大 学 化 学 (双语)
College Chemistry

College of Chemistry and Materials Science

Chapter 8
Precipitation Equilibria and TiTrations

Qianhuo Chen
Fujian Normal University, China

Content

8.1 Basic Concepts

8.2 Factors Affecting the Precipitation Equilibrium

8.3 Fractional Precipitation

8.4 Transformation of the Precipitate

8.5 Gravimetry

8.6 Precipitation Titration

8.7 Organic precipitating agent

8.8 Homogeneous precipitation

Chapter Goals

1. **Apply chemical equilibrium concepts to the solubility of ionic compounds.**
2. **Estimate the solubility of a salt from the value of K_{sp}.**
3. **Understand the side reaction and K'_{sp}.**
4. **Understand the common ion effect, salt effect, acid effect and coordination effect.**

Mineral Barite(重晶石）

Barium sulfate used to examine the digestive tract.

8.1 Basic Concepts

1. Precipitation-dissolution Equilibrium

$$\mathrm{M_mA_n}(s) \rightleftharpoons m\mathrm{M^{n+}}(aq) + n\mathrm{A^{m-}}(aq)$$

$$K^{\circ}_{\mathrm{sp}} = \{a(\mathrm{M}^{n+})\}^{m}\{a(\mathrm{A}^{m-})\}^{n} = \gamma_M{}^{m}[M^{n+}]^{m}\gamma_A{}^{n}[A^{m-}]^{n}$$

$$= \gamma_M{}^{m}\gamma_A{}^{n}[M^{n+}]^{m}[A^{m-}]^{n} = \gamma_M{}^{m}\gamma_A{}^{n}K_{\mathrm{sp}}$$

Activity Product Constant

$$K_{sp} = [M^{n+}]^{m}[A^{m-}]^{n}$$

Solubility Product Constant

2. Solubility Product Constant: K_{sp}

$$\mathrm{MA}(s) \rightleftharpoons \mathrm{M}^+(aq) + \mathrm{A}^-(aq)$$

$$K^\circ_{sp} = a(\mathrm{M}^+)a(\mathrm{A}^-) = \gamma_+\left(\frac{m_+}{m^o}\right)\gamma_-\left(\frac{m_-}{m^o}\right)$$ m^0=1 mol/kg

Given Solubility Product Constant: $K_{sp}=(m_+)(m_-)$

$$\therefore\ K_{sp} = K^\circ_{sp}\frac{m^o m^o}{\gamma_+\gamma_-}$$

$$\xrightarrow{\text{In dilute solution}} \quad K_{sp} = K^\circ_{eq} m^o m^o$$

$$c_B = \frac{n_B}{V_{solution}} = \frac{m_B \times W_{solvent}}{\frac{W_{solution}}{\rho}} = \frac{m_B \times \rho}{\frac{m_{solution}}{W_{solvent}}} = \frac{m_B \times \rho}{\frac{W_B + W_{solvent}}{W_{solvent}}}$$

$$\begin{cases} \rho = \frac{W_{solution}}{V_{solution}} \\ m_B = n_B / w_{solvent} \end{cases}$$

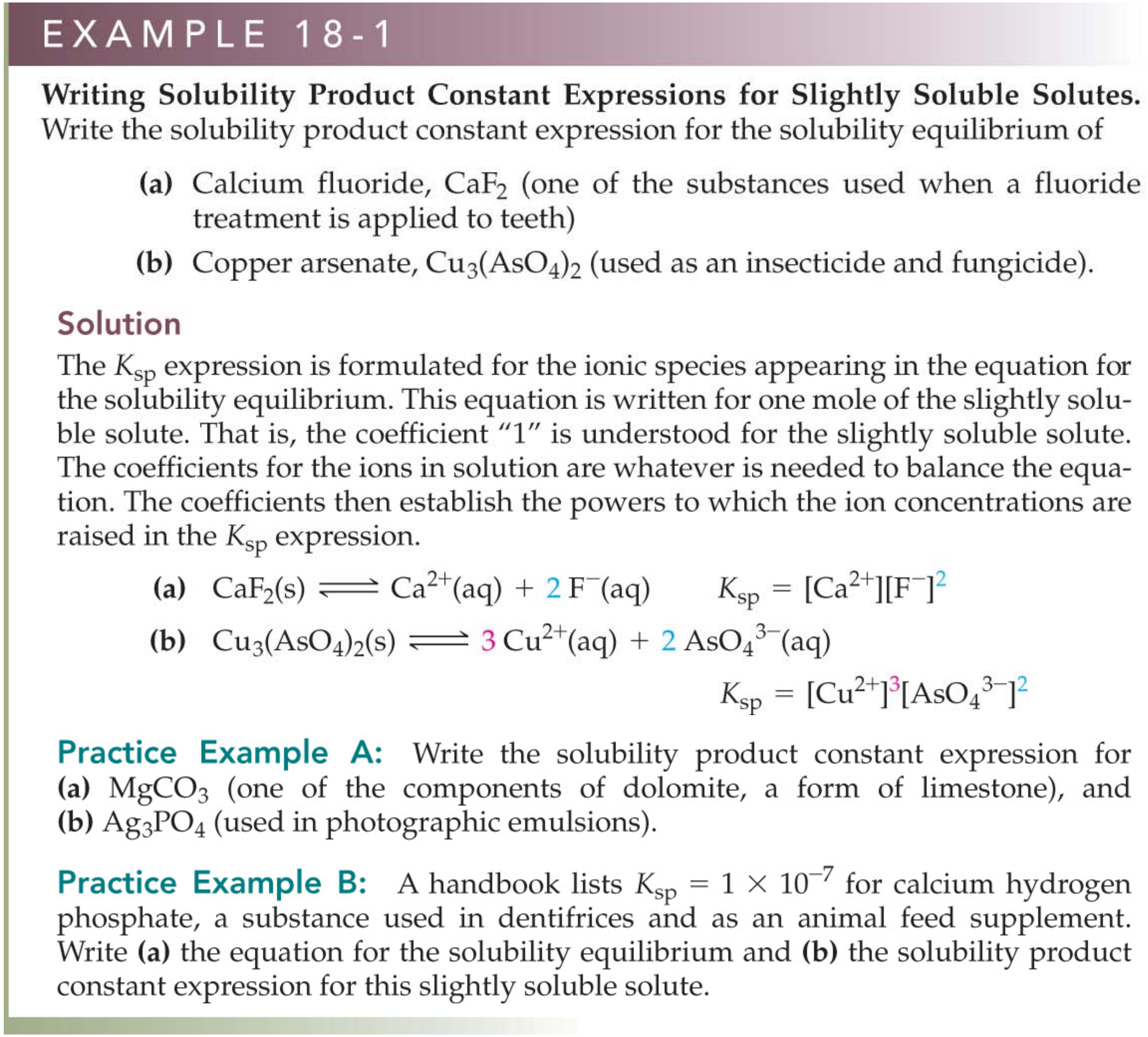
(质量摩尔浓度)

$$\frac{m_B \rho}{1 + \frac{W_B}{W_{solvent}}} = \frac{m_B \rho}{1 + \frac{n_B M_B}{W_{solvent}}} = \frac{m_B \rho}{1 + m_B M_B}$$

where ρ (kg/L) is the density of the solution, M_B (kg/mol) is the molar mass of the solute.

$$\xrightarrow{\text{In dilute solution}} m_B M_B \ll 1, \rho \to 1 \longrightarrow c_B \approx m_B$$

$$\therefore K_{sp} = [M^+][A^-]$$



EXAMPLE 18-1

Writing Solubility Product Constant Expressions for Slightly Soluble Solutes. Write the solubility product constant expression for the solubility equilibrium of

(a) Calcium fluoride, CaF_2 (one of the substances used when a fluoride treatment is applied to teeth)

(b) Copper arsenate, $Cu_3(AsO_4)_2$ (used as an insecticide and fungicide).

Solution

The K_{sp} expression is formulated for the ionic species appearing in the equation for the solubility equilibrium. This equation is written for one mole of the slightly soluble solute. That is, the coefficient "1" is understood for the slightly soluble solute. The coefficients for the ions in solution are whatever is needed to balance the equation. The coefficients then establish the powers to which the ion concentrations are raised in the K_{sp} expression.

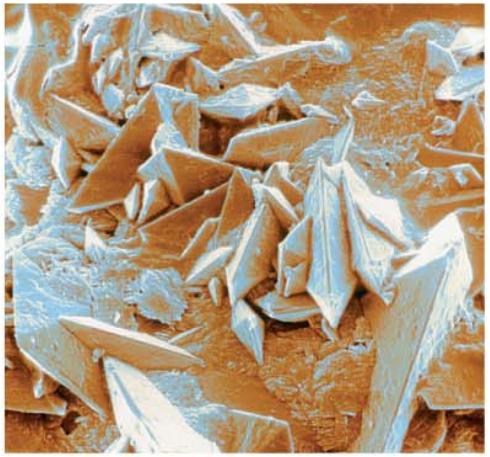
(a) $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq) \qquad K_{sp} = [Ca^{2+}][F^-]^2$

(b) $Cu_3(AsO_4)_2(s) \rightleftharpoons 3\,Cu^{2+}(aq) + 2\,AsO_4^{3-}(aq)$

$$K_{sp} = [Cu^{2+}]^3[AsO_4^{3-}]^2$$

Practice Example A: Write the solubility product constant expression for **(a)** $MgCO_3$ (one of the components of dolomite, a form of limestone), and **(b)** Ag_3PO_4 (used in photographic emulsions).

Practice Example B: A handbook lists $K_{sp} = 1 \times 10^{-7}$ for calcium hydrogen phosphate, a substance used in dentifrices and as an animal feed supplement. Write **(a)** the equation for the solubility equilibrium and **(b)** the solubility product constant expression for this slightly soluble solute.



▲ Some calcium salts, such as calcium fluoride and calcium hydrogen phosphate, have beneficial uses, but another calcium salt, calcium oxalate (CaC_2O_2), can be harmful. The photo is a scanning electron microscope image of calcium oxalate crystals, commonly called kidney stones, which can form in the human kidney.

3. Solubility (s) is defined as the concentration of a dissolved at equilibrium with its undissolved form.

$$\mathrm{M_mA_n}(s) \rightleftharpoons m\mathrm{M^{n+}}(aq) + n\mathrm{A^{m-}}(aq)$$

Equi. ms ns

$$\because \quad K_{sp} = [ms]^m[ns]^n = m^m n^n s^m s^n = m^m n^n s^{m+n}$$

$$\therefore \quad s = \sqrt[m+n]{\frac{K_{sp}}{m^m n^n}} = \sqrt[m+n]{\frac{K^{\circ}_{sp}}{m^m n^n \gamma^m(\mathrm{M})\gamma^n(\mathrm{A})}}$$

Note for the Relationship Between K_{sp} & s

K_{sp} can be used to

- **estimate the solubility of a solid salt;**
- **determine whether a solid will precipitate when solution of its anion and cation are mixed;**
- **compare the solubility of two salts having the same cation-anion ratio.**

Note

1. If $Q = K_{sp}$ the solution is saturated and at equilibrium.
2. If $Q < K_{sp}$, the solution is not saturated. (i) If solid is present, more will dissolve until equilibrium is achieved; (ii) If solid is not already present, more ions could be added to the solution until precipitation of solid begins.
3. If $Q > K_{sp}$, the system is not at equilibrium, the solution is supersaturated.

