فصل 19 (کتاب سیلبربرگ) قسمت سوم

تعادل های ترکیبات یونی کم محلول

K_{sp} و Q_{sp}

For a slightly soluble ionic compound in water, ***equilibrium*** exists between ***solid solute*** and ***aqueous ions***.

$$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^{-}(aq)$$

$$Q_c = \frac{[Pb^{2+}][F^-]^2}{[PbF_2]} \qquad Q_{sp} = Q_c[PbF_2] = [Pb^{2+}][F^-]^2$$

When the solution is saturated, the system is at equilibrium, and $Q_{sp} = K_{sp}$, the ***solubility product constant***.

ثابت حاصل ضرب حلالیت

Sample Problem 19.5 **Writing Ion-Product Expressions**

PROBLEM: Write the ion-product expression at equilibrium for each compound:

(a) magnesium carbonate **(b)** iron(II) hydroxide
(c) calcium phosphate **(d)** silver sulfide

PLAN: We write an equation for a saturated solution of each compound, and then write the ion-product expression at equilibrium, K_{sp}. Note the sulfide in part (d).

SOLUTION:

(a) $MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$ $\quad K_{sp} = [Mg^{2+}][CO_3^{2-}]$

(b) $Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^{-}(aq)$ $\quad K_{sp} = [Fe^{2+}][OH^-]^2$

(c) $Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$ $\quad K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

Table 19.2 Solubility-Product Constants (K_{sp}) of Selected Ionic Compounds at 25° C

Name, Formula	K_{sp}
Aluminum hydroxide, $Al(OH)_3$	$3x10^{-34}$
Cobalt(II) carbonate, $CoCO_3$	$1.0x10^{-10}$
Iron(II) hydroxide, $Fe(OH)_2$	$4.1x10^{-15}$
Lead(II) fluoride, PbF_2	$3.6x10^{-8}$
Lead(II) sulfate, $PbSO_4$	$1.6x10^{-8}$
Mercury(I) iodide, Hg_2I_2	$4.7x10^{-29}$
Silver sulfide, Ag_2S	$8x10^{-48}$
Zinc iodate, $Zn(IO_3)_2$	$3.9x10^{-6}$

پیدا کردن Ksp از روی حلالیت

Sample Problem 19.6 **Determining K_{sp} from Solubility**

PROBLEM: **(a)** Lead(II) sulfate ($PbSO_4$) is a key component in lead-acid car batteries. Its solubility in water at 25° C is $4.25x10^{-3}$ g/100 mL solution. What is the K_{sp} of $PbSO_4$?

(b) When lead(II) fluoride (PbF_2) is shaken with pure water at 25° C, the solubility is found to be 0.64 g/L. Calculate the K_{sp} of PbF_2.

SOLUTION:

(a) $PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2}(aq)$ $K_{sp} = [Pb^{2+}][SO_4^{2-}]$

Converting from g/mL to mol/L:

$$\frac{4.25\text{x}10^{-3}\text{ g } PbSO_4}{100\text{ mL soln}} \text{ x } \frac{1000\text{ mL}}{1\text{ L}} \text{ x } \frac{1\text{ mol } PbSO_4}{303.3\text{ g } PbSO_4} = 1.40\text{x}10^{-4}\ M\ PbSO_4$$

Each mol of $PbSO_4$ produces 1 mol of Pb^{2+} and 1 mol of SO_4^{2-}, so $[Pb^{2+}] = [SO_4^{2-}] = 1.40\text{x}10^{-4}\ M$

$K_{sp} = [Pb^{2+}][SO_4^{2-}] = (1.40\text{x}10^{-4})^2$ **$= 1.96\text{x}10^{-8}$**

(b) $PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + F^{-}(aq)$ $K_{sp} = [Pb^{2+}][F^{-}]^2$

Converting from g/L to mol/L:

$$\frac{0.64\text{ g } PbF_2}{1\text{ L soln}} \text{ x } \frac{1\text{ mol } PbF_2}{245.2\text{ g } PbF_2} = 2.6\text{x}10^{-3}\ M\ PbF_2$$

Each mol of PbF_2 produces 1 mol of Pb^{2+} and 2 mol of F^-, so $[Pb^{2+}] = 2.6\text{x}10^{-3}\ M$ and $[F^-] = 2(2.6\text{x}10^{-3}) = 5.2\text{x}10^{-3}\ M$

$K_{sp} = [Pb^{2+}][F^-]^2 = (2.6\text{x}10^{-3})(5.2\text{x}10^{-3})^2$ **$= 7.0\text{x}10^{-8}$**

Sample Problem 19.7 **Determining Solubility from K_{sp}**

PROBLEM: Calcium hydroxide (slaked lime) is a major component of mortar, plaster, and cement, and solutions of $Ca(OH)_2$ are used in industry as a strong, inexpensive base. Calculate the molar solubility of $Ca(OH)_2$ in water if the K_{sp} is $6.5\text{x}10^{-6}$.

