or a molten mixture of sodium carbonate–lithium sulphide–potassium carbonate. f) Reduction of carbon or natural gas to elemental sulfur.

tirely satisfactory solution because precipitation would eventually occur at some distance. It should be mentioned in this context that very tall stacks have been constructed in the recent past; the tallest of these, at Sudbury, Canada, is 381 m high and has a diameter of 36 m at the bottom which tapers to 16 m at the top. The gas stream from the converters is rich in sulfur dioxide (because fuel is not burnt in the converters and most of the oxygen in the input air forms sulfur dioxide) but is noncontinuous or intermittent (because of the batchwise operation of converters). These difficulties can be overcome, to a limited extent, by combining gas streams. Recently, old converters have been retrofitted with oxygen-enriched blowing systems, and this has brought about a decrease in the total volume of the gas and a corresponding increase in sulfur dioxide concentration to levels suitable for collection. The emergence of flash-smelting furnaces, using oxygen or oxygen-enriched air, has altered the scenario of yesteryear. These furnaces produce off-gases of a smaller volume and with a higher concentration of sulfur dioxide. In International Nickel Company (INCO) flash smelting, approximately 3–5 tons of sulfur dioxide are emitted per ton of copper produced. The gas stream contains around 10–30% sulfur dioxide, and the converter off-gas stream contains about 7–13% sulfur dioxide. The sulfur dioxide contained in these gas streams is easily treated in an acid conversion plant to produce sulfuric acid. These flash-smelting plants continue to use Pierce–Smith converters. Apart from the noncontinuous generation of gas stream, there is an additional problem associated with the operation of the converters, the filling and emptying of which is associated with the generation of considerable amounts of fugitive gas and fumes as well as a large volume of ventilation gas that is too lean in sulfur dioxide to permit acid making.

It may be perceived that a continuous, sulfur dioxide-rich stream can be produced if the smelting and converting operations of conventional technology can be combined in one continuous operation, and this has been attempted in the Noranda process. However, in the largest present-day installation subscribing to this process, the units are used primarily as smelters, with the conversion implemented in separate, conventional converters.

Another way to avoid the generation within a smelter of large volumes of gas that are low in sulfur dioxide is to use electricity rather than fossil fuel for the generation of heat. In electric furnaces there are thus no combustion gases, and the effluent furnace gases are limited to what is produced by the process. In this way only small amounts of (sulfur dioxide rich) gas are produced in the smelter. Electric furnace smelting of copper concentrates to produce blister copper for subsequent electrorefining is economical where electricity costs are low, or for small-scale operation. A wide variety of feed stocks may be smelted using this approach.

As originally conceived, the Noranda process was an attempt to combine smelting and converting in one continuous operation. However, a major difficulty in doing this is to keep the smelting and converting separate within the unit (e.g., to ensure that the slag leaving the unit is representative of a smelter slag – low in copper – rather than a high copper converter slag).

This difficulty is avoided in the Mitsubishi continuous smelter which, as may be recalled from Chapter 4, consists of three separate furnaces for smelting, slag cleaning, and converting with cocurrent flow (by gravity) of slag and matte occurring from the first furnace to the third. This new copper process appears to closely approach the goal of minimal disturbance to the environment. The noncontinuous flow of gas to the acid plant and the fugitive gas problems associated with Pierce–Smith converters are no longer present in this continuous copper production process.

The foregoing has been a brief and general account of the environmental impact that ensues from the processing of sulfidic resources of metals. For obvious reasons, a major emphasis has been placed with regard to the copper industry in the presentations. It will be worthwhile for the reader to become more acquainted with this area, which has featured in as many as twenty papers contained in the proceedings of the EPD-96 Congress (see Literature).

The majority of currently operated nonferrous smelting processes seem avidly to be using high levels of oxygen enrichment, and because of this the processes have become autogenous. The heat of reaction of the iron and the sulfur contained in the feed materials supplies all the heat necessary to maintain the furnace at the required temperatures. Auxiliary fuel in the form of oil, natural gas, or coal is no longer required, thereby reducing air introduction and the consequent generation of nitrogen oxides. Nitrates, even in minor amounts, have always been a source of concern in smelters where sulfur is fixed as sulfuric acid. The nitrate levels must be less than 5 ppm in the acid, and in plants using higher levels of oxygen enrichment, it is no longer necessary to bleed nitrates from the acid plant circuit, thereby avoiding the generation of an effluent that would require neutralization and disposal.

Sulfide ores usually contain small amounts of mercury, arsenic, selenium, and tellurium, and these impurities volatilize during the ore treatment. All the volatilized impurities, with the exception of mercury, are collected in the dust recovery systems. On account of its being present in low concentrations, mercury is not removed by such a system and passes out with the exit gases. The problem of mercury contamination is particularly pertinent to zinc plants since the sulfidic ores of zinc contain traces of mercury (20–300 ppm). The mercury traces in zinc sulfide concentrates volatilize during roasting and contaminate the sulfuric acid that is made from the sulfur dioxide produced. If the acid is then used to produce phosphatic fertilizers, this may lead to mercury entering the food chain as a contaminant. Several processes have been developed for the removal of mercury, but these are not yet widely adopted.

- One such process was developed by the Outokumpu Company in Finland and used in the company's zinc smelter at Kokkola. The gases are scrubbed with concentrated sulfuric acid, whereby mercury is dissolved as mercuric sulfate. After several recycling operations, the mercury concentration reaches saturation level such that crystals of mercuric sulfate form and can be removed.

- In the Odda process, used by Det Norske Zinkkompani in Norway in collaboration with Boliden Kemi, the gases are subjected to scrubbing with a mercuric chloride solution which reacts with mercury, yielding insoluble mercurous chloride; this can be separated by filtering.

- In the Boliden process, developed by Boliden Kemi Company in Sweden, filter beds containing amorphous selenium are used to filter the gases. Mercury in the gas is deposited in the filter as mercury selenide (HgSe). Alternatively, the gases can be scrubbed with a slurry of amorphous selenium, whereupon mercury is precipitated as HgSe. Activated carbon filters are also useful for absorbing mercury vapor from the gas.

- In the process developed at the Centro Nacional de Investigaciones Metalurgicas in Madrid, Spain, mercury is recovered from the stack gases. Mined mercury ore is heated in the usual way in rotary kilns to volatilize mercury as a vapor. After cooling the gases and condensing the mercury, the gases that emerge from the condenser contain about 70 ppm of mercury. In order to recover this mercury and to prevent pollution of the neighborhood of the mercury ore mine, the stack gases are washed with a solution of sodium thiocyanate; this causes a major portion of the mercury to dissolve as a thiocyanate complex, while a minor amount precipitates as the sulfide (HgS). In order to obtain complete precipitation of mercury in its sulfide form, while simultaneously regenerating the sodium thiocyanate solution, a stoichiometric amount of sodium sulfide solution is added to the solution.

