CHEM 1A: GENERAL CHEMISTRY Chapter 4: Three Major Types of Chemical Reactions

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Chapter 4

Three Major Classes of Chemical Reactions





The Major Classes of Chemical Reactions

- 4.1 The Role of Water as a Solvent
- 4.2 Writing Equations for Aqueous Ionic Reactions
- 4.3 Precipitation Reactions
- 4.4 Acid-Base Reactions
- 4.5 Oxidation-Reduction (Redox) Reactions
- 4.6 Elements in Redox Reactions
- 4.7 Reaction Reversibility and the Equilibrium State



Water as a Solvent

- Water is a polar molecule
 - since it has uneven electron distribution
 - and a bent molecular shape.
- Water readily dissolves a variety of substances.
- Water interacts strongly with its solutes and often plays an active role in aqueous reactions.



Figure 4.1 Electron distribution in molecules of H_2 and H_2O .

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A. Electron charge distribution in H_2 is symmetrical.



B. Electron charge distribution in H_2O is asymmetrical.



C. Each bond in H_2O is polar.



D. The whole H_2O molecule is polar.



Figure 4.2 An ionic compound dissolving in water.







Figure 4.3 The electrical conductivity of ionic solutions.

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Using Molecular Scenes to Depict an Ionic Compound in Aqueous Solution

PROBLEM: The beakers shown below contain aqueous solutions of the strong electrolyte potassium sulfate.

- (a) Which beaker best represents the compound in solution? $(H_2O molecules are not shown)$.
- (b) If each particle represents 0.10 mol, what is the total number of particles in solution?





- **PLAN:** (a) Determine the formula and write and equation for the dissociation of 1 mol of compound. Potassium sulfate is a strong electrolyte; it therefore dissociates completely in solution. *Remember that polyatomic ions remain intact in solution.*
 - (b) Count the number of separate particles in the relevant beaker, then multiply by 0.1 mol and by Avogadro's number.

SOLUTION:

(a) The formula is K_2SO_4 , so the equation for dissociation is: K_2SO_4 (s) $\rightarrow 2K^+$ (aq) + SO_4^{2-} (aq)



There should be 2 cations for every 1 anion; beaker C represents this correctly.



(b) Beaker C contains 9 particles, 6 K⁺ ions and 3 SO_4^{2-} ions.

$$9 \times 0.1 - \frac{6.022 \times 10^{23} \text{ particles}}{1 - \frac{1}{1 -$$



PROBLEM: What amount (mol) of each ion is in each solution?

- (a) 5.0 mol of ammonium sulfate dissolved in water
- (b) 78.5 g of cesium bromide dissolved in water
- (c) 7.42x10²² formula units of copper(II) nitrate dissolved in water
- (d) 35 mL of 0.84 *mol/L* zinc chloride
- **PLAN:** Write an equation for the dissociation of 1 mol of each compound. Use this information to calculate the actual number of moles represented by the given quantity of substance in each case.





SOLUTION:

(a) The formula is $(NH_4)_2SO_4$ so the equation for dissociation is:

 $(\mathsf{NH}_4)_2\mathsf{SO}_4\ (s) \to 2\mathsf{NH}_4^+\ (aq) + \mathsf{SO}_4^{2-}\ (aq)$

5.0 mol
$$(NH_4)_2 SO_4 \times \frac{2 \mod NH_4^+}{1 \mod (NH_4)_2 SO_4} = 10. \mod NH_4^+$$

5.0 mol $(NH_4)_2 SO_4 \times \frac{1 \mod SO_4^{2-}}{1 \mod (NH_4)_2 SO_4} = 5.0 \mod NH_4^+$



SOLUTION:

(b) The formula is CsBr so the equation for dissociation is: CsBr (s) \rightarrow Cs⁺ (aq) + Br⁻ (aq)

 $78.5 \frac{\text{g CsBr}}{\text{g CsBr}} \times \frac{1 \text{ mol CsBr}}{212.8 \text{ g CsBr}} \times \frac{1 \text{ mol Cs}^+}{1 \text{ mol CsBr}} = 0.369 \text{ mol Cs}^+$

There is one Cs⁺ ion for every Br⁻ ion, so the number of moles of Br⁻ is also equation to **0.369 mol.**



SOLUTION:

(c) The formula is $Cu(NO_3)_2$ so the formula for dissociation is:

 $Cu(NO_3)_2(s) \rightarrow Cu^{2+}(aq) + 2NO_3^{-}(aq)$

7.42x10²² formula units $Cu(NO_3)_2 x$

<u>1 mol</u> 6.022x10²³ formula units

 $= 0.123 \text{ mol } Cu(NO_3)_2$

0.123 mol Cu(NO₃)₂ x $\frac{1 \text{ mol Cu}^{2+}}{1 \frac{1 \text{ mol Cu}(NO_3)_2}{1 \frac{1 \text{ mol Cu}(NO_3)_2}}} = 0.123 \text{ mol Cu}^{2+} \text{ ions}$

There are 2 NO_3^- ions for every 1 Cu^{2+} ion, so there are **0.246 mol NO**₃⁻ ions.