EXAMPLE

Applying the Criteria for Precipitation of a Slightly Soluble Solute. Three drops of 0.20 M KI are added to 100.0 mL of 0.010 M $Pb(NO_3)_2$. Will a precipitate of lead iodide form?
(1 drop ≈ 0.05 mL)

$$PbI_2(s) \rightarrow Pb^{2+}(aq) + 2\,I^{-}(aq) \qquad K_{sp} = 7.1\times10^{-9}$$

Determine the amount of I^- in the solution:

$$n_{I^-} = 3\ \cancel{\text{drops}}\ \frac{0.05\ \cancel{\text{mL}}}{1\ \cancel{\text{drop}}}\ \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}}\ \frac{0.20\ \cancel{\text{mol KI}}}{1\ \cancel{\text{L}}}\ \frac{1\ \text{mol I}^-}{1\ \cancel{\text{mol KI}}}$$

$$= 3\times10^{-5}\ \text{mol I}^-$$

EXAMPLE

Determine the concentration of I^- in the solution:

$$[I^-] = \frac{3 \times 10^{-5}\ \text{mol}}{0.1000\ \text{L}} = 3\times10^{-4}\ \text{M}$$

Apply the Precipitation Criteria:

$$Q = [Pb^{2+}][I^-]^2 = (0.010)(3\times10^{-4})^2$$

$$= 9\times10^{-10} \quad < \quad K_{sp} = 7.1\times10^{-9}$$


(a)


(b)

Inc.

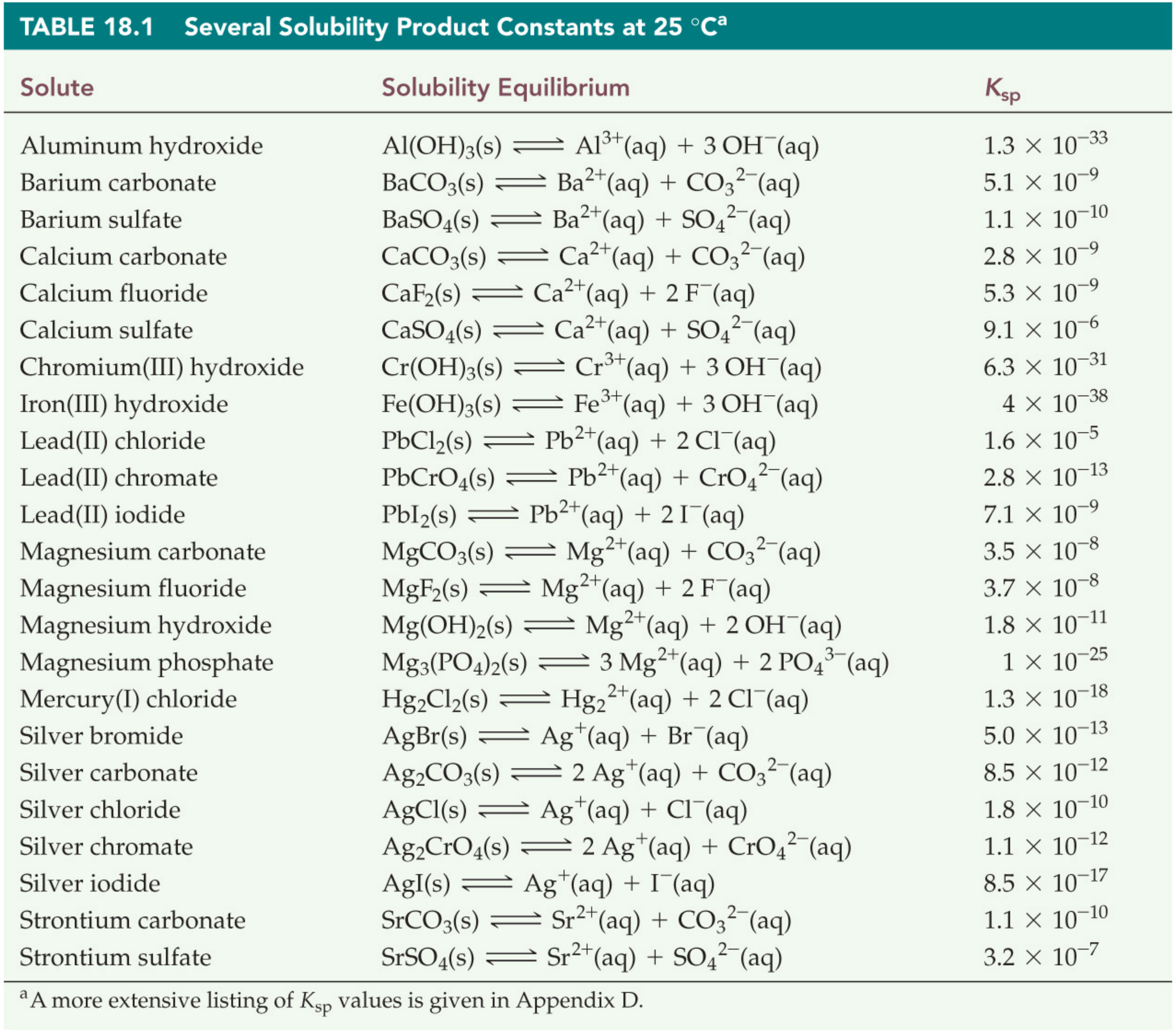
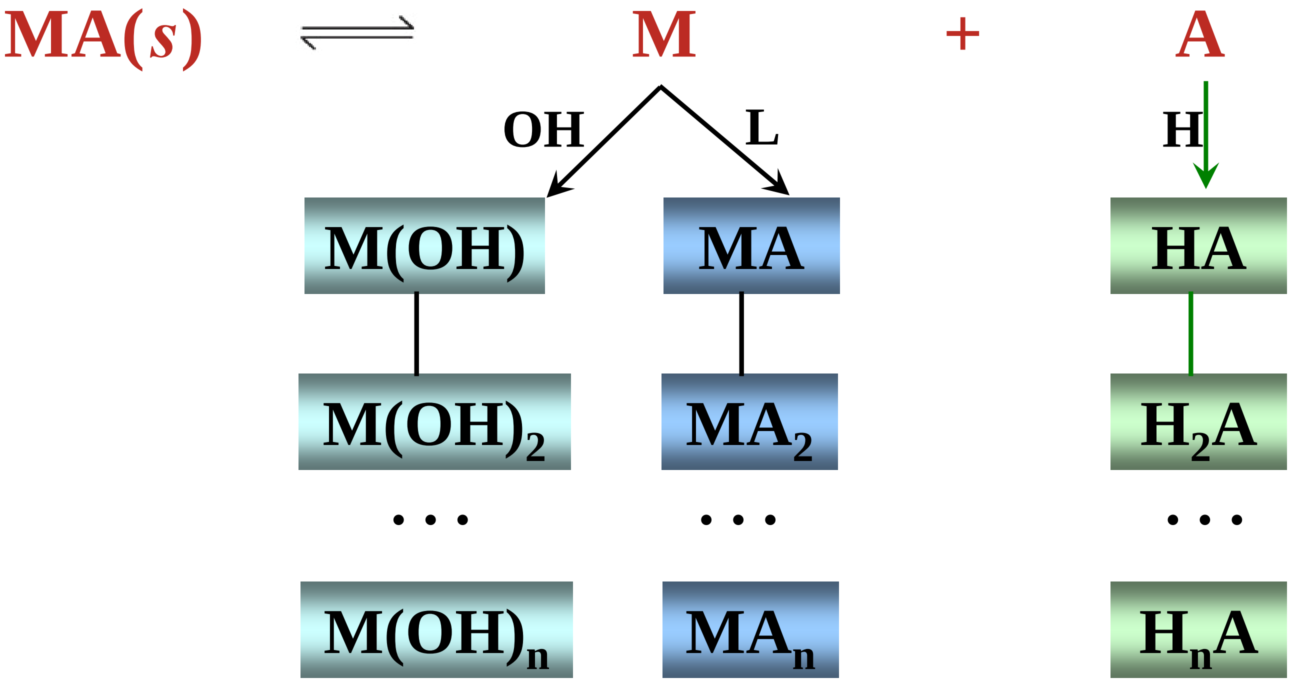


TABLE 18.1 Several Solubility Product Constants at 25 °C[a]

Solute	Solubility Equilibrium	K_{sp}
Aluminum hydroxide	$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3\,OH^-(aq)$	1.3×10^{-33}
Barium carbonate	$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$	5.1×10^{-9}
Barium sulfate	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$	1.1×10^{-10}
Calcium carbonate	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	2.8×10^{-9}
Calcium fluoride	$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$	5.3×10^{-9}
Calcium sulfate	$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$	9.1×10^{-6}
Chromium(III) hydroxide	$Cr(OH)_3(s) \rightleftharpoons Cr^{3+}(aq) + 3\,OH^-(aq)$	6.3×10^{-31}
Iron(III) hydroxide	$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3\,OH^-(aq)$	4×10^{-38}
Lead(II) chloride	$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$	1.6×10^{-5}
Lead(II) chromate	$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$	2.8×10^{-13}
Lead(II) iodide	$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,I^-(aq)$	7.1×10^{-9}
Magnesium carbonate	$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$	3.5×10^{-8}
Magnesium fluoride	$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,F^-(aq)$	3.7×10^{-8}
Magnesium hydroxide	$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$	1.8×10^{-11}
Magnesium phosphate	$Mg_3(PO_4)_2(s) \rightleftharpoons 3\,Mg^{2+}(aq) + 2\,PO_4^{3-}(aq)$	1×10^{-25}
Mercury(I) chloride	$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\,Cl^-(aq)$	1.3×10^{-18}
Silver bromide	$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$	5.0×10^{-13}
Silver carbonate	$Ag_2CO_3(s) \rightleftharpoons 2\,Ag^+(aq) + CO_3^{2-}(aq)$	8.5×10^{-12}
Silver chloride	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	1.8×10^{-10}
Silver chromate	$Ag_2CrO_4(s) \rightleftharpoons 2\,Ag^+(aq) + CrO_4^{2-}(aq)$	1.1×10^{-12}
Silver iodide	$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$	8.5×10^{-17}
Strontium carbonate	$SrCO_3(s) \rightleftharpoons Sr^{2+}(aq) + CO_3^{2-}(aq)$	1.1×10^{-10}
Strontium sulfate	$SrSO_4(s) \rightleftharpoons Sr^{2+}(aq) + SO_4^{2-}(aq)$	3.2×10^{-7}

[a] A more extensive listing of K_{sp} values is given in Appendix D.

4. Side Reaction and Conditional Solubility Product Constant (K'_{sp})



$$MA(s) \rightleftharpoons M + A$$

OH

L

H

$M(OH)$

$M(OH)_2$

…

$M(OH)_n$

MA

MA_2

…

MA_n

HA

H_2A

…

H_nA

For the total concentration of M in the solution:

$$[M'] = [M] + [M(OH)] + [M(OH)_2] + \cdots [M(OH)_n]$$

$$+ [ML] + [ML_2] + \cdots [ML_n]$$

For the total concentration of A in the solution:

$$[A'] = [A] + [HA] + [H_2A] + \cdots$$

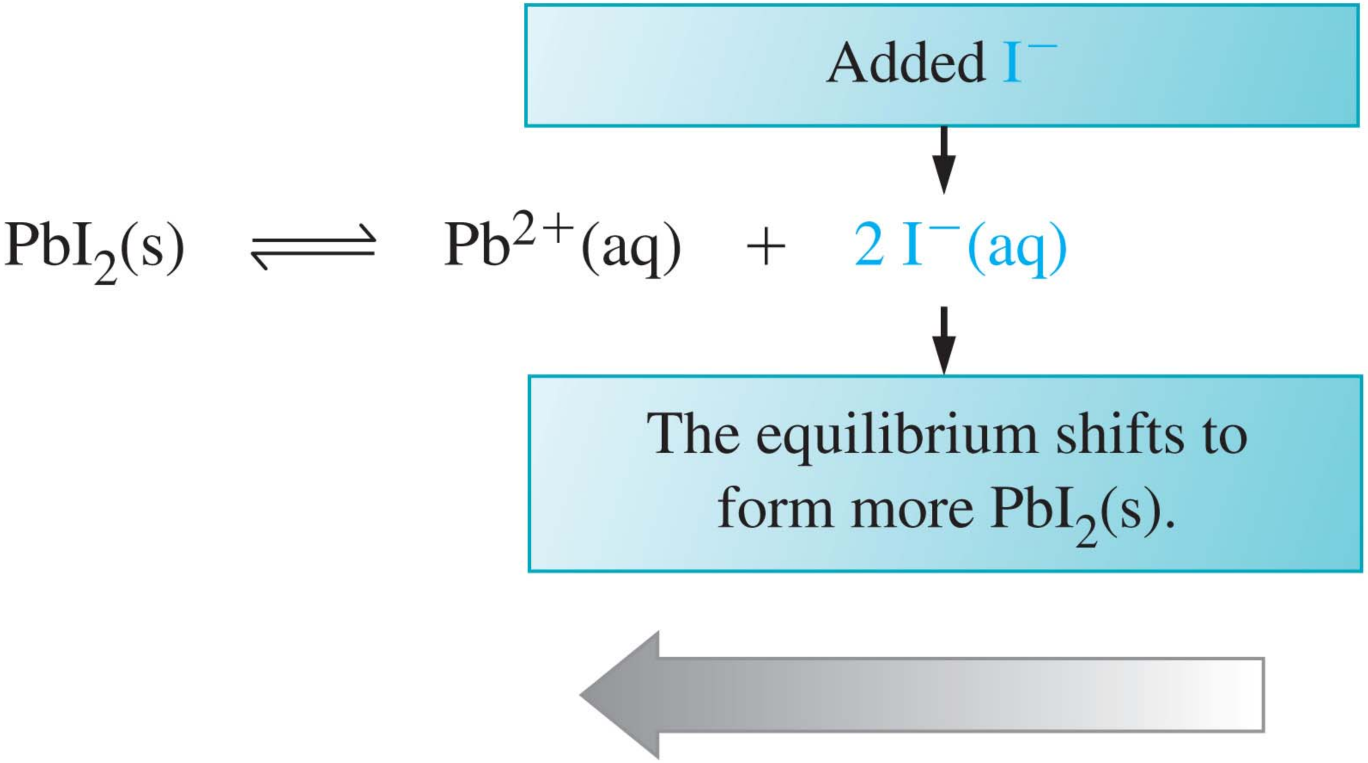
$$K_{sp} = [M][A] = \frac{[M'][A']}{\alpha(M)\alpha(A)}$$

Given $K'_{sp} = [M'][A'] \longrightarrow$ **Conditional Solubility Product**

$$K'_{sp} = K_{sp}\alpha(M)\alpha(A) = \frac{K^{\circ}_{sp}}{\gamma(M)\gamma(A)}\alpha(M)\alpha(A)$$

8.2 Factors Affecting the Precipitation Equilibrium

1. **Common Ion Effect：** **Adding a common ion to a saturated solution of a salt will always lower the salt solubility.**



Added I^-

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,I^-(aq)$$

The equilibrium shifts to form more $PbI_2(s)$.

Note

- **The solubility of a salt will always be reduced by the presence of a common ion, in accordance with Le Chatelier's principle.**
- **We made the approximation that the amount of common ion added to the solution was very large in comparison with the amount of that ion coming from the insoluble salt, which allowed us to simplify our calculation.**

EXAMPLE 18-4

Calculating the Solubility of a Slightly Soluble Solute in the Presence of a Common Ion. What is the molar solubility of PbI_2 in 0.10 M KI(aq)?

Solution

To solve this problem, let's set up an ICE table with s instead of x to represent changes in concentrations. Think of producing a saturated solution of PbI_2, but instead of using pure water as the solvent, we will use 0.10 M KI(aq). Thus, we begin with $[I^-] = 0.10$ M. Now let s represent the amount of PbI_2, in moles, that dissolves to produce 1 L of saturated solution. The additional concentrations appearing in this solution are s mol Pb^{2+}/L and $2s$ mol I^-/L.

$$\mathbf{PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,I^-(aq)}$$

initial concns, M:		0.10
from PbI_2, M:	s	$2s$
equil concns, M:	s	$(0.10 + 2s)$

The usual K_{sp} relationship must be satisfied.

$$K_{sp} = [Pb^{2+}][I^-]^2 = (s)(0.10 + 2s)^2 = 7.1 \times 10^{-9}$$

To simplify the solution to this equation, let's assume that s is much smaller than 0.10 M, so that $0.10 + 2s \approx 0.10$.

$$s(0.10)^2 = 7.1 \times 10^{-9}$$

$$s = \frac{7.1 \times 10^{-9}}{(0.10)^2} = 7.1 \times 10^{-7}\ \text{M}$$

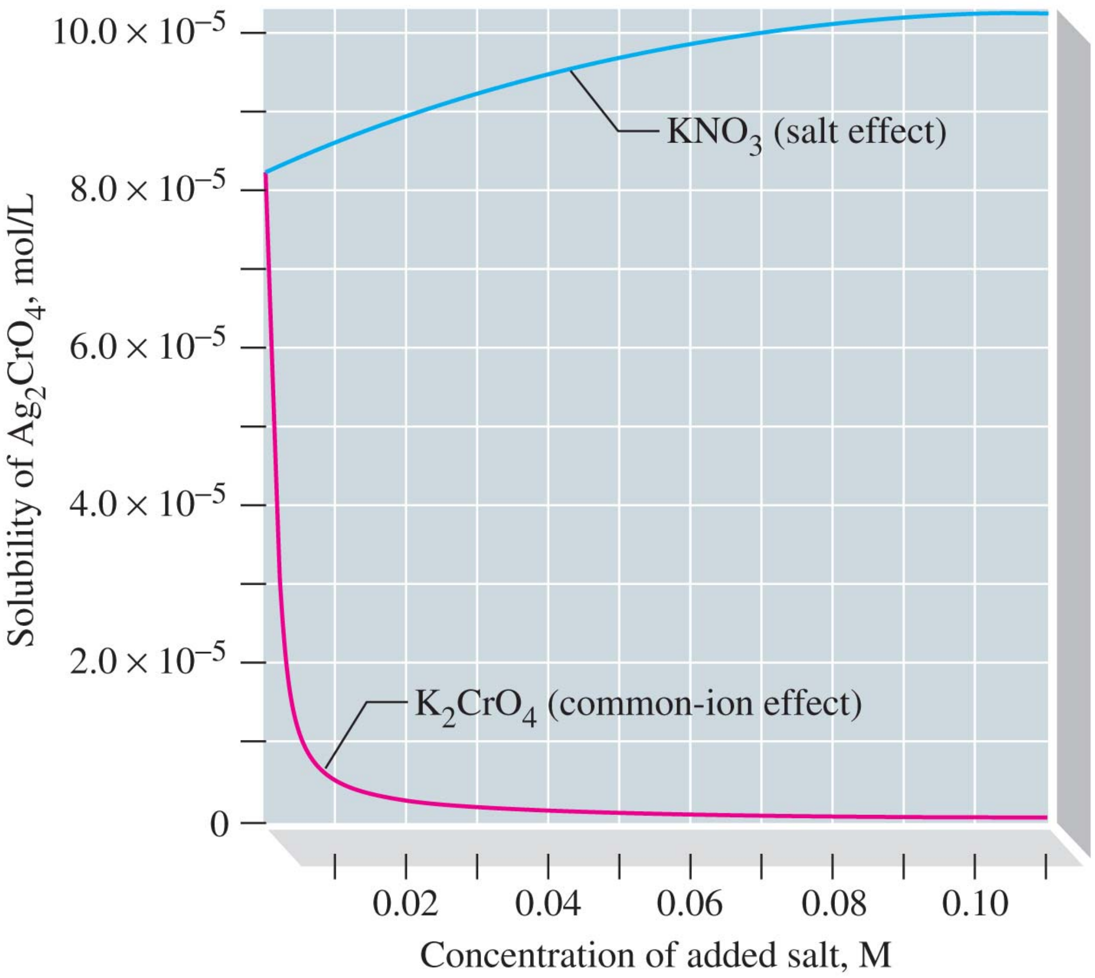
Our assumption is well justified: 7.1×10^{-7} is much smaller than 0.10, and

$$s = \text{molar solubility of } PbI_2 = 7.1 \times 10^{-7}\ \text{M}$$

2. **Salt Effect:** Adding some strong electrolyte (KNO_3、$NaNO_3$) , neither reacting with the precipitate nor having common ions, to a saturated solution of a precipitate will always increase the solubility. The reason of the salt effect is the change of activity coefficient.

$$\left(\mathrm{I} = \frac{1}{2}\sum m_i z_i^2 \rightarrow \lg\gamma_i = -\mathrm{A}z_i^2\sqrt{\mathrm{I}} \rightarrow K_{\mathrm{sp}} = K^{\circ}_{\mathrm{sp}}\frac{m^{\mathrm{o}}m^{\mathrm{o}}}{\gamma_+\gamma_-} \right)$$

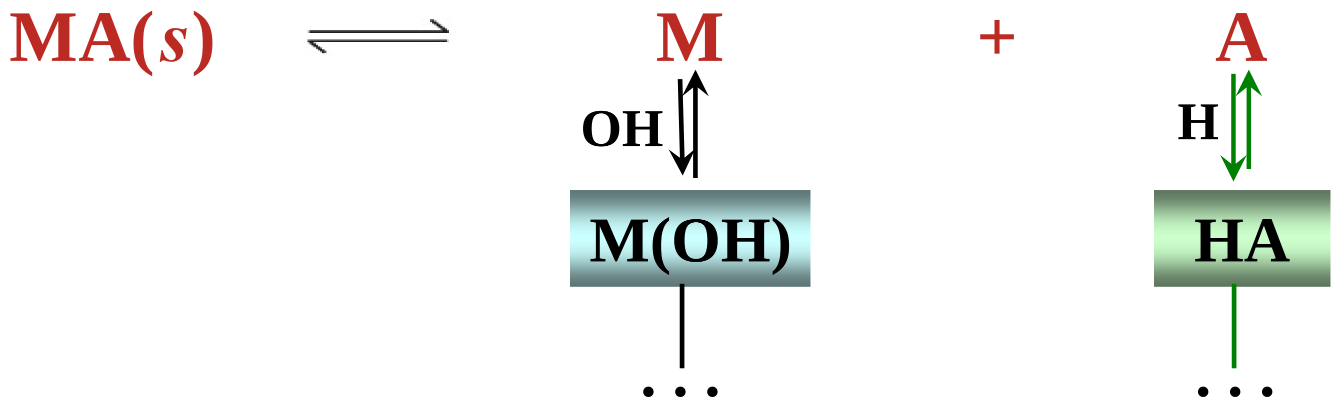
Effects on the Solubility of Ag_2CrO_4



Comparison of the common-ion effect and the salt effect on the molar solubility of Ag_2CrO_4

The presence of CrO_4^{2-} ions, derived from $K_2CrO_4(aq)$ reduces the solubility of Ag_2CrO_4 by a factor of about 35 over the concentration range shown (from 0 to 0.10 M added salt). Over the same concentration range, the solubility of Ag_2CrO_4 is increased by the presence of the uncommon, or diverse, ions from KNO_3, but only by about 25%.