- The St. Joe process, developed by St. Joe Mineral Corporation, USA, is currently in operation at the company's zinc smelter at Monaca, Pennsylvania. A controlled amount of hydrogen sulfide is injected into the mercury-containing gas stream to precipitate mercuric sulfide which is then separated as a slurry in a washing tower. After removing the bulk of mercury by the above process, the sulfuric acid produced from the gases contain traces of mercury which can be removed as a mercuric iodide precipitate by adding potassium iodide. This treatment was developed by the Toho Zinc Company in Japan. The removal of mercury from sulfuric acid can also be effected by injecting sodium thiosulfate: elemental sulfur forms and reacts with mercury to produce insoluble mercury sulfides.

In the production of titanium, the chlorination of rutile generates approximately 0.12 tons of waste for every ton of titanium tetrachloride produced. If ilmenite is directly chlorinated, the amount of waste is 1.5 tons for every ton of titanium tetrachloride. Large amounts of ferric chloride are produced along with volatile chlorides and oxychlorides (e.g., aluminum trichloride, silicon tetrachloride, carbon oxychloride, tin tetrachloride, vanadium tetrachloride, vanadium oxychloride); these can be removed by selective distillation. In fluidized-bed chlorination, the build-up of liquid calcium chloride and magnesium chloride in the fluid bed interferes with the process of fluidization and hence these must be removed.

7.3.3.2 **Solid Effluents**

Solid effluents arising from metallurgical operations occur principally in two forms: fine particulate solids or dusts, and solid wastes. As an example, blast furnace gas may contain up to 170 kg of dust per ton of pig iron produced. Suitable methods must be devised for processing the solid effluents for two reasons: (i) to prevent pollution of the environment and (ii) to recover their valuable content, if any. As far as the latter is concerned, reference may be drawn, as an example, to the recovery of rhenium from the exit gas from molybdenite roasting in a multiple-hearth furnace.

A metallurgical plant using an ore will invariably produce solid residue after the metal values have been removed from the ore. The residue from pyro plants may be disposed of by trucking or conveying, based on techno-economics and feasibility. However, pipeline conveyances of the residue slurry is also in vogue for certain applications where residue quantities are fairly large.

7.3.3.2.1 Dust

In metallurgical processes dust is formed according to two different mechanisms. The first comprises vaporization of the components with high vapor pressure, followed by condensation at lower temperatures in the gas system (chemically formed dust). The chemical dust formation depends on several factors: the process temperature, the composition of the condensed phases (e.g., the melt and/or solid particles), the cooling of the gas, and the composition of the gas. The second of the two mechanisms consists of transportation or movement of small solid and/or liquid particles with process gas (mechanically formed dust). This dust formation depends on several factors: the particle-size distribution of the charged material, the charging system used, and the reactor or furnace design (e.g., the gas velocity and the manner by which injection of gases occurs). The two mechanisms generally take place simultaneously. Hence, the dust, more often than not has a very complex composition. The dust is generally collected in one single gas-clearing device operating at relatively low temperature, and yields a dry dust or a sludge. The complex composition of such dust often does not permit recirculation into the process, and the presence of elements such as zinc and lead in this type of material places them into the hazardous category. A large number of hydrobased processes designed to treat the dust generated in nonferrous processes have been reported in the literature. However, the complexity in the composition of the dust makes it difficult to achieve economical feasibility, and very few processes are known thus far to have been applied on a large scale. The Saganoseki Smelter and Refinery and Kosaka Smelter in Japan may be mentioned as exceptions where hydrometallurgical processes are known to be used for the treatment of dusts produced in copper smelting operations. With regard to the dusts generated in steel-making, some specific examples may be taken. Here, the processes used are pyrometallurgical. Zinc-containing dusts from electric arc furnace processes are treated in Waelz kilns, while the majority of the dusts produced in the stainless steel industry in Nordic countries are processed by Scandust AB in their plasma process. Zinc- and lead-containing wastes can be treated in a Tetronics plasma process or a Horsehead's flame reactor.

A controlled dust generation where the dusts would be enriched in certain products, or where the amount of dust could be reduced or minimized, would greatly facilitate the dust treatment in separate processes. Some possible methods to control dust formation in the metallurgical industry mention include: (i) additions to the condensed or the gaseous phase; (ii) control of the gaseous phase composition in the gas system through controlled amount of air leakage and/or additions to the gas phase; (iii) correct choice of cooling method: possible options are directly by air leakage, by water, by indirect cooling; (iv) separating the dust produced in different time intervals and stages of the process; and (v) correct combination of gas cleaning techniques operating at selected temperatures. Ultimately, to achieve success in this important sphere of controlling dust generation it is fundamentally important to have a basic knowledge of dust-forming mechanisms.

A system known as synthetic mineral immobilization technology (SMITE) is emerging as an important methodology for the treatment of hazardous inorganic wastes. As a typical example, reference may be made to arsenic trioxide flue dust. This is a voluminous by-product that is produced by the of roasting arsenopyrite ores of base and precious metals to reduce sulfur levels sufficiently for smelting. The most durable mineral currently recognized for the incorporation of arsenic at high concentrations is an apatite type (known as

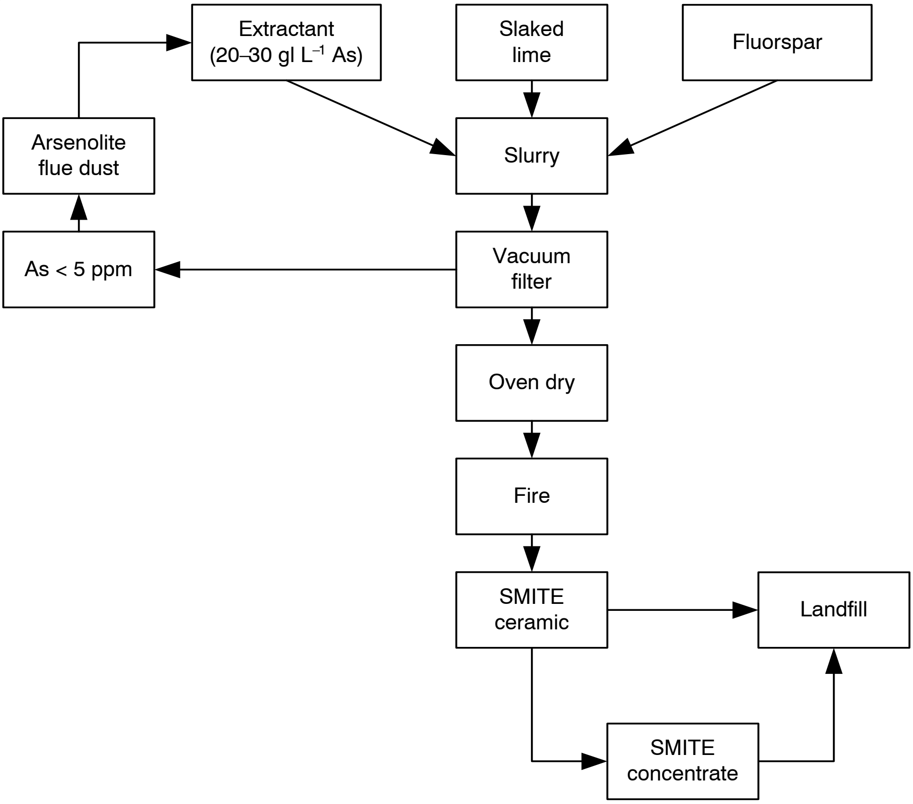

Figure 7.6 Flowsheet of SMITE stabilization of arsenical flue dust.

svabtite), which has the ideal stoichiometry of $Ca_5(AsO_4)_3F$. A basic process for stabilizing arsenic is shown in Figure 7.6.