SOLUTION:

(d) The formula is $ZnCl_2$ so the formula for dissociation is:

 $ZnCl_2(s) \rightarrow Zn^{2+}(aq) + 2Cl^{-}(aq)$



There is 1 mol of Zn^{2+} ions for every 1 mol of $ZnCl_2$, so there are **2.9 x 10⁻² mol Zn²⁺ ions**.



Writing Equations for Aqueous Ionic Reactions

The **molecular equation** shows all reactants and products as if they were *intact, undissociated compounds*.

This gives the least information about the species in solution.

$2AgNO_{3}(aq) + Na_{2}CrO_{4}(aq) \rightarrow Ag_{2}CrO_{4}(s) + 2NaNO_{3}(aq)$

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When solutions of silver nitrate and sodium chromate mix, a brick-red precipitate of silver chromate forms.

The **total ionic equation** shows all soluble ionic substances *dissociated into ions*.

This gives the most accurate information about species in solution.

2Ag ⁺ (<i>aq</i>) + 2NO ₃ ⁻ (<i>aq</i>)	\rightarrow	Ag_2CrO_4 (s)
+ 2Na ⁺ (<i>aq</i>) + CrO ₄ ²⁻ (<i>aq</i>)		+ 2Na ⁺ (<i>aq</i>) + NO ₃ ⁻ (<i>aq</i>)

Spectator ions are ions that are not involved in the actual chemical change. Spectator ions appear unchanged on both sides of the total ionic equation.

2Ag ⁺ (<i>aq</i>) + <mark>2NO₃⁻</mark> (<i>aq</i>)	\rightarrow	Ag_2CrO_4 (s)
+ 2Na ⁺ (aq) + CrO ₄ ²⁻ (aq)		+ <mark>2Na</mark> + (aq) + <mark>2NO₃-</mark> (aq)



The **net ionic equation** eliminates the **spectator ions** and shows only the *actual chemical change*.

$$2Ag^{+}(aq) + CrO_{4}^{2-}(aq) \rightarrow Ag_{2}CrO_{4}(s)$$







Figure 4.4 An aqueous ionic reaction and the three types of equations.





Precipitation Reactions

- In a **precipitation reaction** two soluble ionic compounds react to give an insoluble products, called a **precipitate**.
- The precipitate forms through the net removal of ions from solution.
- It is possible for more than one precipitate to form in such a reaction.





Figure 4.5 The precipitation of calcium fluoride.

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$2NaF(aq) + CaCl_2(aq) \rightarrow CaF_2(s) + 2NaCl(aq)$

 $2 \operatorname{Na}^{+}(aq) + 2 \operatorname{F}^{-}(aq) + \operatorname{Ca}^{2+}(aq) + 2 \operatorname{Cl}^{-}(aq) \longrightarrow \operatorname{CaF}_{2}(s) + 2 \operatorname{Na}^{+}(aq) + 2 \operatorname{Cl}^{-}(aq)$

 $2 \operatorname{NaF}(aq) + \operatorname{CaCl}_2(aq) \longrightarrow \operatorname{CaF}_2(s) + 2 \operatorname{NaCl}(aq)$





Figure 4.6 The precipitation of Pbl₂, a metathesis reaction.



 $2Nal(aq) + Pb(NO_3)_2(aq) \rightarrow Pbl_2(s) + NaNO_3(aq)$

 $2Na^{+}(aq) + 2I^{-}(aq) + Pb^{2+}(aq) + 2NO_{3}^{-}(aq)$ $\longrightarrow PbI_{2}(s) + 2Na^{+}(aq) + 2NO_{3}^{-}(aq)$

 $Pb^{2+}(aq) + 2l^{-}(aq) \longrightarrow Pbl_{2}(s)$

Precipitation reactions are also called **double displacement** reactions or **metathesis**.

 $2\text{Nal}(aq) + \text{Pb}(\text{NO}_3)_2(aq) \rightarrow \text{Pbl}_2(s) + 2\text{NaNO}_3(aq)$



Ions exchange partners and a precipitate forms, so there is an exchange of bonds between reacting species.

Predicting Whether a Precipitate Will Form

- Note the ions present in the reactants.
- Consider all possible cation-anion combinations.
- Use the *solubility rules* to decide whether any of the ion combinations is insoluble.
 - An insoluble combination identifies the precipitate that will form.