3. **Acid Effect:** **If the cation of a substance is a weak acid or the anion is a weak base, the solubility of the substance will be affected by the pH of the solution.**



$MA(s) \rightleftharpoons M + A$

$M \overset{OH}{\rightleftharpoons} M(OH)$ …

$A \overset{H}{\rightleftharpoons} HA$ …

- **Any salt containing an anion that is the conjugate base of a weak acid will dissolve in water to a greater extent than given by K_{sp}.**

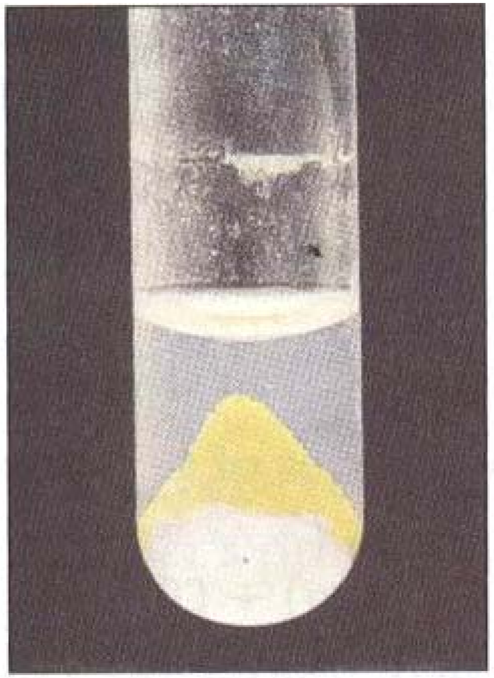
$$\mathbf{PbS(s) \rightleftharpoons Pb^{2+}(aq) + S^{2-}(aq)}$$

$$\mathbf{S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^{-}(aq) + OH^{-}(aq)}$$

$$[Pb^{2+}] = [S^{2-\prime}] = s$$

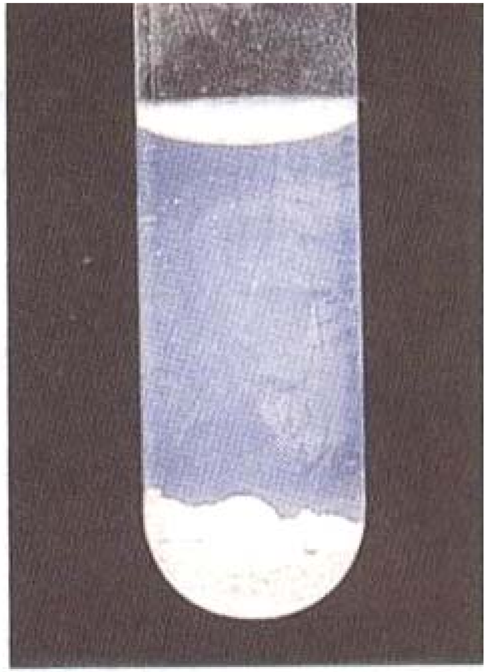
Note

- **In general, the solubility of salt containing the conjugate base of a weak acid is increased by addition of a stronger acid to the solution. In contrast, salts are not soluble in strong acid if the anion is the conjugate base of a strong acid.**



Precipitate of
AgCl and Ag_3PO_4

$\xrightarrow{\text{Add strong acid}}$



Precipitate of
AgCl

4. Coordination effect： **The presence of complexing agents that can combine with either cation or anion of a slightly soluble substance will lead to an increase in its solubility.**

Main reaction : $\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^{+} + Cl^{-}}$ $K_{sp} = 1.8\times10^{-11}$

Complexation reaction : $\mathrm{Ag^{+} + 2NH_3 \rightleftharpoons Ag(NH_3)_2^{+}}$

$$K_{sp} = \frac{[\mathrm{Ag(NH_3)_2}]^{+}}{[\mathrm{Ag^{+}}][\mathrm{NH_3}]^{2}} = 1.6\times10^{7}$$

$$[\mathrm{Ag'}] = [\mathrm{Cl^{-}}] = s$$

TABLE 18.2 Formation Constants for Some Complex Ions[a]

Complex Ion	Equilibrium Reaction[b]	K_f
$[Co(NH_3)_6]^{3+}$	$Co^{3+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$	4.5×10^{33}
$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	1.1×10^{13}
$[Fe(CN)_6]^{4-}$	$Fe^{2+} + 6\,CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$	1×10^{37}
$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6\,CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1×10^{42}
$[PbCl_3]^-$	$Pb^{2+} + 3\,Cl^- \rightleftharpoons [PbCl_3]^-$	2.4×10^{1}
$[Ag(NH_3)_2]^+$	$Ag^+ + 2\,NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.6×10^{7}
$[Ag(CN)_2]^-$	$Ag^+ + 2\,CN^- \rightleftharpoons [Ag(CN)_2]^-$	5.6×10^{18}
$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2\,S_2O_3{}^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	1.7×10^{13}
$[Zn(NH_3)_4]^{2+}$	$Zn^{2+} + 4\,NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$	4.1×10^{8}
$[Zn(CN)_4]^{2-}$	$Zn^{2+} + 4\,CN^- \rightleftharpoons [Zn(CN)_4]^{2-}$	1×10^{18}
$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4\,OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	4.6×10^{17}

[a] A more extensive tabulation is given in Appendix D.

[b] Tabulated here are *overall* formation reactions and the corresponding *overall* formation constants. In Section 25-7, we describe the formation of complex ions in a *stepwise* fashion and introduce formation constants for individual steps.

5. Other Effects

- **Temperature effect;**
- **Solvent effect;**
- **The effect of the size of the precipitate;**
- **The effect of forming colloid solution;**
- **The effect of form of the precipitate.**

EXAMPLE 18-6

Assessing the Completeness of a Precipitation Reaction. The first step in a commercial process in which magnesium is obtained from seawater involves precipitating Mg^{2+} as $Mg(OH)_2(s)$. The magnesium ion concentration in seawater is about 0.059 M. If a seawater sample is treated so that its $[OH^-]$ is maintained at 2.0×10^{-3} M, **(a)** what will be $[Mg^{2+}]$ remaining in solution when precipitation stops ($K_{sp} = 1.8 \times 10^{-11}$)? **(b)** Is the precipitation of $Mg(OH)_2(s)$ complete under these conditions?

◀ One method of maintaining a constant pH during a precipitation is to carry out the precipitation from a buffer solution.

Solution

(a) There is no question that precipitation will occur, because the ion product $Q_{sp} = [Mg^{2+}][OH^-]^2 = (0.059)(2.0 \times 10^{-3})^2 = 2.4 \times 10^{-7}$ exceeds K_{sp}. Precipitation of $Mg(OH)_2(s)$ will continue as long as the ion product exceeds K_{sp}, but will stop when that product is equal to K_{sp}. At the point at which the ion product equals K_{sp}, whatever $[Mg^{2+}]$ is in solution remains in solution.

$$[Mg^{2+}][OH^-]^2 = [Mg^{2+}](2.0 \times 10^{-3})^2 = 1.8 \times 10^{-11} = K_{sp}$$

$$[Mg^{2+}]_{remaining} = \frac{1.8 \times 10^{-11}}{(2.0 \times 10^{-3})^2} = 4.5 \times 10^{-6}\ M$$

(b) $[Mg^{2+}]$ in seawater is reduced from 0.059 M to 4.5×10^{-6} M as a result of the precipitation reaction. Expressed as a percentage,

$$\%[Mg^{2+}]_{remaining} = \frac{4.5 \times 10^{-6}\ M}{0.059\ M} \times 100\% = 0.0076\%$$

Because less than 0.1% of the Mg^{2+} remains, we conclude that precipitation is essentially complete.

Practice Example A: A typical Ca^{2+} concentration in seawater is 0.010 M. Will the precipitation of $Ca(OH)_2$ be complete from a seawater sample in which $[OH^-]$ is maintained at 0.040 M?

8.3 Fractional Precipitation

- A technique in which two or more ions in solution are separated by the proper use of one reagent that can cause precipitation of both ions.
- Significant differences in solubility's are necessary.
- Key to the technique is slow addition of the reagent.

8.3 Fractional Precipitate (continued)

Example: **A solution containing 0.01 mol/L of I^- and 0.01 mol/L of Cl^- was added with $AgNO_3$ solution, which precipitate will form first?**

The concentration of **Ag^+** ***when*** **AgCl** ***begins to precipitate:***

$$[Ag^+] = \frac{K_{sp}(AgCl)}{c(Cl^-)} = \frac{1.8\times10^{-10}}{0.01} = 1.8\times10^{-8}(mol/L)$$

The concentration of **Ag^+** ***when*** **AgI** ***begins to precipitate:***

$$[Ag^+] = \frac{K_{sp}(AgI)}{c(I^-)} = \frac{9.3\times10^{-17}}{0.01} = 9.3\times10^{-15}(mol/L)$$

8.4 Transformation of the Precipitate

$$\mathrm{CaSO_4(s)} \rightleftharpoons \mathrm{Ca^{2+}(aq)} + \mathrm{SO_4^{2-}(aq)}$$

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

$$\mathrm{CaSO_4(s)} + \mathrm{CO_3^{2-}(aq)} \rightleftharpoons \mathrm{CaCO_3(s)} + \mathrm{SO_4^{2-}(aq)}$$

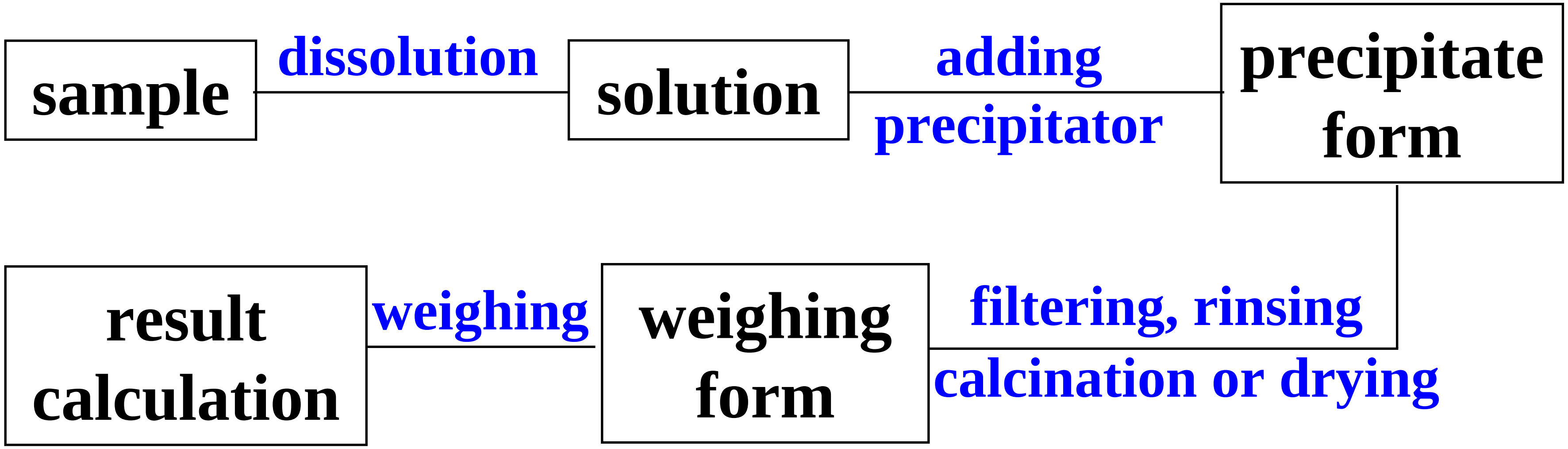
Transformation Reaction

Equilibrium Constant of Transformation Reaction:

$$K = \frac{[\mathrm{SO_4^{2-}}]}{[\mathrm{CO_3^{2-}}]} = \frac{[\mathrm{SO_4^{2-}}][\mathrm{Ca^{2+}}]}{[\mathrm{CO_3^{2-}}][\mathrm{Ca^{2+}}]} = \frac{K_{\mathrm{sp}}(\mathrm{CaSO_4})}{K_{\mathrm{sp}}(\mathrm{CaCO_3})} = \frac{9.1\times10^{-6}}{2.8\times10^{-9}} = 3.3\times10^{3}$$

8.5 Gravimetry (重量测定)

- In gravimetry, or gravimetric analysis as it is sometimes called, the analyte is converted to an insoluble substance (precipitate) which is *isolated* and *weighed*.



sample

dissolution

solution

adding precipitator

precipitate form

filtering, rinsing calcination or drying

weighing form

weighing

result calculation

Requirements for Precipitate

- **For Precipitate Form:**

1. **Highly insoluble;**
2. **Pure；**
3. **Easy to filter and rinse (清洗);**
4. **Easy to change to weighing form.**

- **For weighing form:**

1. **Invariable (恒定的) chemical composition;**
2. **Stable property;**
3. **Large molar mass.**