Methods of dust removal depend mainly on the particle size of the dust and the temperature and moisture content of the gas. The methods used are broadly divided into dry methods and wet methods. The dry methods involve the use of gravity and baffle chambers, cyclones, filters, and electrostatic precipitators, while the wet methods involve the use of spray towers and venturi scrubbers. In principle, wet cleaning is preferred to dry cleaning because of the excessive wear associated with and the difficulty in handling the fine dusty material removed in the dry methods. The wet methods, however, must be followed by such operations as filtration, drying of filter cakes, and recycling of water.

As far as dry methods are concerned, gravity and baffle chambers and cyclones are suitable for separating larger particles, while filters and electrostatic separators are preferred for finer particles.

- The *gravity and baffle chambers* provide the simplest of gas collection techniques. The gas is allowed to travel through a large chamber or a long tunnel to reduce its velocity, causing the dust to drop out by the action of gravity. The gas flow is deflected by baffles, or the flow direction may be reversed in order to enhance the separation.

- *Cyclones* are more efficient than gravity and baffle chambers, and also occupy less space. The dust-laden gas makes a tangential entry into a cylindrical or conical chamber. The dust particles travel outwards to the outer wall due to centrifugal forces; there they collide with the wall and fall downwards to the receiver chamber, whilst the gases escape from an opening provided at the top.
- *Filters* are devices which have woven cloth partitions through which the gases are passed to implement separation of solids from gases, or for cleaning the gas. The material used to construct the filter cloth imposes the upper temperature limit of the hot gases that can be treated. There is also a limitation on the moisture content of the gas which can be successfully handled. In any case, the dust should not adhere strongly to the filter cloth if it is to remain functional throughout its operation.
- The principle of dust separation in *electrostatic precipitators* is based on the fact that if the solid particles in a gas are imparted an electric charge, they will be attracted to a collection device having the opposite charge. The most commonly used type of electrostatic separator consists of a series of ionizing electrodes and an oppositely charged series of collecting electrodes. These are housed in a chamber through which the exhaust gas is routed. The ionizing electrodes are rods, while the collection electrodes are grounded plates or shells. The collecting electrodes have a large surface area compared to the ionizing electrodes. A high voltage of 50 to 80 kV is applied across the two sets of electrodes to maintain the highest electrostatic field without sparking. Under the influence of the electrostatic field, the gas molecules become electrically charged and move away from the ionizing electrodes towards the collecting electrodes. As the suspended dust particles collide with these ionized gas molecules, the electric charge is transferred to the dust particles. Because of their acquired charge, these particles are attracted towards the oppositely charged collecting electrodes where they lose their charge and fall into collecting hoppers.

The wet methods of dust separation involve the use of spray towers and venturi scrubbers. In spray towers, the dust-laden gases pass upwards countercurrent to a falling spray of water. The tower is packed with such materials as wooden grates, ceramic tiles, or metal spirals. This provision increases the contact between the upward-moving gas and the downward-moving water. The part of the tower above the water spray is meant to separate the water droplets from the gaseous medium that exits from the tower. The venturi scrubbing system involves the introduction of water at the throat of a venturi perpendicular to the gas flow. The water is atomized into tiny droplets, thereby creating a large surface area. The venturi is followed by a centrifugal eliminator; this is provided to remove the entrained droplets and the collected dust particles. The gas cleaned in this way is then emitted through the outlet provided.

7.3.3.2.2 **Solid Wastes**

The solid wastes generated from pyrometallurgical processes are in the form of slags which consists of lime, silica, alumina, iron oxides, and minor amounts of alkali oxides and heavy metals. Slags are generated in almost all pyrometallurgical processes in an amount per ton of metal that is mainly governed by the impurities and/or gangue materials that are mandatorily to be extracted into the slag. The world average rate of blast furnace slag production in 1990 was 270 kg t^{-1} hot metal, ranging from 145 to 319 kg t^{-1} for individual operations. While the major slag components are themselves the principal constituents of rock and soil, the minor constituents usually become immobilized in a stable, nonhazardous iron-aluminosilicate matrix. Some of the newer pyrometallurgical techniques produce slags from various dusts containing hazardous chemicals such as arsenic and lead. These slags, however, are stable and have been classified as nonhazardous. Many uses (and thus methods of disposal) have been developed over the years for both ferrous and nonferrous slags, including mine backfill, aggregate for construction, sand blasting, and ballast for rail lines. In addition to these high-tonnage uses of slags there are some minor (but important) uses, including the production of rockwool insulation, filter media, brake linings, and noise-reduction materials. It is interesting to note that since the slag is a stable and nonhazardous matrix for trapping and immobilizing many potentially hazardous materials, nonferrous smelters can provide the environmentally valuable service of safely processing hazardous materials from other industries. The development of superior process technologies in the nonferrous industry will broaden its ability to process a variety of waste products and produce usable products without damaging the environment. An example is the use of the plasma reactor to recycle various industrial catalysts and to treat electric arc furnace dust, as well as more conventional feed materials to produce a nonhazardous slag.

A very well accepted philosophy is the reuse of slags originating from the major metallurgical enterprise, the iron and steel industry. The degree of utilization of steel-making slags differs considerably from one country to another as it depends on various factors such as the composition of the slags, the iron and steel-making practices, and the national and local environmental regulations. In Western Europe and the United States, most of the steel-making slags are re-used especially for road construction, whilst in the Nordic countries, most steel slags are deposited in landfills, despite their possessing superior properties in many respects compared with natural aggregates (e.g., granite and basalt). The problems associated with the reuse of slags are mainly related to the possible leaching of heavy metals and sulfur, the swelling properties of the slag due to formation of hydroxides upon reaction with water, and the eventual disintegration of the aggregates. The swelling is at least partly dependent on the amount of free lime and magnesia in the slag. In this respect, it is also worth mentioning the possibilities for increased recycling or reuse of slags. A decrease in the quantity of slag produced can only be accomplished if the raw materials are purer, or if slags with higher extraction capacities are developed. However, a more extensive hot metal pretreatment could minimize the Basic Oxygen Furnace (BOF) slag in steel-making. The possibility of recycling slag within the plant is limited by its impurity content, the alternative being to expand and extend the reuse of slags in the field of external applications. An increased reuse of slags can be achieved by developing new applications for them and optimizing their composition in order to meet application requirements. Much research has been carried out in the former area, whilst the latter area has attracted very little attention. The adjustment of slag composition could be carried out directly either inside or outside of the main process when the slag is still in a molten condition. Possible ways to optimize slag composition include additions to either change the slag composition or to facilitate the dissolution of slag formers, the use of premelted synthetic slag formers, or optimization to ensure complete melting of slag formers and to minimize the amount required. Knowledge of the mineralogical composition of the slag is essential for its use in civil engineering and road construction, and it is also an important criterion when considering leachability when slag is used for road construction or when it is land-filled. Possible ways of influencing the mineralogical composition of slag include: (i) control of the cooling rate, either through a very rapid solidification to form a glassy slag or a controlled solidification; (ii) the inclusion of additives to the molten slag for stabilizing impurities and hazardous elements, or their extraction into phases that can be separated; (iii) the reduction of BOF slag with carbon to obtain a metal phase containing most of the impurities and a slag that can be recycled to the process; and (iv) slag oxidation to form dicalcium ferrite from the free lime present in steel-making slag.