Table 4.1 Solubility Rules for Ionic Compounds in Water

Soluble Ionic Compounds

- 1. All common compounds of Group 1A(1) ions (Li⁺, Na⁺, K⁺, etc.) and ammonium ion (NH₄⁺) are soluble.
- 2. All common nitrates (NO₃⁻), acetates (CH₃COO⁻ or C₂H₃O₂⁻) and most perchlorates (ClO₄⁻) are soluble.
- All common chlorides (Cl⁻), bromides (Br⁻) and iodides (l⁻) are soluble, except those of Ag⁺, Pb²⁺, Cu⁺, and Hg₂²⁺. All common fluorides (F⁻) are soluble except those of Pb²⁺ and Group 2A(2).
- 4. All common sulfates (SO₂²⁻) are soluble, *except* those of Ca²⁺, Sr²⁺, Ba²⁺, Ag⁺, and Pb²⁺.

Insoluble Ionic Compounds

- All common metal hydroxides are insoluble, *except* those of Group 1A(1) and the larger members of Group 2A(2)(beginning with Ca²⁺).
- 2. All common carbonates (CO_3^{2-}) and phosphates (PO_4^{3-}) are insoluble, *except* those of Group 1A(1) and NH₄⁺.
- 3. All common sulfides are insoluble *except* those of Group 1A(1), Group 2A(2) and NH_4^+ .



PROBLEM: Predict whether or not a reaction occurs when each of the following pairs of solutions are mixed. If a reaction does occur, write balanced molecular, total ionic, and net ionic equations, and identify the spectator ions.

(a) potassium fluoride (aq) + strontium nitrate $(aq) \rightarrow$

(b) ammonium perchlorate (aq) + sodium bromide (aq) \rightarrow

PLAN: Note reactant ions, write the possible cation-anion combinations, and use Table 4.1 to decide if the combinations are insoluble. Write the appropriate equations for the process.



SOLUTION: (a) The reactants are KF and $Sr(NO_3)_2$. The possible products are KNO₃ and SrF_2 . KNO₃ is soluble, but SrF_2 is an insoluble combination.

Molecular equation:

2KF (aq) + Sr(NO₃)₂ (aq) \rightarrow 2 KNO₃ (aq) + SrF₂ (s)

Total ionic equation:

 $2K^{+}(aq) + 2F^{-}(aq) + Sr^{2+}(aq) + 2NO_{3}^{-}(aq) \rightarrow 2K^{+}(aq) + 2NO_{3}^{-}(aq) + SrF_{2}(s)$

K⁺ and NO₃⁻ are spectator ions

Net ionic equation:

 $Sr^{2+}(aq) + 2F^{-}(aq) \rightarrow SrF_{2}(s)$





SOLUTION: (b) The reactants are NH_4CIO_4 and NaBr. The possible products are NH_4Br and $NaCIO_4$. Both are soluble, so no precipitate forms.

Molecular equation:

 $NH_4CIO_4(aq) + NaBr(aq) \rightarrow NH_4Br(aq) + NaCIO_4(aq)$

```
Total ionic equation:

NH_4^+(aq) + CIO_4^-(aq) + Na^+(aq) + Br^-(aq) \rightarrow NH_4^+(aq) + Br^-(aq) + Na^+(aq) + CIO_4^-(aq)
```

All ions are spectator ions and there is no net ionic equation.





Using Molecular Depictions in Precipitation Reactions

PROBLEM: The following molecular views show reactant solutions for a precipitation reaction (with H_2O molecules omitted for clarity).



- (a) Which compound is dissolved in beaker A: KCl, Na_2SO_4 , MgBr₂, or Ag_2SO_4 ?
- (b) Which compound is dissolved in beaker B: NH_4NO_3 , $MgSO_4$, Ba $(NO_3)_2$, or CaF_2 ?





PLAN: Note the number and charge of each kind of ion and use Table 4.1 to determine the ion combinations that are soluble.

SOLUTION:

(a) Beaker A contains two 1+ ion for each 2- ion. Of the choices given, only Na_2SO_4 and Ag_2SO_4 are possible. Na_2SO_4 is soluble while Ag_2SO_4 is not.

Beaker A therefore contains Na₂SO₄.

(b) Beaker B contains two 1- ions for each 2+ ion. Of the choices given, only CaF_2 and $Ba(NO_3)_2$ match this description. CaF_2 is not soluble while $Ba(NO_3)_2$ is soluble.

Beaker B therefore contains Ba(NO₃)₂.





- **PROBLEM:** (c) Name the precipitate and spectator ions when solutions A and B are mixed, and write balanced molecular, total ionic, and net ionic equations for this process.
 - (d) If each particle represents 0.010 mol of ions, what is the maximum mass (g) of precipitate that can form (assuming complete reaction)?
 - **PLAN:** (c) Consider the cation-anion combinations from the two solutions and use Table 4.1 to decide if either of these is insoluble.
- **SOLUTION:** The reactants are $Ba(NO_3)_2$ and Na_2SO_4 . The possible products are $BaSO_4$ and $NaNO_3$. $BaSO_4$ is insoluble while $NaNO_3$ is soluble.