SOLUTION:

$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^{-}(aq)$ $K_{sp} = [Ca^{2+}][OH^-]^2 = 6.5\text{x}10^{-6}$

Concentration (*M*)	$Ca(OH)_2(s) \rightleftharpoons$	$Ca^{2+}(aq)$ +	$2OH^-(aq)$
Initial	-	0	0
Change	-	$+S$	$+2S$
Equilibrium	-	S	$2S$

$$K_{sp} = [Ca^{2+}][OH^-]^2 = (S)(2S)^2 = 4S^3 = 6.5\text{x}10^{-6}$$

$$S = \sqrt[3]{K_{sp}/4} = \sqrt[3]{(6.5\text{x}10^{-6})/4} \quad \boxed{= 1.2\text{x}10^{-2}\ M}$$

عوامل موثر بر حلالیت رسوب:

اثر یون مشترک- هیدرولیز کاتیون- هیدرولیز آنیون- اثر pH- اثر تشکیل کمپلکس

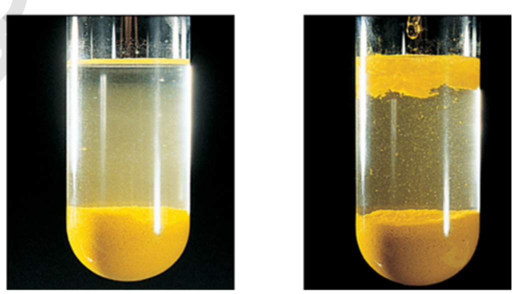
$$\begin{array}{ccccccc} MA\ (\text{solid}) & \rightleftharpoons & MA\ (\text{soln}) & \rightleftharpoons & M^+ & + & A^- \\ & & \upharpoonleft\downharpoonright X & & \upharpoonleft\downharpoonright Y & & \upharpoonleft\downharpoonright Z \\ & & MA(X) & & M^+(Y) & & A^-(Z) \end{array}$$

اثر یون مشترک بر حلالیت رسوب

افزایش کرومات به تعادل زیر، رسوب را افزایش می دهد.

$$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$$

Figure 19.13 The effect of a common ion on solubility.



Sample Problem 19.8	**Calculating the Effect of a Common Ion on Solubility**

PROBLEM: In Sample Problem 19.7, we calculated the solubility of $Ca(OH)_2$ in water. What is its solubility in 0.10 M $Ca(NO_3)_2$? K_{sp} of $Ca(OH)_2$ is $6.5\text{x}10^{-6}$.

SOLUTION:

$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$ $K_{sp} = [Ca^{2+}][OH^-]^2 = 6.5\text{x}10^{-6}$

$[Ca^{2+}]_{init} = 0.10\ M$ because $Ca(NO_3)_2$ is a soluble salt, and dissociates completely in solution.

Concentration (M)	**$Ca(OH)_2(s)$**	**$\rightleftharpoons$**	**$Ca^{2+}(aq)$ +**	**$2OH^-(aq)$**
Initial	-		0.10	0
Change	-		$+S$	$+ 2S$
Equilibrium	-		$0.10 + S$	$2S$

$K_{sp} = [Ca^{2+}][OH^-]^2 = 6.5\text{x}10^{-6} \approx (0.10)(2S)^2 = (0.10)(4S^2)$

$4S^2 \approx \dfrac{6.5\text{x}10^{-6}}{0.10}$ so $S \approx \sqrt{(6.5\text{x}10^{-5})/4}$ $\boxed{\mathbf{= 4.0\text{x}10^{-3}\ \mathit{M}}}$

Checking the assumption: $\dfrac{4.0\text{x}10^{-3}\ M}{0.10\ M} \text{ x } 100 = 4.0\% < 5\%$

اثر pH (افزایش اسید)

The addition of H_3O^+ will ***increase*** the solubility of a salt that contains the ***anion of a weak acid***.