7.3.4
Secondary Metal Production

Secondary metal production is advantageous not only with respect to energy consumption but also to environmental impact as compared to primary metal production. The important environmental problems pertain to the formation of dioxins during thermal processing and the generation of dusts of the oxides of zinc, lead, and other metals in secondary steel, copper, and zinc production.

7.4
Hydrometallurgical Processing

The text so far has pertained mostly to energy- and environment-related considerations that are relevant to certain representative pyrometallurgical and electrometallurgical operations. The present section deals more generally with such considerations in the context of hydrometallurgical operations.

It was noted in Chapter 5 that biohydrometallurgy represents the only area in the field of hydrometallurgy that is not associated with the consumption of large amounts of energy. However, its application on a commercial scale is still confined to a very limited number of metals. It may also be recalled that hydrometallurgy presents itself as a lower energy consuming option only in situations where pyrometallurgical operations tend to be highly energy-intensive. An example that is often cited in this context pertains to the case of lean and complex resources of metals and materials. A lean and complex resource, such as ocean bed mined manganese nodules for instance, cannot be processed pyrometallurgically in an energy-efficient manner. Even the feasibility of processing such resources exclusively by the pyrometallurgical route is often doubtful. Processing the resource off-shore, carrying the resource in a concentrated form (thereby saving on the huge costs involved in transportation of the lean resource as such), and finally going through hydro or combined hydro-pyro processes appear to constitute an economically acceptable scheme.

Hydrometallurgy has frequently been praised for not having any highly adverse impact on the environment. The problems associated with sulfur dioxide emission to the atmosphere from the roasters and the smelters of sulfidic sources have created much interest in treating these resources by hydrometallurgical methods. Moreover, the extreme amount of effort that has gone into the development of hydro-based processes for the sulfidic sources of metals (particularly of copper) is too well known to require further elaboration. It is, indeed, quite true that some of these hydro-based processes tend to be economical and hence hold attraction for further development and growth – especially in situations where the scale of operation or the tonnage handled are small but where major problems of accessibility exist due to the remote location of a resource. It is also true that the question of sulfur dioxide emission from these hydro-based processes does not arise. Some of these processes yield elemental sulfur, this being the most desirable and nonpolluting form in which the sulfur bound with the source can be extracted. Sulfur in this form is cheap to transport and, depending upon necessity, it can readily be converted into sulfur dioxide or sulfuric acid. By contrast, some hydro-based processes produce hydrogen sulphide, which is readily convertible into elemental sulfur: $H_2S + 0.5\ O_2 \rightarrow S + H_2O$.

Although these hydro-based processes, when applied to sulfidic sources, do not cause air pollution due to sulfur dioxide emission, they – and many other hydrometallurgical operations that are generally used for a wide variety of raw materials and resources – can create both land and water pollution problems.

At this point it is valid to provide a general account of industrial waste-water treatment. Liquid industrial wastes can – and do – adversely influence aquatic life, impair property, and alter the ecology of the receiving water bodies of soil media, resulting ultimately in degradation of the biosphere. Mounting worries about health hazards and groundwater pollution have coerced the regulatory bodies to be more strict and industries to be more aware of sources of reduction and appropriate treatment. The quantity of waste water produced varies with the type of industry, technology or process adopted, reuse, recycling, and conservation of water utilized. A very general statement can be made as regards the nature of composition of industrial water wastes – they simply vary widely because of the diverse raw materials and process technology. The methods for industrial waste treatment can be broadly classified into three types:

- *physical:* the unit operations adopted are screening, flocculation, oil skimming, sedimentation, flotation, filtration, stripping, and some others;
- *chemical:* application of chemical unit processes are neutralization removal of toxic and nontoxic pollutants by chemical precipitation, mast transfer, disinfection, oxidation, and some others;
- *biological:* bio treatment is usually the most economical method of reducing organic content, toxicity, and unwelcome appearance. Quite often, an extensive pretreatment is required before a given waste is biologically treated; this can be aerobic, anaerobic, or a combination of these processes.

In future, the developments in hydrometallurgy will need to be concerned more with environmental problems associated with pertinent processes. Hydrometallurgical processes produce a variety of waste liquors and unwanted solid products which must be treated before their final disposal. There are two main objectives in such waste treatments: the first is to recover valuable impurities and unused reagents from the solutions; and the second is to ensure that the release of associated materials does not pollute the environment to an unacceptable extent.

Disposal of the residues of leaching operations can pose particular problems when they come into contact with natural waters, as this can eventually lead to the contamination of streams and water supplies. The long-term stability of the solids is, therefore, a problem which warrants serious consideration.

Aqueous waste solutions should be disposed of properly, and in particular solutions carrying heavy metals need to be treated. Untreated solutions, if released, can contaminate the geological environment.

In mineral beneficiation and hydrometallurgical plants slurry transportation is generally adopted since the residue/tailings are already moist. The tailings, when disposed of in dry form, are dumped into valleys or previously mined-out areas for backfilling. After back-filling work, the area may be covered with top soil and planted out for the rehabilitation and/or restoration of the land. Conventionally, tailings in the form of slurry are discharged into a tailing pond, while the supernatant is re-used in the process and/or recycled for repulping the tailings. Large tailing ponds are generally located in valleys surrounded by hills such that the construction of one or two dams will provide the requisite hold-up for tailings. One recent such method is called "thickened tailings", whereby at a suitably high solid consistency, the waste is pumped to a disposal site above ground. This slurry consistency is high enough to produce a sloped deposit on the ground, and the water run-off (including rainwater) is collected in a holding pond. This hold water is recycled to the plant, or it can also be used for sprinkling should dust emission be experienced in the disposal area.

Generally, the process liquid effluents released in the metallurgical industry are manageable both in quantity and quality. The process liquid effluent consists of water containing small amounts of dissolved solids, and extensive recycling of the effluent is carried out with a view not only to obtain zero effluent discharge but also to minimize freshwater input to the plant.