Molecular equation: Ba(NO₃)₂ (aq) + Na₂SO₄ (aq) \rightarrow 2NaNO₃ (aq) + BaSO₄ (s)

Total ionic equation:

 $\begin{array}{l} \mathsf{Ba}^{2^{+}}\left(aq\right)+2\mathsf{NO}_{3}^{-}\left(aq\right)+2\mathsf{Na}^{+}\left(aq\right)+\mathsf{SO}_{4}^{2^{-}}\left(aq\right)\to 2\mathsf{Na}^{+}\left(aq\right)+2\mathsf{NO}_{3}^{-}\left(aq\right)\\ &+\mathsf{BaSO}_{4}\left(s\right)\end{array}$

Na⁺ and NO₃⁻ are spectator ions

Net ionic equation: Ba²⁺ (aq) + SO₄²⁻ (aq) \rightarrow BaSO₄ (s)





PLAN: (d) Count the number of each kind of ion that combines to form the solid. Multiply the number of each reactant ion by 0.010 mol and calculate the mol of product formed from each. Decide which ion is the limiting reactant and use this information to calculate the mass of product formed.

SOLUTION: There are 4 Ba²⁺ particles and 5 SO₄²⁻ particles depicted.

4 Ba²⁺ particles x $0.010 \text{ mol Ba}^{2+}$ x $1 \text{ mol Ba}SO_4$ = 0.040 mol BaSO₄ 1 particle 1 mol Ba²⁺ = 0.040 mol BaSO₄

 $4 \text{ SO}_{4}^{2-} \text{ particles x } \frac{0.010 \text{ mol SO}_{4}^{2-} \text{ x }}{1 \text{ particle}} \frac{1 \text{ mol BaSO}_{4}}{1 \text{ mol SO}_{4}^{2-}} = 0.050 \text{ mol BaSO}_{4}$



Ba²⁺ ion is the limiting reactant, since it yields less BaSO₄.

$$0.040 \text{ mol } BaSO_4 \times \frac{233.4 \text{ g } BaSO_4}{1 \text{ mol } BaSO_4} = 9.3 \text{ g } BaSO_4$$



Acid-Base Reactions

An **acid** is a substance that produces H^+ ions when dissolved in H_2O .

$$\mathsf{HX} \stackrel{\mathsf{H}_2\mathsf{O}}{\longrightarrow} \mathsf{H}^+(aq) + \mathsf{X}^-(aq)$$

A **base** is a substance that produces OH^{-} ions when dissolved in H_2O .

$$\begin{array}{rcl} \mathsf{MOH} & \stackrel{\mathsf{H}_2\mathsf{O}}{\longrightarrow} & \mathsf{mol/L}^+ (aq) + \mathsf{OH}^- \\ (aq) \end{array}$$

An acid-base reaction is also called a neutralization reaction.





Figure 4.7 The H⁺ ion as a solvated hydronium ion.



H⁺ interacts strongly with H_2O , forming H_3O^+ in aqueous solution.





Table 4.2Selected Acids and Bases

Acids

Strong

hydrochloric acid, HCl hydrobromic acid, HBr hydriodic acid, HI nitric acid, HNO₃ sulfuric acid, H_2SO_4 perchloric acid, HClO₄

Weak

- hydrofluoric acid, HF
- phosphoric acid, H₃PO₄
- acetic acid, CH_3COOH (or $HC_2H_3O_2$)

Bases

Strong

sodium hydroxide, NaOH potassium hydroxide, KOH calcium hydroxide, Ca(OH)₂ strontium hydroxide, Sr(OH)₂ barium hydroxide, Ba(OH)₂

Weak

ammonia, NH₃




Figure 4.8 Acids and bases as electrolytes.

Strong acids and strong bases dissociate completely into ions in aqueous solution.

They are *strong electrolytes* and conduct well in solution.



A Strong acid (or base) = strong electrolyte





Figure 4.8 Acids and bases as electrolytes.

Weak acids and weak bases dissociate very little into ions in aqueous solution.

They are weak electrolytes and conduct poorly in solution.



B Weak acid (or base) = weak electrolyte



Determining the Number of H⁺ (or OH⁻) lons in Solution

- **PROBLEM:** How many H⁺(*aq*) ions are in 25.3 mL of 1.4 *mol/L* nitric acid?
- **PLAN:** Use the volume and concentration to determine the mol of acid present. Since HNO_3 is a strong acid, moles acid = moles H⁺.

volume of HNO₃

convert mL to L and multiply by mol of $HNO_3^{mol/L}$

mole of H^+ = mol of HNO_3

mol of H⁺

multiply by Avogadro's number

number of H⁺ ions





SOLUTION: 35.3 mL soln x $\frac{1}{10^3}$ x $\frac{1.4 \text{ mol HNO}_3}{1 \text{ L soln}} = 0.035 \text{ mol HNO}_3$ One mole of $H^+(aq)$ is released per mole of nitric acid (HNO_3) . H_2O $HNO_3(aq) \xrightarrow{2} H^+(aq) + NO_3^-(aq)$ = 0.035 mol HNO₃ x $\frac{1 \text{ mol } \text{H}^+}{1 \text{ mol } \text{HNO}_3}$ x $\frac{6.022 \times 10^{23} \text{ ions}}{1 \text{ mol } \text{HNO}_3}$ = 2.1x10²² H⁺ ions