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

$$CO_3^{2-}(aq) + H_3O^+(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$$

$$HCO_3^-(aq) + H_3O^+(aq) \rightarrow [H_2CO_3(aq)] + H_2O(l) \rightarrow CO_2(g) + 2H_2O(l)$$

Figure 19.14 **Test for the presence of a carbonate.**

When a carbonate mineral is treated with HCl, bubbles of CO_2 form.

نمونه مسئله 19-9

Sample Problem 19.9 **Predicting the Effect on Solubility of Adding Strong Acid**

PROBLEM: Write balanced equations to explain whether addition of H_3O^+ from a strong acid affects the solubility of each ionic compound:

(a) lead(II) bromide **(b)** copper(II) hydroxide **(c)** iron(II) sulfide

SOLUTION:

(a) $PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$

Br^- is the anion of HBr, a strong acid, so it does not react with H_3O^+. The addition of strong acid has **no effect** on its solubility.

(b) $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$

OH^- is the anion of H_2O, a very weak acid, and is in fact a strong base. It will react with H_3O^+:

$$\mathbf{OH^-(aq) + H_3O^+(aq) \rightarrow 2H_2O(l)}$$

The addition of strong acid will cause an **increase in solubility**.

(c) $FeS(s) \rightleftharpoons Fe^{2+}(aq) + S^{2-}(aq)$

S^{2-} is the anion of HS^-, a weak acid, and is a strong base. It will react completely with water to form HS^- and OH^-. Both these ions will react with added H_3O^+:

$$\mathbf{HS^-(aq) + H_3O^+(aq) \rightarrow H_2S(aq) + H_2O(l)}$$
$$\mathbf{OH^-(aq) + H_3O^+(aq) \rightarrow 2H_2O(l)}$$

The addition of strong acid will cause an **increase in solubility**.

پیش بینی تشکیل رسوب

وقتی دو محلول حاوی یونهای تشکیل دهنده رسوب با هم مخلوط شوند:

If $Q_{sp} = K_{sp}$,
the solution is saturated and no change will occur.

If $Q_{sp} > K_{sp}$,
a precipitate will form until the remaining solution is saturated.

If $Q_{sp} < K_{sp}$,
no precipitate will form because the solution is unsaturated.

نمونه مسئله 19–10

Sample Problem 19.10 **Predicting Whether a Precipitate Will Form**

PROBLEM: A common laboratory method for preparing a precipitate is to mix solutions containing the component ions. Does a precipitate form when 0.100 L of 0.30 *M* $Ca(NO_3)_2$ is mixed with 0.200 L of 0.060 *M* NaF?

SOLUTION:

The ions present are Ca^{2+}, NO_3^-, Na^+, and F^-. All Na^+ and NO_3^- salts are soluble, so the only possible precipitate is CaF_2 ($K_{sp} = 3.2\text{x}10^{-11}$).

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = [Ca^{2+}][F^-]^2$$

$Ca(NO_3)_2$ and NaF are soluble, and dissociate completely in solution.

We need to calculate $[Ca^{2+}]$ and $[F^-]$ in the final solution.

Amount (mol) of Ca^{2+} = 0.030 M Ca^{2+} x 0.100 L = 0.030 mol Ca^{2+}.

$$[Ca^{2+}]_{init} = \frac{0.030 \text{ mol } Ca^{2+}}{0.100 \text{ L} + 0.200 \text{ L}} = 0.10\ M\ Ca^{2+}$$

Amount (mol) of F^- = 0.060 M F^- x 0.200 L = 0.012 mol F^-.

$$[F^-]_{init} = \frac{0.012 \text{ mol } F^-}{0.100 \text{ L} + 0.200 \text{ L}} = 0.040\ M\ F^-$$

$Q_{sp} = [Ca^{2+}]_{init}[F^-]^2_{init} = (0.10)(0.040)^2 = \mathbf{1.6x10^{-4}}$

Since $Q_{sp} > K_{sp}$, **CaF_2 will precipitate** until $Q_{sp} = 3.2x10^{-11}$.

رسوب گیری انتخابی

اگر دو یا چند یون با یک واکنشگر رسوب دهنده رسوب دهند، در صورتی که حلالیت متفاوتی داشته باشند با کنترل غلظت واکنشگر رسوب دهنده، امکان جداسازی یونها وجود دارد. یونی زودتر رسوب می کند که Qsp آن زودتر به Ksp برسد.