Hydrometallurgical processes utilizing an acidic medium most commonly use sulfuric or hydrochloric acids, both of which are relatively safe from an environmental viewpoint. Hydrometallurgy, as applied to nuclear metals and materials processing and reprocessing, has particularly important waste treatment and disposal constraints. Wastes generated in this particular field invariably have associated radioactivity – a feature which renders them different from other wastes. Depending upon the level of the associated radioactivity, the wastes are classified into low-, intermediate-, and high-level grades. The waste management procedure to be adopted depends on the form of the wastes (solid, liquid, or gaseous) and, of course, on the level of radioactivity associated with them. In fact, radioactive waste management has developed into a separate and fully fledged branch of nuclear technology. The disposal methods are basically different from those applicable to nonradioactive wastes. For example, the basic sequence of operations for the disposal of a highly radioactive liquid waste involves: (i) interim storage in liquid form; (ii) solidification and packaging after a period of decay of the radioactivity; (iii) engineered storage of solidified and packaged waste for further decay of radioactivity; and (iv) final disposal of the solidified and packaged waste, after a sufficient period of decay of radioactivity, into geological formations or the oceans.

7.4.1
Niobium/Tantalum Metallurgy

At this point, it may be worthwhile referring to a specific example that is relevant to the information provided in the previous section, and the extraction of niobium/tantalum can be considered for this purpose.

The flowsheet depicting the extractive metallurgy of niobium/tantalum, presented previously in Chapter 5, underscores the important role played by the relevant hydrometallurgical operations. Figure 7.7 presents a review of the processing of niobium/tantalum raw materials into a variety of intermediate products: niobium and tantalum pentoxides (Nb_2O_5 and Ta_2O_5), potassium tantalum fluoride (K_2TaF_7), and niobium and tantalum carbides (NbC and TaC). The by-products generated in the different steps have also been indicated.

The processing of natural ores is perhaps not relevant to this discussion because the upgrading processes involve mechanical, electrical, or magnetic separation. These processes and their by-products normally do not contribute to environmental hazards.

Tin slags account for a sizeable fraction of the world's tantalum production. These slags are melted in electric arc furnaces, together with coke and lime (as flux), and this pyrometallurgical process leads to the production of synthetic niobium/tantalum concentrates. The waste products of this operation are mechanically separated slags which can be used, for instance, as landfill. The exhaust gases from this process are of minor consequence if dust is eliminated by the use of filters.

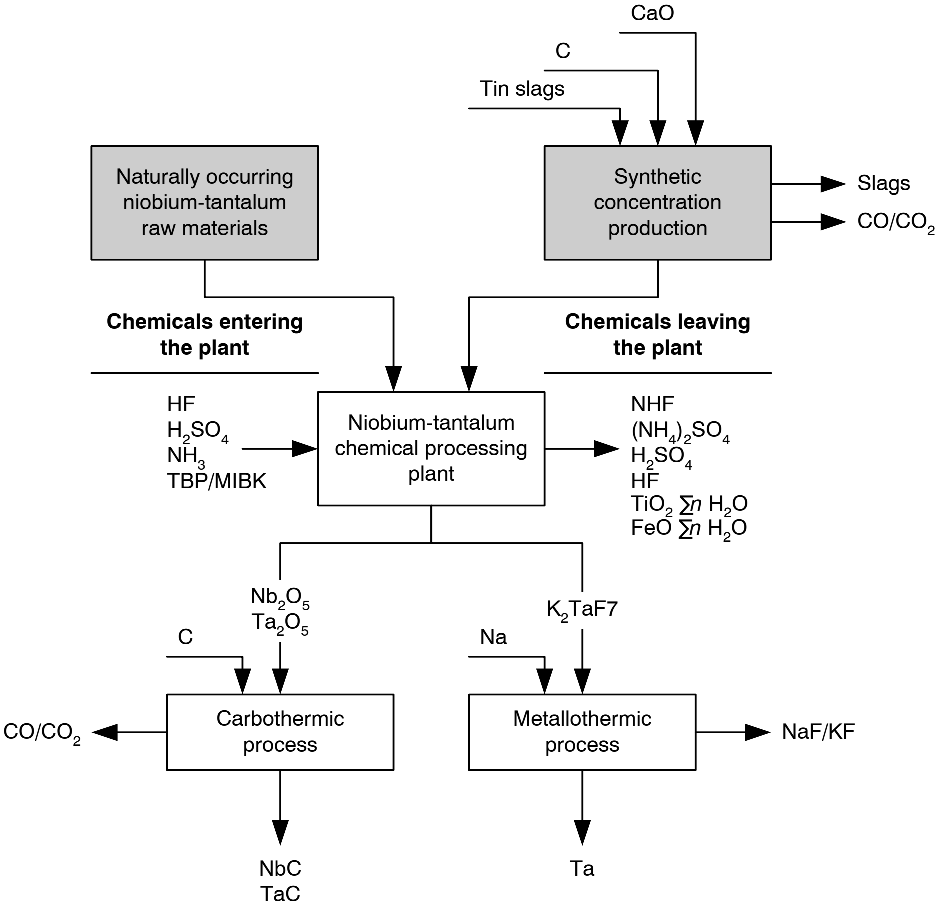

Figure 7.7 Niobium-tantalum chemical processing.

Natural ore concentrates (columbite-tantalite) and synthetic concentrates (obtained from tin slags) essentially constitute the feed materials supplied to niobium/tantalum chemical processing plants. A variety of chemicals are formed during the operation of these plants, and this aspect is of considerable relevance to the present discussion. The niobium/tantalum source materials are dissolved in a hydrofluoric and sulfuric acid mixture to form the heptafluorides of niobium and tantalum (H_2NbF_7 and H_2TaF_7). These fluoroacids are extracted by an organic solvent, methylisobutyl ketone (MIBK)/tributyl phosphate (TBP), while most of the dissolved impurities remain in the raffinate. The organic phase, loaded with niobium/tantalum, is scrubbed with sulfuric acid in order to remove the impurities that might be co-extracted along with niobium/tantalum during the extraction stage. The scrubbed organic phase is then stripped of its niobium value by using sulfuric acid as the stripping reagent. Further chemical treatments involve the use of ammonia to precipitate niobium and tantalum hydroxides (these are calcined to form the respective oxides) and of potassium fluoride to precipitate potassium tantalum fluoride (K_2TaF_7). The oxides are carbothermically reduced to the corresponding carbides, while the fluoride salt is chemically reduced with sodium to produce tantalum metal powder. The various wastes generated in the course of the entire operation are shown in Figure 7.8.

The opening of the niobium/tantalum feed involves digestion with a hydrofluoric and sulfuric acid mixture, and generates residues that still contain these acids. Normally these residues are carefully neutralized (e.g., by treating with lime) and then disposed of.