Writing Ionic Equations for Acid-Base Reactions

- **PROBLEM:** Write balanced molecular, total ionic, and net ionic equations for the following acid-base reactions and identify the spectator ions.
 - (a) hydrochloric acid (aq) + potassium hydroxide $(aq) \rightarrow$
 - (b) strontium hydroxide (aq) + perchloric acid $(aq) \rightarrow$
 - (c) barium hydroxide (aq) + sulfuric acid $(aq) \rightarrow$
 - PLAN: All reactants are strong acids and bases (see Table 4.2). The product in each case is H₂O and an ionic salt. Write the molecular reaction in each case and use the solubility rules to determine if the product is soluble or not.





(a) hydrochloric acid (aq) + potassium hydroxide $(aq) \rightarrow$

```
Molecular equation:
HCl (aq) + KOH (aq) \rightarrow KCl (aq) + H<sub>2</sub>O (I)
```

```
Total ionic equation:
H<sup>+</sup> (aq) + Cl<sup>-</sup> (aq) + K<sup>+</sup> (aq) + OH<sup>-</sup> (aq) \rightarrow K<sup>+</sup> (aq) + Cl<sup>-</sup> (aq) + H<sub>2</sub>O (I)
```

```
Net ionic equation:
H<sup>+</sup> (aq) + OH<sup>-</sup> (aq) \rightarrow H<sub>2</sub>O (/)
```

Spectator ions are K⁺ and Cl⁻





(b) strontium hydroxide (aq) + perchloric acid $(aq) \rightarrow$

Molecular equation: Sr(OH)₂ (aq) + 2HClO₄ (aq) \rightarrow Sr(ClO₄)₂ (aq) + 2H₂O (*I*)

Total ionic equation: $Sr^{2+}(aq) + 2OH^{-}(aq) + 2H^{+}(aq) + 2CIO_{4}^{-}(aq) \rightarrow Sr^{2+}(aq) + 2CIO_{4}^{-}(aq) + 2H_{2}O(l)$

Net ionic equation: 2H⁺ (aq) + 2OH⁻ (aq) \rightarrow 2H₂O (*I*) or H⁺ (aq) + OH⁻ (aq) \rightarrow H₂O (*I*)

Spectator ions are Sr²⁺ and ClO₄⁻



(c) barium hydroxide (aq) + sulfuric acid $(aq) \rightarrow$

```
Molecular equation:
Ba(OH)<sub>2</sub> (aq) + H<sub>2</sub>SO<sub>4</sub> (aq) \rightarrow BaSO<sub>4</sub> (s) + 2H<sub>2</sub>O (l)
```

Total ionic equation: Ba²⁺ (aq) + 2OH⁻ (aq) + 2H⁺ (aq) + SO₄²⁻ (aq) \rightarrow BaSO₄ (s) + H₂O (/)

The net ionic equation is the **same** as the total ionic equation since there are **no spectator ions**.

This reaction is both a neutralization reaction and a precipitation reaction.



Figure 4.9 An aqueous strong acid-strong base reaction as a proton-transfer process.



Figure 4.11 A gas-forming reaction with a weak acid.

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Molecular equation

NaHCO₃ (aq) + CH₃COOH(aq) \rightarrow CH₃COONa (aq) + CO₂ (g) + H₂O (/)

Total ionic equation

Na⁺ (aq)+ HCO₃⁻ (aq) + CH₃COOH (aq) \rightarrow CH₃COO⁻ (aq) + Na⁺ (aq) + CO₂ (g) + H₂O (*l*)

Net ionic equation

 $\begin{aligned} \mathsf{HCO}_3^{-}(aq) + \mathsf{CH}_3\mathsf{COOH}(aq) &\longrightarrow \\ \mathsf{CH}_3\mathsf{COO}^{-}(aq) + \mathsf{CO}_2(g) + \mathsf{H}_2\mathsf{O}(l) \end{aligned}$



Writing Proton-Transfer Equations for Acid-Base Reactions

- **PROBLEM:** Write balanced total and net ionic equations for the following reactions and use curved arrows to show how the proton transfer occurs.
 - (a) hydriodic acid (aq) + calcium hydroxide $(aq) \rightarrow$

Give the name and formula of the salt present when the water evaporates.

(b) potassium hydroxide (aq) + propionic acid $(aq) \rightarrow$

Note that propionic acid is a weak acid. Be sure to identify the spectator ions in this reaction.