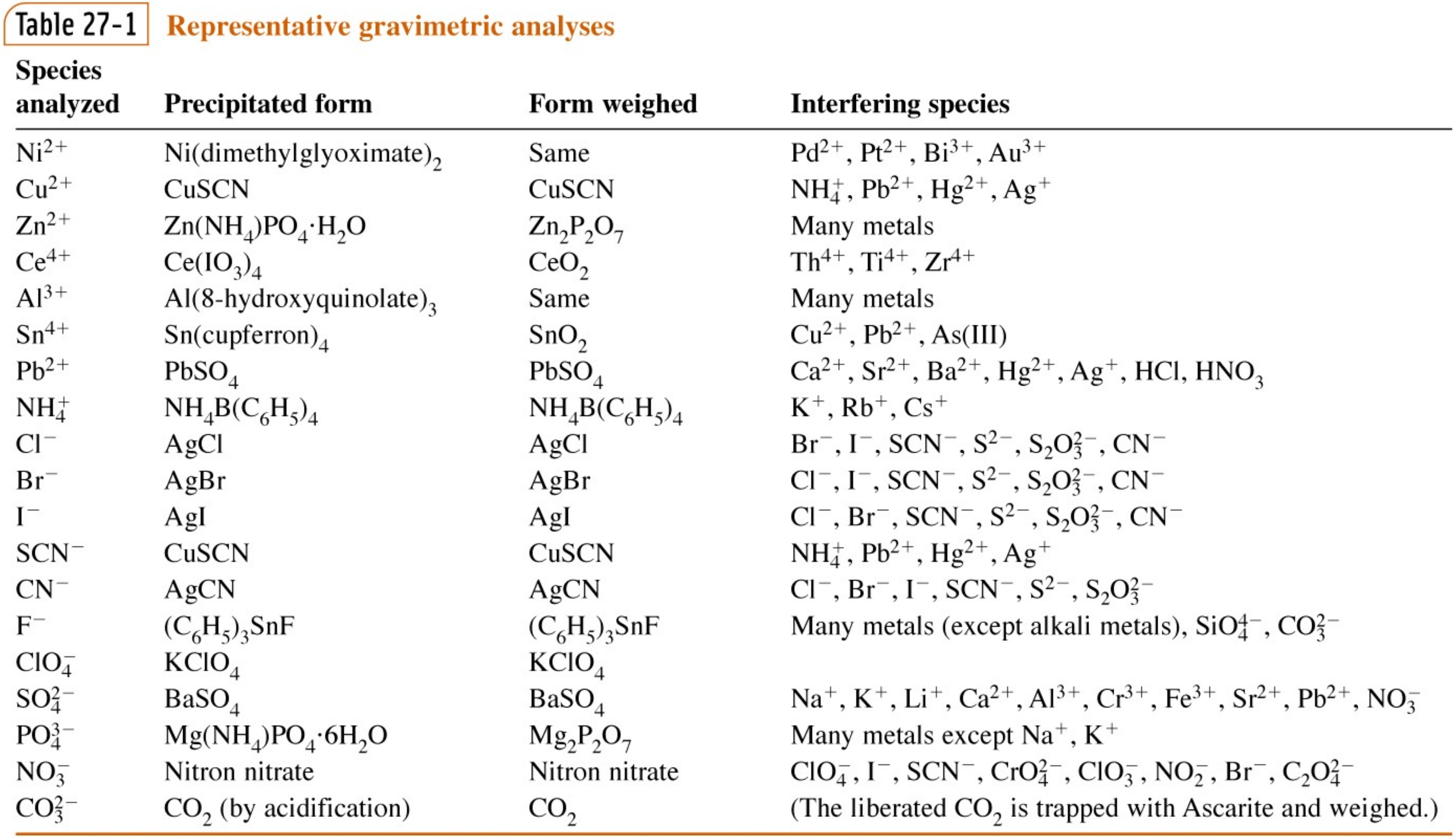


Table 27-1 Representative gravimetric analyses

Species analyzed	Precipitated form	Form weighed	Interfering species
Ni^{2+}	$Ni(dimethylglyoximate)_2$	Same	Pd^{2+}, Pt^{2+}, Bi^{3+}, Au^{3+}
Cu^{2+}	$CuSCN$	$CuSCN$	NH_4^+, Pb^{2+}, Hg^{2+}, Ag^+
Zn^{2+}	$Zn(NH_4)PO_4 \cdot H_2O$	$Zn_2P_2O_7$	Many metals
Ce^{4+}	$Ce(IO_3)_4$	CeO_2	Th^{4+}, Ti^{4+}, Zr^{4+}
Al^{3+}	$Al(8\text{-hydroxyquinolate})_3$	Same	Many metals
Sn^{4+}	$Sn(cupferron)_4$	SnO_2	Cu^{2+}, Pb^{2+}, As(III)
Pb^{2+}	$PbSO_4$	$PbSO_4$	Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg^{2+}, Ag^+, HCl, HNO_3
NH_4^+	$NH_4B(C_6H_5)_4$	$NH_4B(C_6H_5)_4$	K^+, Rb^+, Cs^+
Cl^-	$AgCl$	$AgCl$	Br^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
Br^-	$AgBr$	$AgBr$	Cl^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
I^-	AgI	AgI	Cl^-, Br^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
SCN^-	$CuSCN$	$CuSCN$	NH_4^+, Pb^{2+}, Hg^{2+}, Ag^+
CN^-	$AgCN$	$AgCN$	Cl^-, Br^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$
F^-	$(C_6H_5)_3SnF$	$(C_6H_5)_3SnF$	Many metals (except alkali metals), SiO_4^{4-}, CO_3^{2-}
ClO_4^-	$KClO_4$	$KClO_4$	
SO_4^{2-}	$BaSO_4$	$BaSO_4$	Na^+, K^+, Li^+, Ca^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Sr^{2+}, Pb^{2+}, NO_3^-
PO_4^{3-}	$Mg(NH_4)PO_4 \cdot 6H_2O$	$Mg_2P_2O_7$	Many metals except Na^+, K^+
NO_3^-	Nitron nitrate	Nitron nitrate	ClO_4^-, I^-, SCN^-, CrO_4^{2-}, ClO_3^-, NO_2^-, Br^-, $C_2O_4^{2-}$
CO_3^{2-}	CO_2 (by acidification)	CO_2	(The liberated CO_2 is trapped with Ascarite and weighed.)

Calculating the Results

Analyte	weighing form	gravimetric factor F
Ba	$BaSO_4$	$M(Ba)/M(BaSO_4)$
MgO	$Mg_2P_2O_7$	$2M(MgO)/M(Mg_2P_2O_7)$
Fe_3O_4	Fe_2O_3	$2M(Fe_3O_4)/M(Fe_2O_3)$
NH_3	Pt	$2M(NH_3)/M(Pt)$

8.6 Precipitation Titration

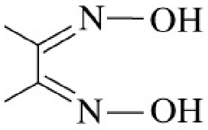
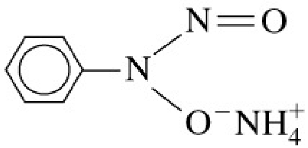
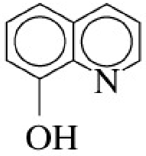
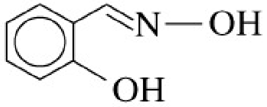
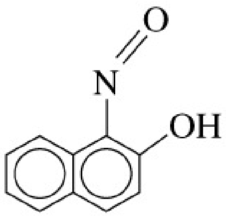
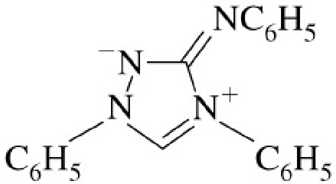
Silver method

- **Mohr's method** — **K_2CrO_4 indicator**
  莫尔法
- **Volhard method** — **$NH_4Fe(SO_4)_2$ indicator**
  伏哈德法
- **Fajans method** — **Adsorption indicator**
  法杨司法

8.7 Organic precipitating agent

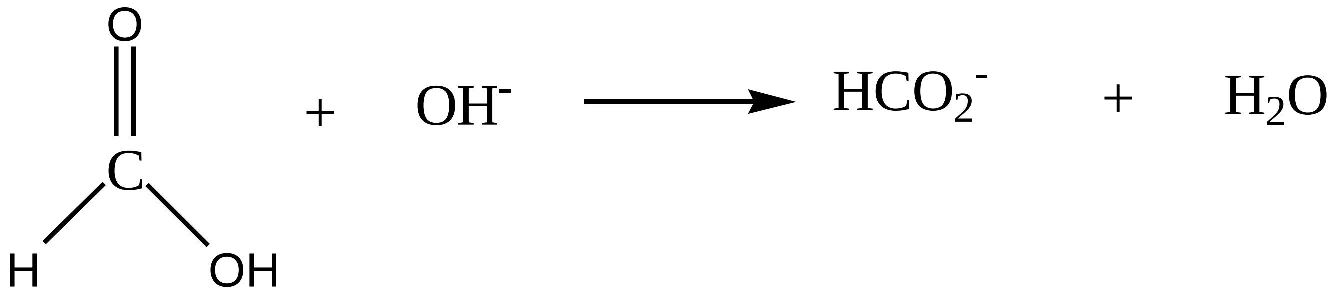
- **High selectivity**
- **Low solubility of the precipitation**
- **The adsorption capacity of the precipitation to inorganic impurities is very small, and easy to obtain the pure precipitation.**
- **Large molar mass.**
- **The composition of sedimentation is constant, the precipitation can be weighed by the drying**

Table 27-2 Common organic precipitating agents

Name	Structure	Ions precipitated
Dimethylglyoxime 丁二酮肟		Ni^{2+}, Pd^{2+}, Pt^{2+}
Cupferron 铜铁试剂		Fe^{3+}, VO_2^+, Ti^{4+}, Zr^{4+}, Ce^{4+}, Ga^{3+}, Sn^{4+}
8-Hydroxyquinoline (oxine) 8-羟基喹啉		Mg^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+}, Bi^{3+}, Ga^{3+}, Th^{4+}, Zr^{4+}, UO_2^{2+}, TiO^{2+}
Salicylaldoxime 水杨醛肟		Cu^{2+}, Pb^{2+}, Bi^{3+}, Zn^{2+}, Ni^{2+}, Pd^{2+}
1-Nitroso-2-naphthol 1-亚硝基2-萘酚		Co^{2+}, Fe^{3+}, Pd^{2+}, Zr^{4+}
Nitron 硝酸灵		NO_3^-, ClO_4^-, BF_4^-, WO_4^{2-}
Sodium tetraphenylborate	$Na^+B(C_6H_5)_4^-$	K^+, Rb^+, Cs^+, NH_4^+, Ag^+, organic ammonium ions
Tetraphenylarsonium chloride	$(C_6H_5)_4As^+Cl^-$	$Cr_2O_7^{2-}$, MnO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}, ClO_4^-, I_3^-

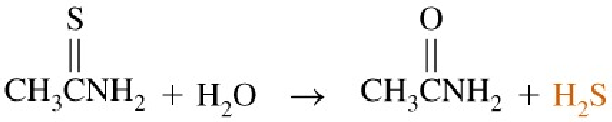
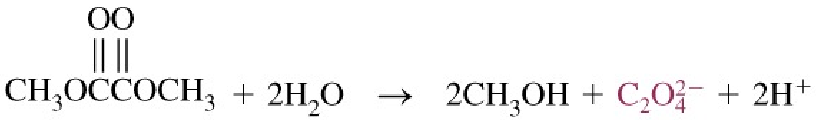
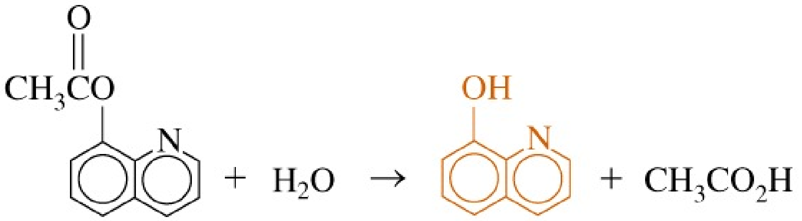
8.8 Homogeneous precipitation