The raffinate, containing hydrofluoric and sulfuric acids, together with the sulfuric acid-containing washing liquid of the solvent extraction process, must also be neutralized with lime, and this produces a large amount of calcium fluoride and calcium sulfate sludge. During the precipitation process, filtrates containing ammonium fluoride and ammonium sulfate are produced, and these too are treated with lime to recycle the ammonia. A considerable amount of calcium sulfate/calcium fluoride is produced at this stage also. The potassium tantalum fluoride precipitation effluent gives rise to calcium fluoride after treatment with lime. The sludges thus generated from the raffinate of solvent extraction, from the precipitation of niobium and tantalum hydroxides, and from the crystallization of potassium tantalum fluoride can be processed to recover calcium fluoride and calcium sulfate as potential feed stock for other chemical operations, and this results in a reduction in the amount of the sludge for disposal.

It is useful to treat the raffinate to recover the two acids it contains. The raffinate can first be subjected to a thermal treatment which decomposes it into insoluble metallic oxides, hydrofluoric acid and sulfuric acid. In a first scrubbing, sulfuric acid is recovered, whilst in a second stage, hydrofluoric acid is absorbed. When put into operation, this process not only causes a reduction in the amount of sludges but also leads to acid production for return to the process.

While the emphasis here has been on the reduction of the amount of waste sludges, it is also equally important to address the problem of regulating the effluents and emissions. In this context, special mention may be made of ammonia which must be carefully regulated. The procedure for processing ammonium fluoride or ammonium sulfate containing solutions begins with lime treatment. The filtrates are fed continuously into a column and stripped with live steam and upgraded. In this way it is possible (with improved equipment and carefully controlled operation) to attain ammonia contents of less than 50 ppm in the effluent.

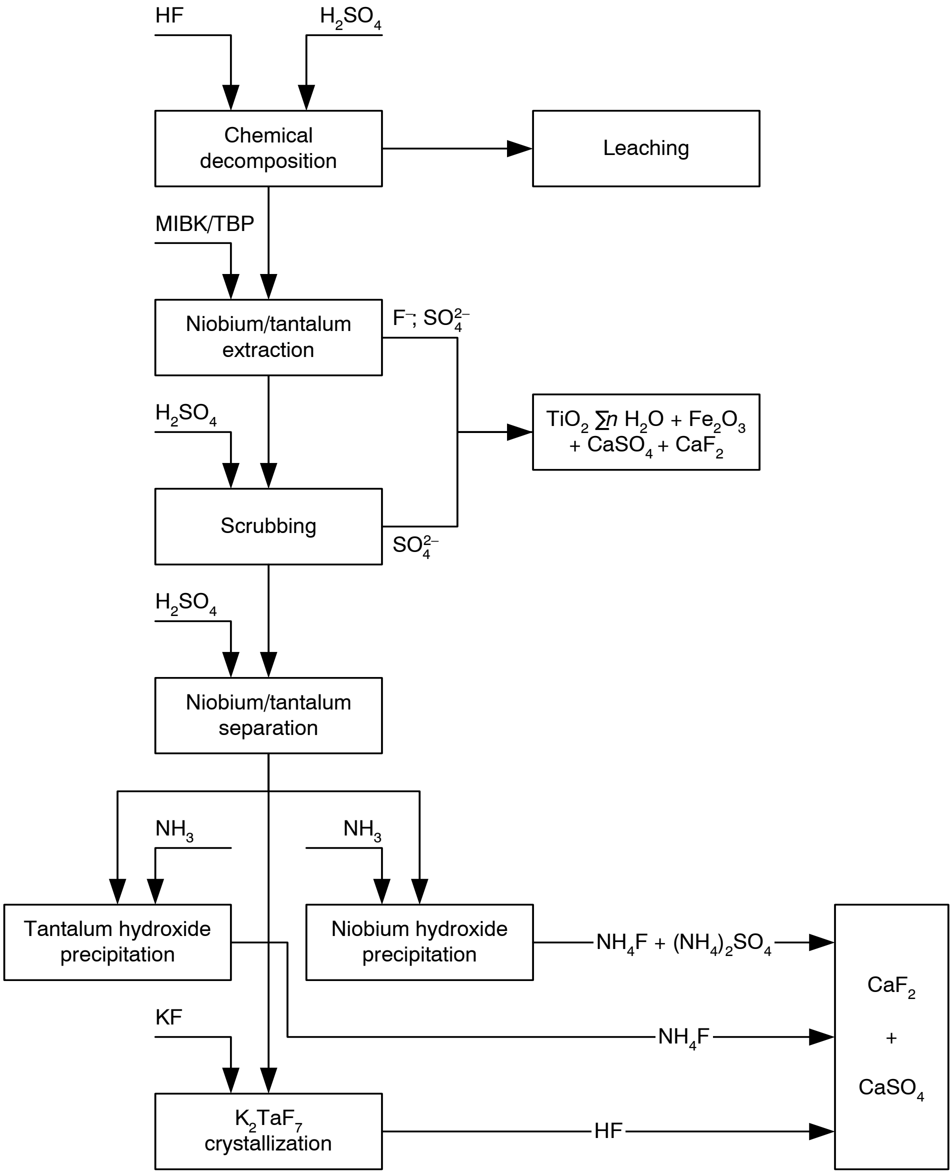

Figure 7.8 Wastes arising from nobium/tantalum resource processing.

As a final comment, it should be noted that many of the treatments described above for minimizing environmental pollution are quite energy-intensive. However, when taking a long-term view of the present state of our surroundings, it is mandatory that this extra energy input should be accommodated by the metallurgical industry.

7.4.2
Uranium

Uranium is the only naturally occurring fissile nuclear fuel, and has provenly and responsibly played this premier role by being responsible for most of the nuclear power generated to date. As in all energy-generation systems, the use of nuclear power has both advantages and disadvantages. Two advantages for nuclear power plants are worth recording over conventional power plants. First, for a given energy output, nuclear power plants consume much less fuel. The fuel cost is also relatively low, despite the cost of mining the uranium, purifying it, conducting isotopic enrichment (which depends on the nuclear reactor design system), and packaging it in a form suitable for use in a reactor. Other advantages include the generation of power without air pollution or with any contribution to the greenhouse effect.

Uranium mining and milling (ore processing) constitute important ingredients of the front end of the nuclear fuel cycle. The back end of the cycle primarily involves those operations which are carried out after the nuclear fuel is discharged from a nuclear reactor after having fulfilled its utility period. A description of the front-end stages with an emphasis on environmental issues constitutes an interesting example. In the case of uranium, there is the additional concern over the associated radioactivity. Uranium mining and milling operators must obtain appropriate approvals before carrying out their activities. Such approvals, which are issued by national and local governments, specify operating conditions that are designed to ensure safe operation of the facilities and protection of the environment. The operations following the reactor use of nuclear fuel are much more involved, mainly because of the fact that after discharge the fuel is much more unsuitable and so requires very careful handling; this implies that, immediately after discharge from the reactor, the fuel is intensely radioactive and requires extremely rigorous and careful handling at every stage of its processing.