PLAN: In (a) the reactants are a strong acid and a strong base. The acidic species is therefore H_3O^+ , which transfers a proton to the OH⁻ from the base.

SOLUTION:



 $H_3O^+(aq) + OH^-(aq) \rightarrow + H_2O(l)$

When the water evaporates, the salt remaining is Cal_2 , calcium iodide.





PLAN: In (b) the acid is weak; therefore it does not dissociate much and largely exists as intact molecules in solution.

SOLUTION:

Total Ionic Equation:

$$\mathsf{H}^{+} \text{ transferred to OH}^{-}$$

$$\mathsf{K}^{+} (aq) + \mathsf{OH}^{-} (aq) + \mathsf{CH}_{3}\mathsf{CH}_{2}\mathsf{COOH} (aq) \rightarrow \mathsf{K}^{+} (aq) + \mathsf{H}_{2}\mathsf{O} (l) + \mathsf{CH}_{3}\mathsf{CH}_{2}\mathsf{COO}^{-} (aq)$$

Net Ionic Equation:

 $CH_3CH_2COOH(aq) + OH^-(aq) \rightarrow CH_3CH_2COO^-(aq) + H_2O(l)$

K⁺ is the only spectator ion in the reaction.





Acid-Base Titrations

- In a *titration*, the concentration of one solution is used to determine the concentration of another.
- In an acid-base titration, a standard solution of base is usually added to a sample of acid of unknown concentration.
- An *acid-base indicator* has different colors in acid and base, and is used to monitor the reaction progress.
- At the equivalence point, the mol of H⁺ from the acid equals the mol of OH⁻ ion produced by the base.

– Amount of H^+ ion in flask = amount of OH^- ion added

• The *end point* occurs when there is a slight excess of base and the indicator changes color permanently.



Figure 4.11

An acid-base titration.

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Finding the Concentration of Acid from a Titration

PROBLEM: A 50.00 mL sample of HCl is titrated with 0.1524 mol/L NaOH. The buret reads 0.55 mL at the start and 33.87 mL at the end point. Find the concentration of the HCl solution. Write a balanced equation for the reaction. Use the volume of PLAN: base to find amount of OH^{-} (mol), then amount of H^{+} (mol) and finally concentration (*mol/L*) for the acid. volume of base (difference in buret readings) multiply by concentration (*mol/L*) of base amount of OH⁻ use mole ratio to find amount of acid amount of H⁺ and acid divide by volume (L) of acid

concentration (*mol/L*) of acid



SOLUTION: NaOH (aq) + HCl $(aq) \rightarrow$ NaCl (aq) + H₂O (I)

volume of base = 33.87 mL - 0.55 mL = 33.32 mL

33.32 mL soln x $1 - x = 0.1524 \text{ mol NaOH} = 5.078 \times 10^{-3} \text{ mol NaOH}$ $10^3 \text{ mL} = 1 - 5.078 \times 10^{-3} \text{ mol NaOH}$

Since 1 mol of HCl reacts with 1 mol NaOH, the amount of HCl = 5.078×10^{-3} mol.

$$\frac{5.078 \times 10^{-3} \text{ mol HCl}}{50.00 \text{ mL}} \times \frac{10^3 \text{ mL}}{1 \text{ L}} = 0.1016 \text{ mol/L HCl}$$



Oxidation-Reduction (Redox) Reactions

Oxidation is the *loss* of electrons. The *reducing agent* loses electrons and is oxidized.

> **Reduction** is the *gain* of electrons. The *oxidizing agent* gains electrons and is reduced.

A **redox reaction** involves **electron transfer** Oxidation and reduction occur together.





Figure 4.12 The redox process in compound formation.



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Table 4.3 Rules for Assigning an Oxidation Number (O.N.)

General rules

- 1. For an atom in its elemental form (Na, O₂, Cl₂, etc.): O.N. = 0
- 2. For a monoatomic ion: O.N. = ion charge
- 3. The sum of O.N. values for the atoms in a compound equals zero. The sum of O.N. values for the atoms in a polyatomic ion equals the ion's charge.

Rules for specific atoms or periodic table groups

1. For Group 1:	O.N. = +1 in all compounds
2. For Group 2:	O.N. = +2 in all compounds
3. For hydrogen:	O.N. = +1 in combination with nonmetals
4. For fluorine:	O.N. = -1 in combination with metals and boron
5. For oxygen:	O.N. = -1 in peroxides
	O.N. = -2 in all other compounds(except with F)
6. For Group 17:	O.N. = -1 in combination with metals, nonmetals (except O), and other halogens lower in the group



Sample Problem 4.9 Determining the Oxidation Number of Each Element in a Compound (or Ion)

PROBLEM: Determine the oxidation number (O.N.) of each element in these species:
 (a) zinc chloride
 (b) sulfur trioxide
 (c) nitric acid

PLAN: The O.N.s of the ions in a polyatomic ion add up to the charge of the ion and the O.N.s of the ions in the compound add up to zero.