- **In homogeneous precipitation, the precipitant is generated slowly by a chemical reaction. For example, urea decomposes in boiling water to produce OH^-.**
- **By this means, the pH of a solution can be raised very gradually. Slow OH^- formation enhances the particle size of Fe(III) formate precipitate:**



$$HCO_2^- + Fe^{3+} \longrightarrow Fe(HCO_2)_3\ nH_2O$$

Table 27-3 **Common reagents used for homogeneous precipitation**

Precipitant	Reagent	Reaction	Some elements precipitated
OH^-	Urea 尿素	$(H_2N)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$	Al, Ga, Th, Bi, Fe, Sn
OH^-	Potassium cyanate 氰酸钾	$HOCN + 2H_2O \rightarrow NH_4^+ + CO_2 + OH^-$ Hydrogen cyanate	Cr, Fe
S^{2-}	Thioacetamide[a] 硫代乙酰胺	 $CH_3\overset{\overset{S}{\|}}{C}NH_2 + H_2O \rightarrow CH_3\overset{\overset{O}{\|}}{C}NH_2 + H_2S$	Sb, Mo, Cu, Cd
SO_4^{2-}	氨基磺酸 Sulfamic acid	$H_3\overset{+}{N}SO_3^- + H_2O \rightarrow NH_4^+ + SO_4^{2-} + H^+$	Ba, Ca, Sr, Pb
$C_2O_4^{2-}$	草酸(二)甲酯 Dimethyl oxalate	 $CH_3O\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}OCH_3 + 2H_2O \rightarrow 2CH_3OH + C_2O_4^{2-} + 2H^+$	Ca, Mg, Zn
PO_4^{3-}	Trimethyl phosphate 磷酸三甲酯	$(CH_3O)_3P{=}O + 3H_2O \rightarrow 3CH_3OH + PO_4^{3-} + 3H^+$	Zr, Hf
CrO_4^{2-}	Chromic ion plus bromate	$2Cr^{3+} + BrO_3^- + 5H_2O \rightarrow 2CrO_4^{2-} + Br^- + 10H^+$	Pb
8-Hydroxyquinoline	8-Acetoxyquinoline 乙酸基喹啉		Al, U, Mg, Zn

a. Hydrogen sulfide is volatile and toxic; it should be handled only in a well-vented hood. Thioacetamide is a carcinogen that should be handled with gloves. If thioacetamide contacts your skin, wash yourself thoroughly immediately. Leftover reagent is destroyed by heating at 50°C with 5 mol of NaOCl per mole of thioacetamide, and then washing down the drain. [H. Elo, *J. Chem. Ed.* **1987**, *64*, A144.]

EXAMPLE 18-8

Determining Whether a Precipitate Will Form in a Solution in Which There Is Also an Ionization Equilibrium. Should $Mg(OH)_2(s)$ precipitate from a solution that is 0.010 M $MgCl_2$ and also 0.10 M NH_3?

Solution

The key here is in understanding that $[OH^-]$ is established by the ionization of $NH_3(aq)$.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

If we set this up in the usual way, the equilibrium values are $x = [NH_4^+] = [OH^-]$ and $[NH_3] = (0.10 - x) \approx 0.10$. Then we obtain

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x \cdot x}{0.10} = 1.8 \times 10^{-5}$$

$$x^2 = 1.8 \times 10^{-6} \qquad x = [OH^-] = 1.3 \times 10^{-3}\ \text{M}$$

Now we can rephrase the original question: Should $Mg(OH)_2(s)$ precipitate from a solution in which $[Mg^{2+}] = 1.0 \times 10^{-2}$ M and $[OH^-] = 1.3 \times 10^{-3}$ M? We must compare the ion product, Q_{sp}, with K_{sp}.

$$Q_{sp} = [Mg^{2+}][OH^-]^2 = (1.0 \times 10^{-2})(1.3 \times 10^{-3})^2$$

$$= 1.7 \times 10^{-8} > K_{sp} = 1.8 \times 10^{-11}$$

Precipitation should occur.

Practice Example A: Should $Mg(OH)_2(s)$ precipitate from a solution that is 0.010 M $MgCl_2(aq)$ and also 0.10 M $NaC_2H_3O_2$? $K_{sp} = [Mg(OH)_2] = 1.8 \times 10^{-11}$; $K_a(HC_2H_3O_2) = 1.8 \times 10^{-5}$.

[*Hint:* What equilibrium expression establishes $[OH^-]$ in the solution?]

EXAMPLE 18-9

Controlling an Ion Concentration, Either to Cause Precipitation or to Prevent It. What $[NH_4^+]$ must be maintained to prevent precipitation of $Mg(OH)_2(s)$ from a solution that is 0.010 M $MgCl_2$ and 0.10 M NH_3?

Solution

The maximum value of the ion product, Q_{sp}, before precipitation occurs is 1.8×10^{-11}, the value of K_{sp} for $Mg(OH)_2$. This fact allows us to determine the maximum concentration of OH^- that can be tolerated.

$$[Mg^{2+}][OH^-]^2 = (1.0 \times 10^{-2})[OH^-]^2 = 1.8 \times 10^{-11}$$
$$[OH^-]^2 = 1.8 \times 10^{-9}$$
$$[OH^-] = 4.2 \times 10^{-5}\ M$$

Next let's determine what $[NH_4^+]$ must be present in 0.10 M NH_3 to maintain $[OH^-] = 4.2 \times 10^{-5}$ M.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{[NH_4^+](4.2 \times 10^{-5})}{0.10} = 1.8 \times 10^{-5}$$

$$[NH_4^+] = \frac{0.10 \times 1.8 \times 10^{-5}}{4.2 \times 10^{-5}} = 0.043\ M$$

To keep the $[OH^-]$ at 4.2×10^{-5} M *or less*, and thus prevent the precipitation of $Mg(OH)_2(s)$, $[NH_4^+]$ should be maintained at 0.043 M or *greater*.

Practice Example A: What minimum $[NH_4^+]$ must be present to prevent precipitation of $Mn(OH)_2(s)$ from a solution that is 0.0050 M $MnCl_2$ and 0.025 M NH_3? For $Mn(OH)_2$, $K_{sp} = 1.9 \times 10^{-13}$.

EXAMPLE 18-10

Predicting Reactions Involving Complex Ions. Predict what will happen if nitric acid is added to a solution of $[Ag(NH_3)_2]Cl$ in $NH_3(aq)$.

Solution

Nitric acid neutralizes free NH_3 in the solution. Because $HNO_3(aq)$ is a strong acid, we represent it as being completely ionized and write only the net ionic equation.

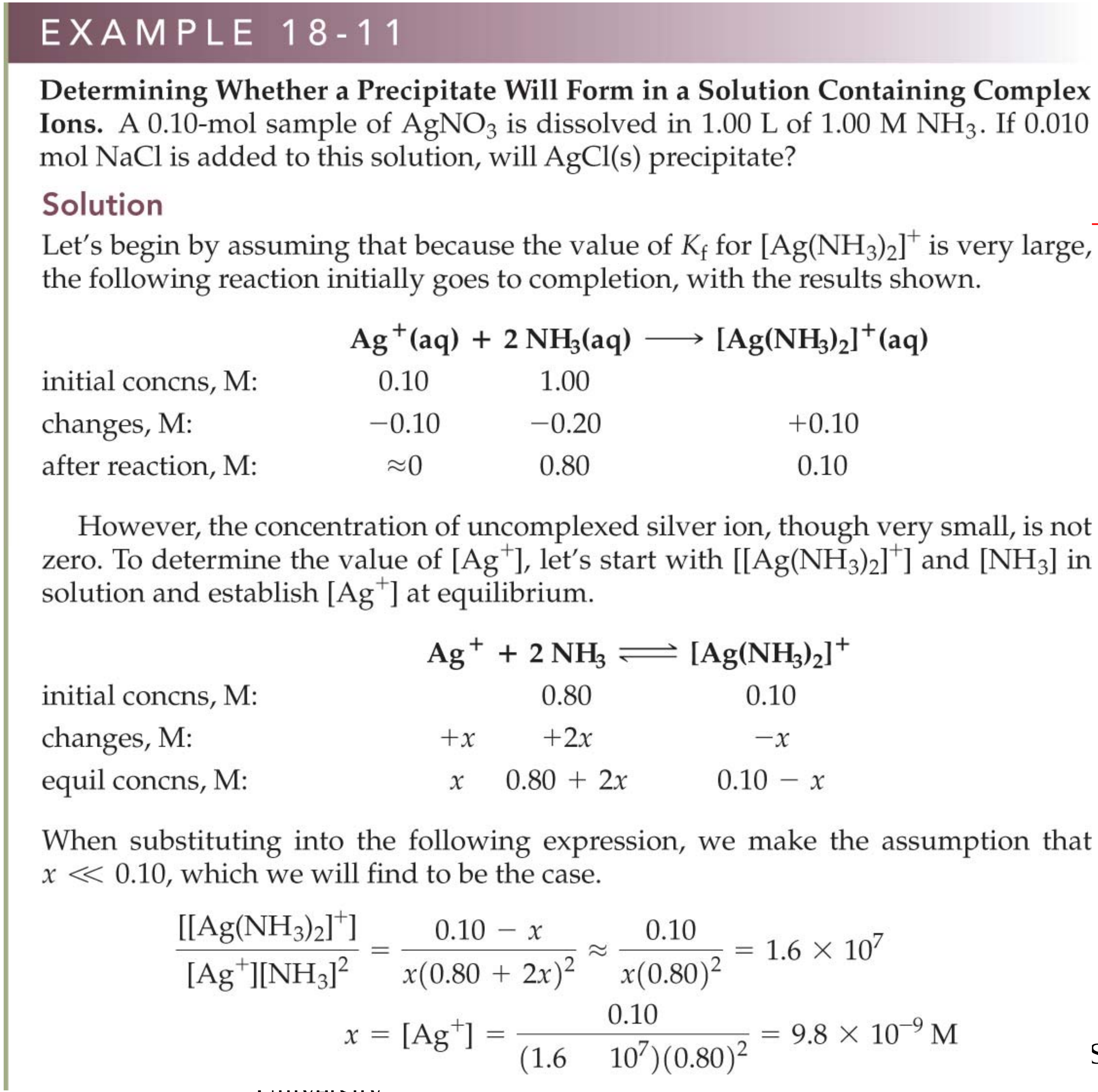
$$H_3O^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq) + H_2O(l)$$

To replace free NH_3 lost in this neutralization, equilibrium in reaction (18.7) shifts to the *left*. As a result, $[Ag^+]$ increases. When $[Ag^+]$ increases to the point at which the ion product $[Ag^+][Cl^-]$ exceeds K_{sp}, AgCl(s) precipitates (Fig. 18-6).

Practice Example A: Copper(II) ion forms both an insoluble hydroxide and the complex ion $[Cu(NH_3)_4]^{2+}$. Write equations to represent the expected reaction when **(a)** $CuSO_4(aq)$ and NaOH(aq) are mixed; **(b)** an excess of $NH_3(aq)$ is added to the product of part (a); and **(c)** an excess of $HNO_3(aq)$ is added to the product of part (b).

Practice Example B: Zinc(II) ion forms both an insoluble hydroxide and the complex ions $[Zn(OH)_4]^{2-}$ and $[Zn(NH_3)_4]^{2+}$. Write four equations to represent the reactions of **(a)** $NH_3(aq)$ with $ZnSO_4(aq)$, followed by **(b)** enough $HNO_3(aq)$ to make the product of part (a) acidic; **(c)** enough NaOH(aq) to make the product of part (b) slightly basic; **(d)** enough NaOH(aq) to make the product of part (c) strongly basic.

▲ **FIGURE 18-6**
Reprecipitating AgCl(s)
The reagent being added to the solution containing $[Ag(NH_3)_2]^+$ and Cl^- is $HNO_3(aq)$. H_3O^+ from the acid reacts with $NH_3(aq)$ to form $NH_4^+(aq)$.
As a result, equilibrium between $[Ag(NH_3)_2]^+$, Ag^+, and NH_3 is upset. The complex ion is destroyed, $[Ag^+]$ quickly rises to the point at which K_{sp} for AgCl is exceeded, and a precipitate forms.