Mining operations of all types pose potential hazards both to the environment and to health and safety. Indeed, most countries have legislation in place to control these activities as well as general legislation for occupational health and safety. The nonradiation hazards in uranium mining and milling operations are no different from those found at other mines and mills, as the operators are instructed to take precautions, including the provision of health and safety training, to minimize any impact on the health of workers and to avoid accidents. Appropriate protective equipment is provided for those working in the facilities, and safety audits are conducted to ensure that such equipment is being properly used and that the work is being carried out in a safe manner. Public access to areas where uranium mining and milling operations are taking place is controlled as a safety measure.

The presence of radiation in the workplace – which is an inevitable consequence of the radioactivity of uranium – requires that additional safety precautions be taken over and above those observed in other similar workplaces. There are generally three sources from which radiation exposure may occur: (i) radiation emitted from uranium ore in-situ and/or during handling; (ii) airborne radiation resulting from the decay of radon gas released from the ore and uranium dust; and (iii) contamination by ore dust or concentrate. Radiation levels around uranium mining and milling facilities are quite low – for the most part only a few times the natural background levels – and they decrease rapidly as the distance from the operations increases. Radon gas liberated from mining operations is rapidly diluted to background levels in open air; as a result, radiation doses to the public from such operations are low. The extent of precautions needed to control the radiation dose of mine and mill workers is, for the most part, a function of the ore being mined. When the ore is relatively high in uranium content, greater protection is needed than in low-grade ore mines. Monitoring of both the radiation levels at the facilities and the exposure of workers is an essential component of radiation protection procedures. Where workers are likely to receive radiation doses that are a significant fraction of the regulatory limit, individual records of exposures are kept. Personal dosimeters are used routinely for this purpose, and a program of medical surveillance is also implemented.

In mining operations where the ore grade is high, the mining technique and operating procedures are selected so as to control the radiation exposure of workers. This is particularly true for underground mines, and in some cases, non-entry mining methods may be required. When high-grade uranium is milled, radiation shielding may be required to control exposure of the equipment operators. Once the uranium is separated from other materials, including its decay products, it emits very little direct radiation in the milling process and, consequently, the likelihood of workers receiving significant direct radiation exposure is reduced.

As mentioned earlier, one of the decay products of uranium is a gas, radon, which is released into the surrounding environment. While radon itself does not present a significant radiation hazard, its immediate decay products constitute a potential source of radiation exposure, if inhaled. The most effective way to limit radiation exposure from this source is to provide adequate ventilation, and this is required whenever workers are in an enclosed area with uranium ore. It is particularly important in underground mines, and in one open-pit, two powerful fans can provide ventilation to a depth of 100 meters under certain weather conditions in the winter to avoid high radon levels. Airborne materials are diluted in the open air and rapidly dispersed, and so radon from uranium mining and milling operations presents no health hazard for the general public. Uranium dust in the air may be inhaled by workers, but where this is a potential problem wetting of the ore is the most commonly used control mechanism. In areas where high concentrations of dust are regularly present, such as concentrate packing facilities, respiratory protection is required.

The supply of clothing and a program of personal hygiene, such as the provision of washing facilities, is usually sufficient to mitigate against any risk of the contamination of personnel.

Most countries require that an assessment be carried out to identify potential environmental impacts of proposed uranium mining and milling operations. In preparing such assessments, mine and mill operators identify the steps that they intend to implement in order to limit such impacts. These steps are subjected to the approval of government regulatory agencies and are monitored by them when the facilities are in operation. The two principal pathways by which contamination might reach the environment from uranium mining and milling operations are air and water. Consequently, frequent sampling of air and water is carried out and monitoring of the receiving environment is undertaken to ensure that environmental impacts are adequately controlled. Such monitoring normally includes sampling of air, soil, water, plants, and animals such as fish. Extensive research has been carried out by the uranium industry in order to develop operating strategies that limit any long-term impact on the environment and to demonstrate that facilities can be decommissioned successfully.

Dust created by mining and milling activities blown by the wind from ore stockpiles is a potential source of environmental contamination. The watering of stockpiles or erection of enclosures is resorted to when necessary in order to prevent the spread of dust. Where ventilation systems collect significant amounts of uranium dust in mills, scrubbers are used to remove the dust from the air before it is discharged to the environment.

The quantities of fresh water used in milling operations are limited due to practical considerations; however, certain operations require clean water. Extensive use is made of recirculated water, especially in areas with scarce supply of water. Contaminated water resulting from mining and milling operations that cannot be re-used is handled as waste and is not discharged directly into the environment. In certain areas, evaporation from water dams is sufficient to avoid water discharges, and in some situations engineered barriers such as dams are installed to prevent the contamination of surface or ground water by uranium mining and milling operations. These barriers serve to isolate the uranium mine or mill from water in the environment.

There are three principal types of wastes that arise in mining and milling operations: (i) mine wastes; (ii) milling wastes; and (iii) waste water. Each type of waste is subjected to an appropriate management strategy.

- *Mine wastes* consist of rock that must be removed in order to access the ore. Generally, this material presents no risk of environmental contamination and it may be piled alongside the mining facility. In some cases, however, waste rock contains minerals that might be leached by water passing through waste piles. When this is considered likely, steps are taken to ensure that the leachate does not enter surface water bodies.

- *Milling wastes* (tailings) contain uranium decay products and may also contain other minerals associated with the uranium ore. The general approach to prevent undesirable constituents in the mill tailings from leaching into the environment is to retain these materials in an area where they can be managed during the life of the facility and where their long-term impact on the environment will be minimal. At some uranium mining and milling sites, it is practicable to place the mill tailings in a mined-out open-pit. Such methods have, for instance, been developed in the province of Saskatchewan, Canada, where the disposal of tailings in mined-out open pits is used to achieve a very low water flow through the tailings after decommissioning. Mill tailings are generally in the form of a slurry, i.e., water and solid mixture. After placement into a tailings management facility, the solid tends to settle and the water can be decanted. This water contains a high concentration of radium as well as other potential contaminants and is, therefore, treated before being released into the environment.

- *Waste water* from a number of sources in mining and milling operations, which cannot be re-used, must be treated before discharge to the environment. Standards have been established for the maximum permissible concentrations of specific contaminants in the discharged water.

In general, radium – a decay product of uranium – is the critical contaminant which controls the suitability for release of the treated water. Radium is relatively easily removed from water.

On the completion of mining and milling operations, the facility must be decommissioned. Decommissioning plans are subject to the approval of government regulatory agencies and are generally based on the principle that the area should be returned, as much as possible, to the state in which it was before the operations commenced. When a mine or mill facility closes, monitoring is required for an extended period to ensure that any significant long-term environmental impact would be unlikely.