Sample Problem 19.12 **Separating Ions by Selective Precipitation**

PROBLEM: A solution consists of 0.20 M $MgCl_2$ and 0.10 M $CuCl_2$. Calculate the $[OH^-]$ that would separate the metal ions as their hydroxides. K_{sp} of $Mg(OH)_2$= is $6.3x10^{-10}$; K_{sp} of $Cu(OH)_2$ is $2.2x10^{-20}$.

SOLUTION:

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = [Mg^{2+}][OH^-]^2 = 6.3\text{x}10^{-10}$

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = [Cu^{2+}][OH^-]^2 = 2.2\text{x}10^{-20}$

$[OH^-] = \sqrt{K_{sp}/[Mg^{2+}]} = \sqrt{6.3\text{x}10^{-10}/0.20} = \mathbf{5.6x10^{-5}}\ \boldsymbol{M}$

This is the maximum $[OH^-]$ that will *not* precipitate Mg^{2+} ion.

Calculating the $[Cu^{2+}]$ remaining in solution with this $[OH^-]$

$$[Cu^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{2.2\text{x}10^{-20}}{(5.6\text{x}10^{-5})^2} = 7.0\text{x}10^{-12}\ M$$

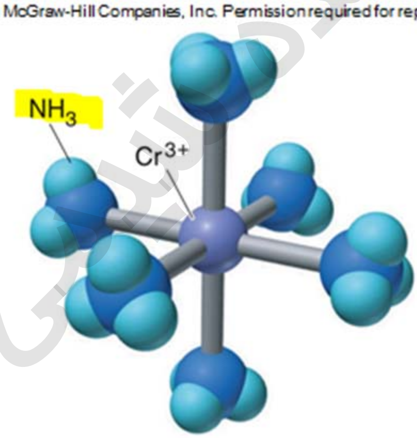
Since the initial $[Cu^{2+}]$ is 0.10 M, virtually all the Cu^{2+} ion is precipitated.

تشکیل کمپلکس

تعادلات تشکیل کمپلکس

اثر تشکیل کمپلکس بر حلالیت رسوب

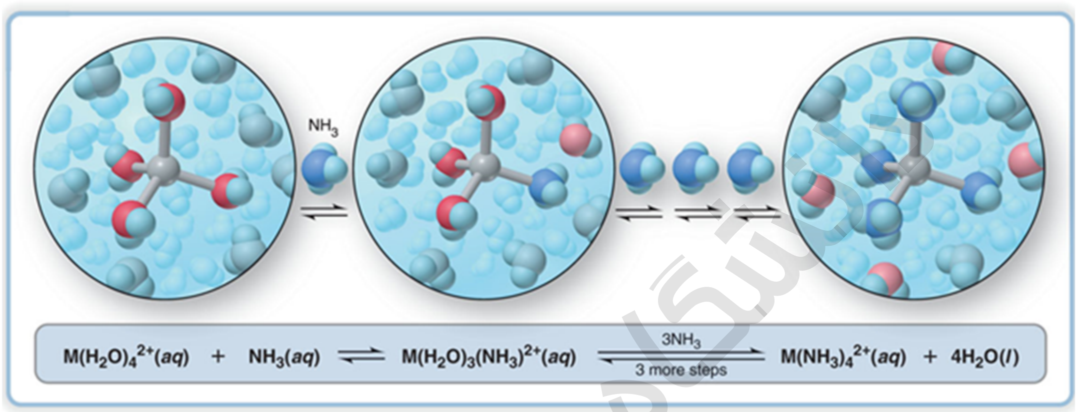
Figure 19.16 $Cr(NH_3)_6^{3+}$, a typical complex ion.



A ***complex ion*** consists of a central metal ion covalently bonded to two or more anions or molecules, called ***ligands***.

تبادل مرحله ای آمونیاک با آب

Figure 19.17 The stepwise exchange of NH_3 for H_2O in $M(H_2O)_4^{2+}$.