SOLUTION:

- (a) **ZnCl₂**. The O.N. for zinc is +2 and that for chloride is -1.
- (b) SO_3 . Each oxygen is an oxide with an O.N. of -2. The O.N. of sulfur must therefore be +6.
- (c) HNO_3 . H has an O.N. of +1 and each oxygen is -2. The N must therefore have an O.N. of +5.



Identifying Redox Reactions

PROBLEM: Use oxidation numbers to decide whether each of the following is a redox reaction or not.

(a) CaO (s) + CO₂(g) \rightarrow CaCO₃(s)

(b) $4 \text{ KNO}_3(s) \rightarrow 2 \text{ K}_2 \text{O}(s) + 2 \text{ N}_2(g) + 5 \text{ O}_2(g)$

(c) NaHSO₄ (aq) + NaOH (aq) \rightarrow Na₂SO₄ (aq) + H₂O (l)

PLAN: Use Table 4.3 to assign an O.N. to each atom. A change in O.N. for any atom indicates electron transfer.

This is not a redox reaction, since no species change O.N.



This is a redox reaction.

- N changes O.N. from +5 to 0 and is reduced.
- O changes O.N. from -2 to 0 and is oxidized.





This is not a redox reaction since no species change O.N.





Figure 4.13 A summary of terminology for redox reactions.



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Identifying Oxidizing and Reducing Agents

PROBLEM: Identify the oxidizing agent and reducing agent in each of the following reactions:

(a) $2AI(s) + 3H_2SO_4(aq) \rightarrow AI_2(SO_4)_3(aq) + 3H_2(g)$ (b) $PbO(s) + CO(g) \rightarrow Pb(s) + CO_2(g)$ (c) $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

PLAN: Assign an O.N. to each atom and look for those that change during the reaction.

The reducing agent contains an atom that is oxidized (increases in O.N.) while the oxidizing agent contains an atom that is reduced (decreases in O.N.).







Al changes O.N. from 0 to +3 and is *oxidized*. Al is the *reducing* agent.

H changes O.N. from +1 to 0 and is *reduced*. H_2SO_4 is the *oxidizing* agent.







Pb changes O.N. from +2 to 0 and is *reduced*. PbO is the *oxidizing* agent.

C changes O.N. from +2 to +4 and is *oxidized*. CO is the *reducing* agent.







 H_2 changes O.N. from 0 to +1 and is *oxidized*. H_2 is the *reducing* agent.

O changes O.N. from 0 to -2 and is *reduced*. O_2 is the *oxidizing* agent.





Balancing Redox Equations (oxidation number method)

- 1. Assign O.N.s to all atoms.
- 2. Identify the reactants that are oxidized and reduced.
- 3. Compute the numbers of electrons transferred, and draw tie-lines from each reactant atom to the product atom to show the change.
- 4. Multiply the numbers of electrons by factor(s) that make the electrons lost equal to the electrons gained.
- 5. Use the factor(s) as balancing coefficients.
- 6. Complete the balancing by inspection and add states of matter.





Sample Problem 4.12 Balancing Redox Equations by the Oxidation Number Method

PROBLEM: Use the oxidation number method to balance the following equations:

(a) Cu (s) + HNO₃ (aq)
$$\rightarrow$$
 Cu(NO₃)₂ (aq) + NO₂ (g) + H₂O (/)

SOLUTION:

Assign oxidation numbers and identify oxidized and reduced species:



loses 2e⁻; oxidation

$$Cu(s) + HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + NO_2(g) + H_2O(l)$$

gains 1e⁻; reduction

Multiply to make e^{-1} lost = e^{-1} gained:

 $\operatorname{Cu}(s) + 2\operatorname{HNO}_{3}(aq) \rightarrow \operatorname{Cu}(\operatorname{NO}_{3})_{2}(aq) + 2\operatorname{NO}_{2}(g) + \operatorname{H}_{2}O(l)$

Balance other atoms by inspection:

 $Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$





(b) $PbS(s) + O_2(g) \rightarrow PbO(s) + SO_2(g)$

SOLUTION:

Assign oxidation numbers and identify oxidized and reduced species:





PbS (s) +
$$O_2(g) \rightarrow PbO(s) + SO_2(g)$$

qains 2e⁻ per O; reduction

Multiply to make e^{-1} lost = e^{-1} gained:

$$PbS(s) + \frac{3}{2}O_2(g) \rightarrow PbO(s) + SO_2(g)$$

Balance other atoms by inspection, and multiply to give whole-number coefficients:

$$2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$$



Figure 4.14 The redox titration of $C_2O_4^{2-}$ with MnO_4^{-} Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display. Before At end titration point $KMnO_4(aq) Na_2C_2O_4(aq)$ © The McGraw-Hill Companies, Inc./Stephen Frisch Photographe © The McGraw-Hill Companies, Inc./Stephen Frisch Photographera Net ionic equation: $\begin{array}{c} +7 & +3 \\ I & 1 \\ 2MnO_4^{-}(aq) + 5C_2O_4^{2-}(aq) + 16H^{+}(aq) \longrightarrow \\ \end{array} \begin{array}{c} +2 & +4 \\ I & 1 \\ 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l) \end{array}$