EXAMPLE 18-11

Determining Whether a Precipitate Will Form in a Solution Containing Complex Ions. A 0.10-mol sample of $AgNO_3$ is dissolved in 1.00 L of 1.00 M NH_3. If 0.010 mol NaCl is added to this solution, will AgCl(s) precipitate?

Solution

Let's begin by assuming that because the value of K_f for $[Ag(NH_3)_2]^+$ is very large, the following reaction initially goes to completion, with the results shown.

	$Ag^+(aq)$	$+\ 2\,NH_3(aq)$	$\longrightarrow [Ag(NH_3)_2]^+(aq)$
initial concns, M:	0.10	1.00	
changes, M:	−0.10	−0.20	+0.10
after reaction, M:	≈0	0.80	0.10

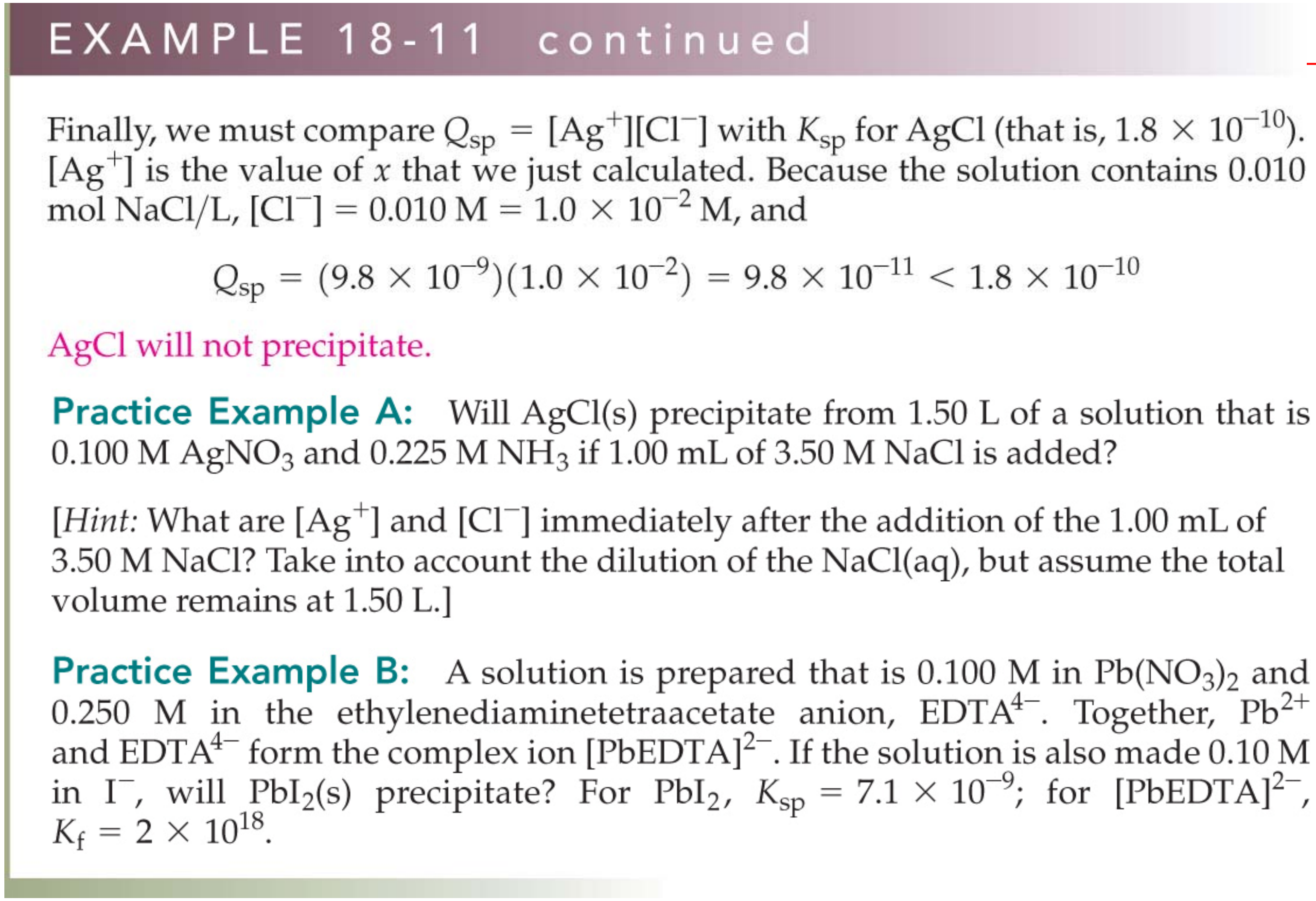
However, the concentration of uncomplexed silver ion, though very small, is not zero. To determine the value of $[Ag^+]$, let's start with $[[Ag(NH_3)_2]^+]$ and $[NH_3]$ in solution and establish $[Ag^+]$ at equilibrium.

	Ag^+	$+\ 2\,NH_3$	$\rightleftharpoons [Ag(NH_3)_2]^+$
initial concns, M:		0.80	0.10
changes, M:	$+x$	$+2x$	$-x$
equil concns, M:	x	$0.80 + 2x$	$0.10 - x$

When substituting into the following expression, we make the assumption that $x \ll 0.10$, which we will find to be the case.

$$\frac{[[Ag(NH_3)_2]^+]}{[Ag^+][NH_3]^2} = \frac{0.10 - x}{x(0.80 + 2x)^2} \approx \frac{0.10}{x(0.80)^2} = 1.6 \times 10^7$$

$$x = [Ag^+] = \frac{0.10}{(1.6 \quad 10^7)(0.80)^2} = 9.8 \times 10^{-9}\ M$$



EXAMPLE 18-11 continued

Finally, we must compare $Q_{sp} = [Ag^+][Cl^-]$ with K_{sp} for AgCl (that is, 1.8×10^{-10}). $[Ag^+]$ is the value of x that we just calculated. Because the solution contains 0.010 mol NaCl/L, $[Cl^-] = 0.010\ M = 1.0 \times 10^{-2}$ M, and

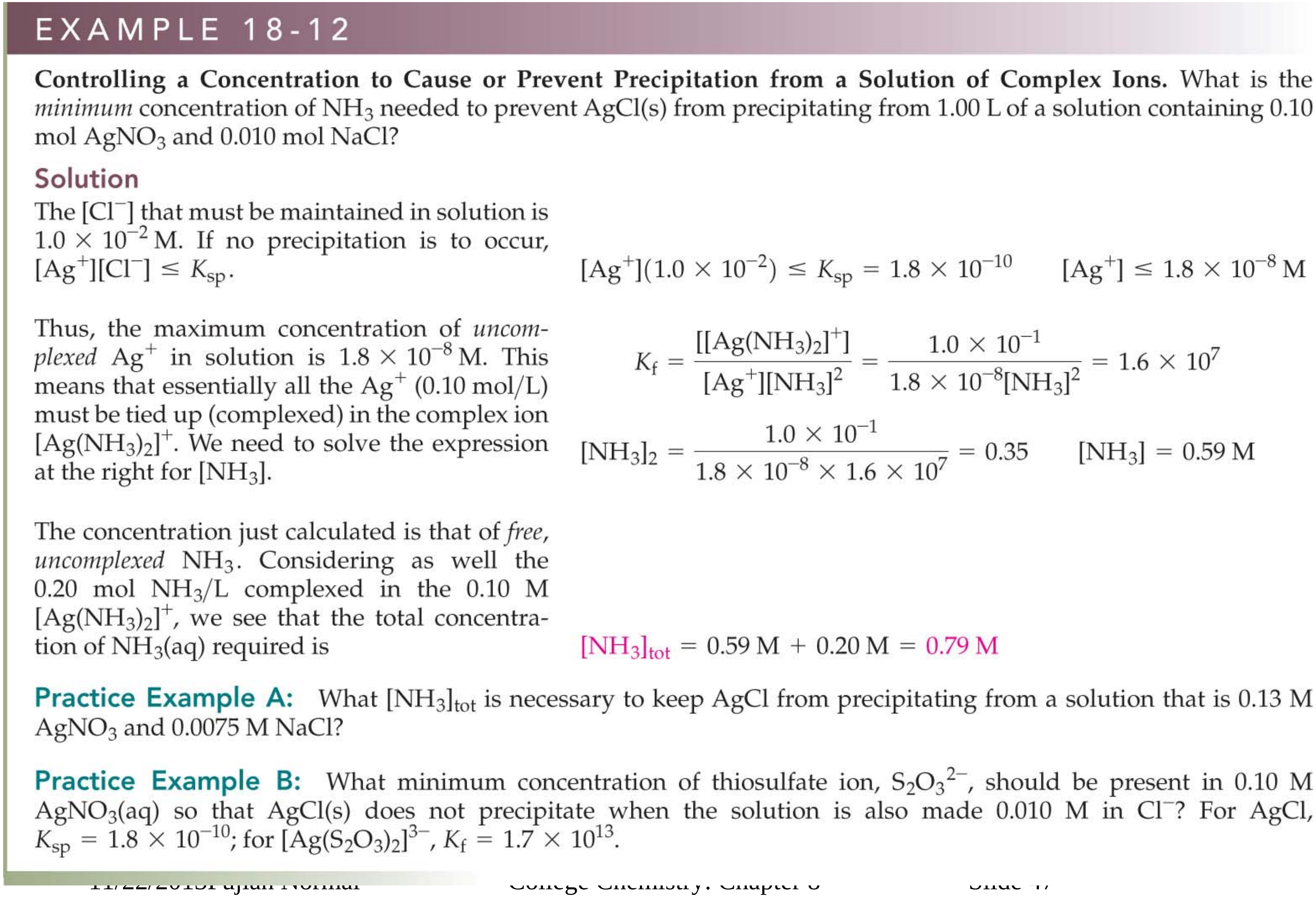
$$Q_{sp} = (9.8 \times 10^{-9})(1.0 \times 10^{-2}) = 9.8 \times 10^{-11} < 1.8 \times 10^{-10}$$

AgCl will not precipitate.

Practice Example A: Will AgCl(s) precipitate from 1.50 L of a solution that is 0.100 M $AgNO_3$ and 0.225 M NH_3 if 1.00 mL of 3.50 M NaCl is added?

[*Hint:* What are $[Ag^+]$ and $[Cl^-]$ immediately after the addition of the 1.00 mL of 3.50 M NaCl? Take into account the dilution of the NaCl(aq), but assume the total volume remains at 1.50 L.]

Practice Example B: A solution is prepared that is 0.100 M in $Pb(NO_3)_2$ and 0.250 M in the ethylenediaminetetraacetate anion, $EDTA^{4-}$. Together, Pb^{2+} and $EDTA^{4-}$ form the complex ion $[PbEDTA]^{2-}$. If the solution is also made 0.10 M in I^-, will $PbI_2(s)$ precipitate? For PbI_2, $K_{sp} = 7.1 \times 10^{-9}$; for $[PbEDTA]^{2-}$, $K_f = 2 \times 10^{18}$.



EXAMPLE 18-12

Controlling a Concentration to Cause or Prevent Precipitation from a Solution of Complex Ions. What is the *minimum* concentration of NH_3 needed to prevent AgCl(s) from precipitating from 1.00 L of a solution containing 0.10 mol $AgNO_3$ and 0.010 mol NaCl?