The overall ***formation constant*** is given by

$$K_f = \frac{[M(NH_3)_4^{2+}]}{[M(H_2O)_4^{2+}][NH_3]^4}$$

Table 19.4 Formation Constants (K_f) of Some Complex Ions at 25° C

Complex Ion	K_f
$Ag(CN)_2^-$	3.0×10^{20}
$Ag(NH_3)_2^+$	1.7×10^{7}
$Ag(S_2O_3)_2^{3-}$	4.7×10^{13}
AlF_6^{3-}	4×10^{19}
$Al(OH)_4^-$	3×10^{33}
$Be(OH)_4^{2-}$	4×10^{18}
CdI_4^{2-}	1×10^{6}
$Co(OH)_4^{2-}$	5×10^{9}
$Cr(OH)_4^-$	8.0×10^{29}
$Cu(NH_3)_4^{2+}$	5.6×10^{11}
$Fe(CN)_6^{4-}$	3×10^{35}
$Fe(CN)_6^{3-}$	4.0×10^{43}
$Hg(CN)_4^{2-}$	9.3×10^{38}
$Ni(NH_3)_6^{2+}$	2.0×10^{8}
$Pb(OH)_3^-$	8×10^{13}
$Sn(OH)_3^-$	3×10^{25}
$Zn(CN)_4^{2-}$	4.2×10^{19}
$Zn(NH_3)_4^{2+}$	7.8×10^{8}
$Zn(OH)_4^{2-}$	3×10^{15}

Sample Problem 19.13 **Calculating the Concentration of a Complex Ion**

PROBLEM: An industrial chemist converts $Zn(H_2O)_4^{2+}$ to the more stable $Zn(NH_3)_4^{2+}$ by mixing 50.0 L of 0.0020 *M* $Zn(H_2O)_4^{2+}$ and 25.0 L of 0.15 *M* NH_3. What is the final $[Zn(H_2O)_4^{2+}]$ at equilibrium? K_f of $Zn(NH_3)_4^{2+}$ is 7.8×10^8.

PLAN: We write the reaction equation and the K_f expression, and use a reaction table to calculate equilibrium concentrations. To set up the table, we must first find $[Zn(H_2O)_4^{2+}]_{init}$ and $[NH_3]_{init}$ using the given volumes and molarities. With a large excess of NH_3 and a high K_f, we assume that almost all the $Zn(H_2O)_4^{2+}$ is converted to $Zn(NH_3)_4^{2+}$.

SOLUTION:

$$Zn(H_2O)_4^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Zn(NH_3)_4^{2+}(aq) + 4H_2O(l)$$

$$K_f = \frac{[Zn(NH_3)_4^{2+}]}{[Zn(H_2O)_4^{2+}][NH_3]^4}$$

Sample Problem 19.13

$$[Zn(H_2O)_4^{2+}]_{initial} = \frac{50.0\ L \times 0.0020\ M}{50.0\ L + 25.0\ L} = 1.3\times10^{-3} M$$

$$[NH_3]_{initial} = \frac{25.0\ L \times 0.15\ M}{50.0\ L + 25.0\ L} = 5.0\times10^{-2}\ M$$

4 mol of NH_3 is needed per mol of $Zn(H_2O_4)^{2+}$, so
$[NH_3]_{reacted} \approx 4(1.3\times10^{-3}\ M) = 5.2\times10^{-3}\ M$ and
$[Zn(NH_3)_4^{2+}] \approx 1.3\times10^{-3}\ M$

Concentration (*M*)	$Zn(H_2O)_4^{2+}(aq)$	$+ 4NH_3(aq)$ ⇌	$Zn(NH_3)_4^{2+}(aq)$	$+ 4H_2O(l)$
Initial	1.3×10^{-3}	5.0×10^{-2}	0	-
Change	$\sim(-1.3\times10^{-3})$	$\sim(-5.2\times10^{-3})$	$\sim(+1.3\times10^{-3})$	-
Equilibrium	x	$\sim 4.5\times10^{-2}$	$\sim 1.3\times10^{-3}$	-

$$K_f = \frac{[Zn(NH_3)_4^{2+}]}{[Zn(H_2O)_4^{2+}][NH_3]^4} = 7.8\times10^8 \approx \frac{(1.3\times10^{-3})}{x(4.5\times10^{-2})^4}$$

$$x = [Zn(H_2O)_4^{2+}] \approx 4.1\times10^{-7}\ M$$

Sample Problem 19.14 **Calculating the Effect of Complex-Ion Formation on Solubility**

PROBLEM: In black-and-white film developing, excess AgBr is removed from the film negative by "hypo", an aqueous solution of sodium thiosulfate ($Na_2S_2O_3$), which forms the complex ion $Ag(S_2O_3)_2^{3-}$. Calculate the solubility of AgBr in **(a)** H_2O; **(b)** 1.0 *M* hypo.
K_f of $Ag(S_2O_3)_2^{3-}$ is $4.7\text{x}10^{13}$ and K_{sp} AgBr is $5.0\text{x}10^{-13}$.