The technology of "in situ leaching" can be used to recover uranium from certain porous ores. In this method, a number of holes are drilled down to the ore zone and an alkaline or acidic solution is then pumped through pipes down to the ore zone, through the porous ore, and up through other pipes. The solution takes up the uranium in the ore, and this uranium is recovered from the leachate by ion exchangers at the surface. Since virtually no ore is brought to the surface, handling of radiation protection aspects and environmental releases are very much less or negligible in comparison to the uranium ore mined underground, hauled up to the surface, and subjected to milling at the mine site. However, the ground water around the in situ leaching area must be carefully monitored.

In conclusion, a general comment should be added, that, today, uranium mining and milling are moving towards sustainable development in the sense that the impact on the environment is small; thus, future generations will be able to use decommissioned areas for their needs. Mining and milling of uranium involve only very small releases to the air of acid gases and carbon dioxide that are known to cause the "greenhouse effect". Thus, uranium mining and milling in combination with nuclear power, contribute much less to global environmental issues such as acid rain and global warming as compared to the burning of fossil fuels for the generation of electricity. It must be realized, of course, that the natural resource uranium is expended and cannot be mined again by future generations. This story is the same as for other fossil fuels.

It was mentioned at the start of this section that nuclear power generation is not without any misgivings. Nuclear power plants are quite expensive to build, primarily due to the extremely dangerous nature of the radioactive products of nuclear fission. Fission products comprise large neutron-rich, unstable nuclei, ranging in atomic number from 25 to 60, and even if these are handled successfully during the normal operation of a nuclear plant, there remains the difficulty of their eventual disposal. Although many of the unstable nuclei produced by fission are short-lived, some have quite long half-lives, and accordingly must be stored for many hundreds of years before enough nuclei decompose to reduce their radioactivity to a safe level. Generally, radioactive materials should be stored as inert solids and this is, by and large, the current policy which forms a major operation among the massive efforts that constitute the back-end of the nuclear fuel cycle, especially for those countries which have opted for reprocessing the spent nuclear fuel. Liquids (or gases) can escape from containers and pollute the atmosphere; solids, obviously, cannot. Moreover, the solids are required to be chemically inert so that air, water, and even strong acids and bases fail to attack the radioactive solid. In addition to the problems associated with strong radioactive waste, other disadvantages include the costs involved with decommissioning a nuclear reactor which has outlived its useful life.

It is relevant and, of course, not out of context to touch briefly on the technologies used for the reduction of carbon dioxide emissions from many origins, including several examples referred to in the present text. The up-swing in global temperature over the previous few decades has heightened concerns that warming derives partly from anthropogenic conditions of so-called greenhouse gases – that is, those gases that linger the near Earth's surface. Premier among the greenhouse gases generated by human activity is carbon dioxide; this acts as an insulator, preventing the Earth from radiating heat. The greenhouse effect derives its name from this phenomenon, since a blanket of CO_2 acts like a greenhouse, letting light energy in during the day but blocking heat losses at night. It is very well known that although carbon dioxide is a natural constituent of the atmosphere, its concentration has risen by one-third since the onset of the industrial age. A continuum annual increase in carbon dioxide levels has been estimated at 0.4%. Mutual concern over the global impact of greenhouse emissions has compelled many world nations to devise common means to reduce the emission of carbon dioxide. To provide some idea of the quantum involved, reference may be made to the USA, which is to reduce its output of carbon and carbon equivalents by the year 2010 to 7% below the levels prevailing in 1990. It is important to note that, at the time of writing, the US emissions of carbon dioxide from carbon have risen to 18% above the 1990 levels. In the event of nations adhering to current trends for the next decade, the forecast is that there will be an increase in those releases or emissions of a further 16%. Hence, the directives for reducing these emissions form the basis of an aspiring contest.

The enhanced focus on carbon dioxide rather than other greenhouse gases is due to its current dominant position (of potential contributions of gases to global warming, carbon dioxide accounts for 83% of the total; methane, 9%; nitrous oxides, 6%; and halocarbons and other gases, 2%). The bulk of carbon dioxide emissions in the US are from the burning of fossil fuels, which in turn accounts for about 90% of energy use. Thus, the introduction of energy-efficient and other low-carbon technologies would help the US to reduce its carbon dioxide production by minimizing the need to burn fossil fuels while still propelling the economy on an upward course.

Greenhouse gas reductions relate mainly to three end-use sectors: buildings, industry, and transportation. The consumption of energy in buildings relates to the provision of lighting, air-conditioning, refrigeration, water, and to the powering of electrical appliances. Technological advances have led to reductions in the energies required for refrigeration, whilst advanced coatings for windows have greatly reduced heat losses. In fact, it has been estimated that before 1973, almost 5% of national energy consumption was attributed to windows, i.e., to the heating, cooling, and lighting needed to compensate for buildings having windows). The new technology had the potential to make windows net sources rather than sinks of energy, particularly in cold climates. Within the industrial sector, energy use is both exceptionally complex and heterogeneous, and encompasses not only manufacturing but also agriculture, mining, and construction. In the reduction of carbon dioxide production by the industrial sector, attention has been directed towards technologies that reduce emissions without necessarily reducing end-use demand. These technologies involve using by-product fuels more efficiently, and retrofilling boilers for the combined generation of heat and power. On the demand side, an economic gain might result from the high-efficiency motors and advanced motor system drives and controls that can be applied to many diverse types of industry. Many additional low-carbon, energy-proficient technologies are distinctly possible and are also industry-specific. In the steel industry, for example, new advances in the steel-making process might reduce energy use by 30% relative to the current blast furnace approach. In the case of nonferrous metals, a reduction in the emission of carbon or its equivalents is possible by the use of a carbon-less anode in an advanced electrolytic cell used to produce aluminum. In the case of nonmetals, cement manufacture, i.e., the calcination of limestone, now accounts for the largest single source of carbon emissions. Here, a reduction in emissions is inevitable, and is estimated to be 1–2 million tons of carbon per year (MtC yr^{-1}) by 2010. This could be effected by substituting waste products such as fly ash and blast furnace slag for a part of the calcined cement clinker which is an intermediate product in cement manufacture.

The transportation sector accounts for nearly one-fourth of the total US primary energy consumption, and one-third of carbon emissions. Here, the reduction of carbon emissions is inevitable on the basis of ongoing research and development, including reduced aerodynamic drag, lower rolling resistance of tires, reduced engine friction, and leaner-burning engines. Associated with this is the call to raise fuel economy by deploying direct-injection diesel engines, and direct-injection gasoline engines. All of these, when introduced, have provided more control of the combustion process and, in turn, greater efficiency than is achievable in the conventional internal combustion engine.

Ultimately, many opportunities will be derived to harvest benefits in energy efficiency, and some of these technologies are already in place, while others will be adopted in due course. However, even with an appropriate performance guarantee, some technologies are still likely to encounter nontechnical obstacles to their adoption. The need of the hour is that meeting such requirements will also require significant commitment to governmental policies that encourage the adoption of superior efficiency and technologies characterized by low carbon emissions, as described herein.

7.5
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Subject Index

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