Sample Problem 4.13 Finding the Amount of Reducing Agent by Titration

PROBLEM: To measure the Ca²⁺ concentration in human blood, 1.00 mL of blood was treated with Na₂C₂O₄ solution to precipitate the Ca²⁺ as CaC₂O₄. The precipitate was filtered and dissolved in dilute H₂SO₄ to release C₂O₄²⁻, which was titrated with KMnO₄ solution. The solution required 2.05mL of 4.88x10⁻⁴ *mol/L* KMnO₄ to reach the end point. The balanced equation is 2 KMnO₄(*aq*) + 5 CaC₂O₄(*s*) + 8 H₂SO₄(*aq*) \rightarrow 2 MnSO₄(*aq*) + K₂SO₄(*aq*) + 5 CaSO₄(*s*) + 10 CO₂(*g*) + 8 H₂O

Calculate the amount (mol) of Ca²⁺ in 1.00 mL of blood.



(/)
PLAN: Calculate the mol of KMnO₄ from the volume and concentration of the solution. Use this to calculate the mol of $C_2O_4^{2-}$ and hence the mol of Ca^{2+} ion in the blood sample.

volume of KMnO₄ soln

convert mL to L and multiply by mol of KMnO₄

molar ratio

mol of CaC₂O₄

ratio of elements in formula

mol of Ca²⁺





SOLUTION:





Elements in Redox Reactions Types of Reaction

- Combination Reactions
 - Two or more reactants combine to form a new compound:
 - $\hspace{0.1cm} X + Y \rightarrow Z$
- Decomposition Reactions
 - A single compound decomposes to form two or more products:

 $- Z \rightarrow X + Y$

- Displacement Reactions
 - double diplacement: $AB + CD \rightarrow AC + BD$
 - single displacement: $X + YZ \rightarrow XZ + Y$
- Combustion
 - the process of combining with O_2



Figure 4.15 Combining elements to form an ionic compound.





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Figure 4.16 Decomposition of the compound mercury(II) oxide to its elements.

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4-77



Figure 4.17 The active metal lithium displaces H₂ from water.

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Figure 4.18 The displacement of H₂ from acid by nickel.

O.N. increasing
oxidation
occurring
reducing agentImage: Comparison of the second se



Ni (s) + 2H⁺ (aq) \rightarrow Ni²⁺ (aq) + H₂ (g)



Figure 4.19 A more reactive metal (Cu) displacing the ion of a less reactive metal (Ag⁺) from solution.

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Figure 4.20

The activity series of the metals.

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Strength as reducing agent





Sample Problem 4.14 Identifying the Type of Redox Reaction

PROBLEM: Classify each of the following redox reactions as a combination, decomposition, or displacement reaction. Write a balanced molecular equation for each, as well as total and net ionic equations for part (c), and identify the oxidizing and reducing agents:

- (a) magnesium (s) + nitrogen (g) \rightarrow magnesium nitride (aq)
- (b) hydrogen peroxide (I) \rightarrow water (I) + oxygen gas
- (c) aluminum (s) + lead(II) nitrate $(aq) \rightarrow$ aluminum nitrate (aq) + lead (s)
- **PLAN:** Combination reactions combine reactants, decomposition reactions involve more products than reactants and displacement reactions have the same number of reactants and products.



SOLUTION:

(a) This is a combination reaction, since Mg and N_2 combine:

Mg is the reducing agent; N_2 is the oxidizing agent.





(b) This is a decomposition reaction, since H_2O_2 breaks down:

$$\begin{array}{ccc} 2 \operatorname{H}_2\operatorname{O}_2(l) \longrightarrow + 2\operatorname{H}_2\operatorname{O}(l) + \operatorname{O}_2(g) \\ \uparrow & \uparrow & \uparrow & \uparrow \\ +1 & +1 & 0 \\ -2 & -2 & -2 \end{array}$$

 H_2O_2 is *both* the reducing and the oxidizing agent.





(c) This is a displacement reaction, since Al displaces Pb²⁺ from solution.

Al is the reducing agent; $Pb(NO_3)_2$ is the oxidizing agent.

The total ionic equation is:

2AI (s) + 3Pb²⁺ (aq) + 2NO₃⁻ (aq) \rightarrow 2AI³⁺ (aq) + 3NO₃⁻ (aq) + 3Pb (s)

The net ionic equation is:

 $2AI(s) + 3Pb^{2+}(aq) \rightarrow 2AI^{3+}(aq) + 3Pb(s)$