PLAN: After writing the equation and the K_{sp} expression, we use the given K_{sp} value to solve for *S*, the molar solubility of AgBr. For **(b)** we note that AgBr forms a complex ion with $S_2O_3^{2-}$, which shifts the equilibrium and dissolves more AgBr. We write an overall equation for the process and set up a reaction table to solve for *S*.

SOLUTION:

(a) $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \quad K_{sp} = [Ag^+][Br^-] = 5.0\text{x}10^{-13}$

$S = [AgBr]_{dissolved} = [Ag^+] = [Br^-]$

$K_{sp} = [Ag^+][Br^-] = S^2 = 5.0\text{x}10^{-13}$

$S = 7.1\text{x}10^{-7}$ *M*

(b) Write the overall equation:

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

$$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq)$$

$$AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons Br^-(aq) + Ag(S_2O_3)_2^{3-}(aq)$$

$$K_{overall} = K_{sp} \times K_f = \frac{[Br^-][Ag(S_2O_3)_2^{3-}]}{[S_2O_3^{2-}]^2} = (5.0\text{x}10^{-13})(4.7\text{x}10^{13}) = 24$$

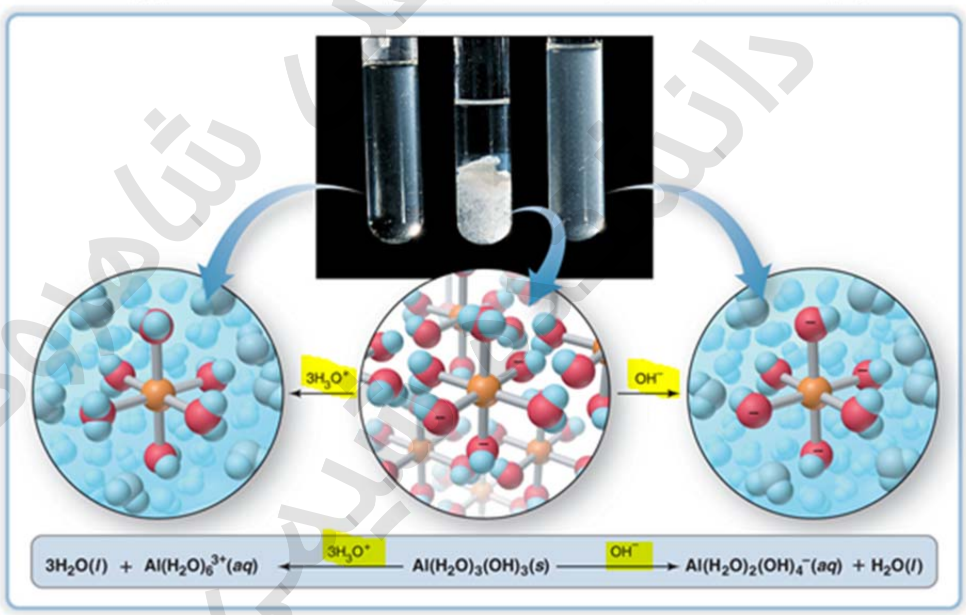
Concentration (M)	$AgBr(s)$ +	$2S_2O_3^{2-}(aq)$ ⇌	$Br^-(aq)$ +	$Ag(S_2O_3)_2^{3-}(aq)$
Initial	-	1.0	0	0
Change	-	$-2S$	$+S$	$+S$
Equilibrium	-	$1.0 - 2S$	S	S

$$K_{overall} = \frac{S^2}{(1.0-2S)^2} = 24 \qquad \text{so} \quad \frac{S}{1.0-2S} = \sqrt{24} = 4.9$$

$$S = [Ag(S_2O_3)_2^{3-}] = 0.45\ M$$

رفتار آمفوتری آلومینیوم هیدروکسید

Figure 19.18 The amphoteric behavior of aluminum hydroxide.



When solid $Al(OH)_3$ is treated with H_3O^+ (*left*) or with OH^- (*right*), it dissolves as a result of the formation of soluble complex ions.

منبع:

فصل 19 کتاب شیمی عمومی تالیف سیلبربرگ

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