Solution

The $[Cl^-]$ that must be maintained in solution is 1.0×10^{-2} M. If no precipitation is to occur, $[Ag^+][Cl^-] \le K_{sp}$.

$$[Ag^+](1.0 \times 10^{-2}) \le K_{sp} = 1.8 \times 10^{-10} \qquad [Ag^+] \le 1.8 \times 10^{-8}\ M$$

Thus, the maximum concentration of *uncomplexed* Ag^+ in solution is 1.8×10^{-8} M. This means that essentially all the Ag^+ (0.10 mol/L) must be tied up (complexed) in the complex ion $[Ag(NH_3)_2]^+$. We need to solve the expression at the right for $[NH_3]$.

$$K_f = \frac{[[Ag(NH_3)_2]^+]}{[Ag^+][NH_3]^2} = \frac{1.0 \times 10^{-1}}{1.8 \times 10^{-8}[NH_3]^2} = 1.6 \times 10^7$$

$$[NH_3]_2 = \frac{1.0 \times 10^{-1}}{1.8 \times 10^{-8} \times 1.6 \times 10^7} = 0.35 \qquad [NH_3] = 0.59\ M$$

The concentration just calculated is that of *free, uncomplexed* NH_3. Considering as well the 0.20 mol NH_3/L complexed in the 0.10 M $[Ag(NH_3)_2]^+$, we see that the total concentration of $NH_3(aq)$ required is

$$[NH_3]_{tot} = 0.59\ M + 0.20\ M = 0.79\ M$$

Practice Example A: What $[NH_3]_{tot}$ is necessary to keep AgCl from precipitating from a solution that is 0.13 M $AgNO_3$ and 0.0075 M NaCl?

Practice Example B: What minimum concentration of thiosulfate ion, $S_2O_3^{2-}$, should be present in 0.10 M $AgNO_3(aq)$ so that AgCl(s) does not precipitate when the solution is also made 0.010 M in Cl^-? For AgCl, $K_{sp} = 1.8 \times 10^{-10}$; for $[Ag(S_2O_3)_2]^{3-}$, $K_f = 1.7 \times 10^{13}$.

EXAMPLE 18-13

Determining the Solubility of a Solute When Complex Ions Form. What is the molar solubility of AgCl in 0.100 M $NH_3(aq)$?

Solution

As we have already seen, equation (18.5) describes the solubility equilibrium.

$$AgCl(s) + 2\,NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq) \qquad (18.5)$$

Let's base our calculation on the equilibrium constant K for reaction (18.5). There are two ways to obtain this value. By one method, equation (18.5) is written as the sum of equations (18.6) and (18.7) on page 761. Then its K value is obtained as the product of a K_{sp} and a K_f.

$$\begin{array}{rlr}
AgCl(s) \rightleftharpoons \cancel{Ag^+(aq)} + Cl^-(aq) & & K_{sp} = 1.8 \times 10^{-10} \\
\cancel{Ag^+(aq)} + 2\,NH_3(aq) \rightleftharpoons [Ag(NH_3)_2{}^+](aq) & & K_f = 1.6 \times 10^7 \\
\hline
AgCl(s) + 2\,NH_3(aq) \rightleftharpoons [Ag(NH_3)_2{}^+](aq) + Cl^-(aq) & &
\end{array}$$

$$K = K_{sp} \times K_f = 1.8 \times 10^{-10} \times 1.6 \times 10^7 = 2.9 \times 10^{-3}$$

By a second method, the equilibrium constant expression for reaction (18.5) is written first, and then the numerator and denominator are multiplied by $[Ag^+]$.

$$K = \frac{[Ag(NH_3)_2{}^+][Cl^-]}{[NH_3]^2} = \frac{[Ag(NH_3)_2{}^+][Cl^-][Ag^+]}{[NH_3]^2[Ag^+]} = K_f \times K_{sp} = 2.9 \times 10^{-3}$$

EXAMPLE 18-13 continued

The expression printed in red is K_f for $[Ag(NH_3)_2]^+$; the one in blue is K_{sp} for AgCl. The K value for reaction (18.5) is the product of the two.

According to equation (18.5), if s mol AgCl/L dissolves (the molar solubility), the expected concentrations of $[Ag(NH_3)_2]^+$ and Cl^- are also equal to s.

	$AgCl(s) \; +$	$2\,NH_3(aq) \rightleftharpoons$	$[Ag(NH_3)_2]^+(aq) \; +$	$Cl^-(aq)$
initial concns, M:		0.100		
changes, M:		$-2s$	$+s$	$+s$
equil concns, M:		$(0.100 - 2s)$	s	s

$$K = \frac{[[Ag(NH_3)_2]^+][Cl^-]}{[NH_3]^2} = \frac{s \cdot s}{(0.100 - 2s)^2} = \left(\frac{s}{0.100 - 2s}\right)^2 = 2.9 \times 10^{-3}$$

We can solve this equation by taking the square root of both sides.

$$\frac{s}{0.100 - 2s} = \sqrt{2.9 \times 10^{-3}} = 5.4 \times 10^{-2}$$

$$s = 5.4 \times 10^{-3} - 0.11s$$

$$1.11s = 5.4 \times 10^{-3}$$

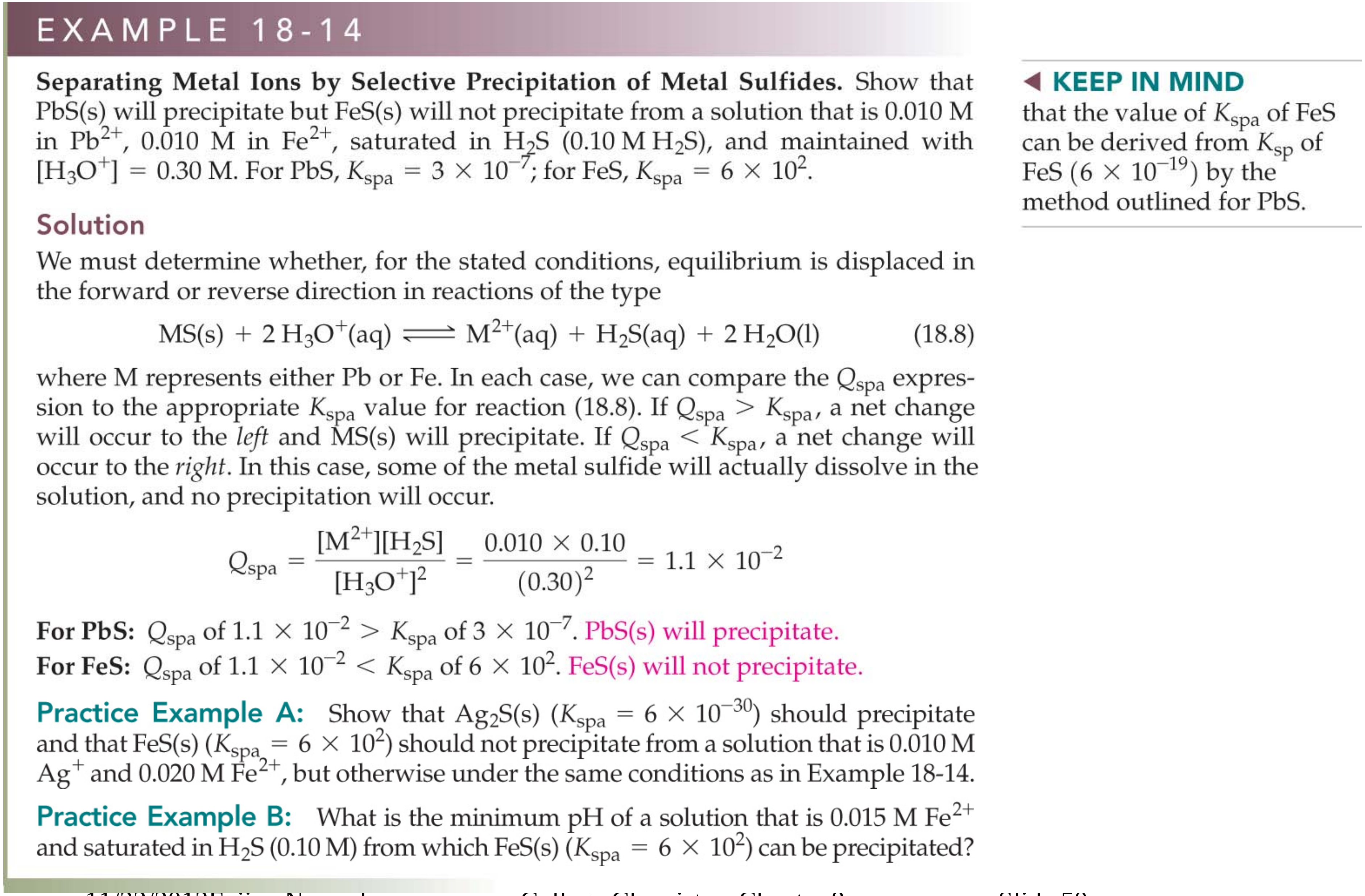
$$s = 4.9 \times 10^{-3}$$

The molar solubility of AgCl(s) in 0.100 M $NH_3(aq)$ is 4.9×10^{-3} M.

NOTE: The usual simplifying assumption, that is, $(0.100 - 2s) \approx 0.100$, would not have worked well in this calculation. The value of s obtained would have been 5.4×10^{-3} M, and $0.100 - (2 \times 0.0054) \neq 0.100$. Also, the molar solubility is actually the *total* concentration of silver in solution: $[Ag^+] + [Ag(NH_3)_2]^+]$. Only when K_f is large and the concentration of complexing agent sufficiently high can we ignore the concentration of uncomplexed metal ion, as was the case here.

Practice Example A: What is the molar solubility of $Fe(OH)_3$ in a solution containing 0.100 M $C_2O_4{}^{2-}$? For $[Fe(C_2O_4)_3]^{3-}$, $K_f = 2 \times 10^{20}$.

Practice Example B: *Without doing detailed calculations*, show that the order of *decreasing* solubility in 0.100 M $NH_3(aq)$ should be AgCl > AgBr > AgI.



EXAMPLE 18-14

Separating Metal Ions by Selective Precipitation of Metal Sulfides. Show that PbS(s) will precipitate but FeS(s) will not precipitate from a solution that is 0.010 M in Pb^{2+}, 0.010 M in Fe^{2+}, saturated in H_2S (0.10 M H_2S), and maintained with $[H_3O^+] = 0.30$ M. For PbS, $K_{spa} = 3 \times 10^{-7}$; for FeS, $K_{spa} = 6 \times 10^2$.

Solution

We must determine whether, for the stated conditions, equilibrium is displaced in the forward or reverse direction in reactions of the type

$$MS(s) + 2\,H_3O^+(aq) \rightleftharpoons M^{2+}(aq) + H_2S(aq) + 2\,H_2O(l) \qquad (18.8)$$

where M represents either Pb or Fe. In each case, we can compare the Q_{spa} expression to the appropriate K_{spa} value for reaction (18.8). If $Q_{spa} > K_{spa}$, a net change will occur to the *left* and MS(s) will precipitate. If $Q_{spa} < K_{spa}$, a net change will occur to the *right*. In this case, some of the metal sulfide will actually dissolve in the solution, and no precipitation will occur.

$$Q_{spa} = \frac{[M^{2+}][H_2S]}{[H_3O^+]^2} = \frac{0.010 \times 0.10}{(0.30)^2} = 1.1 \times 10^{-2}$$

For PbS: Q_{spa} of $1.1 \times 10^{-2} > K_{spa}$ of 3×10^{-7}. PbS(s) will precipitate.

For FeS: Q_{spa} of $1.1 \times 10^{-2} < K_{spa}$ of 6×10^2. FeS(s) will not precipitate.

Practice Example A: Show that $Ag_2S(s)$ ($K_{spa} = 6 \times 10^{-30}$) should precipitate and that FeS(s) ($K_{spa} = 6 \times 10^2$) should not precipitate from a solution that is 0.010 M Ag^+ and 0.020 M Fe^{2+}, but otherwise under the same conditions as in Example 18-14.

Practice Example B: What is the minimum pH of a solution that is 0.015 M Fe^{2+} and saturated in H_2S (0.10 M) from which FeS(s) ($K_{spa} = 6 \times 10^2$) can be precipitated?

◀ **KEEP IN MIND** that the value of K_{spa} of FeS can be derived from K_{sp} of FeS (6×10^{-19}) by the method outlined for PbS.