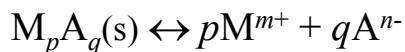


19.3 Equilibria of Slightly Soluble Ionic Compounds

- Slightly soluble ionic solids reach equilibrium with their saturated solutions at very low concentrations of the dissolved solute
- The **dissolved portion** of the ionic solid is assumed to be **completely dissociated to ions** (not always the case)

The Solubility-Product Constant (K_{sp})

- For an ionic solid, M_pA_q , in equilibrium with its saturated solution, the equilibrium constant of the dissolution process is called **solubility-product**



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

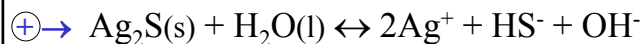
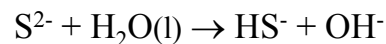
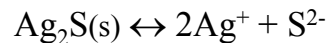
Example: Write the solubility-product expression for $Al(OH)_3$.

→ The subscripts in the formula become powers in the solubility-product expression

$$\Rightarrow K_{sp} = [Al^{3+}][OH^-]^3$$

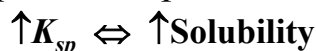
- Sulfides are slightly different since S^{2-} acts as a strong base in water and converts entirely to OH^-

Example: Ag_2S



$$\Rightarrow K_{sp} = [Ag^+]^2[HS^-][OH^-]$$

- K_{sp} is a measure of the extent to which the solubility equilibrium proceeds to the right



- K_{sp} depends on temperature

Calculations Involving K_{sp}

- **Molar solubility (s)** – the molarity of the saturated solution (mol/L)

- The solubility is often expressed in g/L or grams/100 mL of solution → can be easily converted to mol/L

- K_{sp} can be experimentally determined by measuring the molar solubility, s

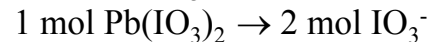
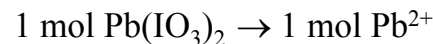
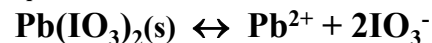
- s can be calculated if K_{sp} is known

Example: The solubility of $Pb(IO_3)_2$ is 0.022 g/L at 25°C. Calculate K_{sp} of $Pb(IO_3)_2$.

→ Convert the solubility to molar solubility, s

$$s = 0.022 \frac{\text{g } Pb(IO_3)_2}{L} \times \frac{1 \text{ mol } Pb(IO_3)_2}{557 \text{ g } Pb(IO_3)_2} = 3.9 \times 10^{-5} \frac{\text{mol}}{L}$$

→ Express K_{sp} through the molar solubility, s



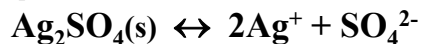
$$\Rightarrow [Pb^{2+}] = s \quad \text{and} \quad [IO_3^-] = 2s$$

$$\Rightarrow K_{sp} = [Pb^{2+}][IO_3^-]^2 = s(2s)^2 = 4s^3$$

$$\Rightarrow K_{sp} = 4 \times (3.9 \times 10^{-5})^3 = \boxed{2.5 \times 10^{-13}}$$

Example: The K_{sp} of Ag_2SO_4 is 1.4×10^{-5} at 24°C . Calculate the molar solubility of Ag_2SO_4 .

→ Express K_{sp} through the molar solubility, s



$$\Rightarrow [\text{Ag}^+] = 2s \quad \text{and} \quad [\text{SO}_4^{2-}] = s$$

$$\Rightarrow K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = (2s)^2s = 4s^3$$

$$\Rightarrow s^3 = K_{sp}/4 \quad \Rightarrow \quad s = (K_{sp}/4)^{1/3}$$

$$\Rightarrow s = (1.4 \times 10^{-5}/4)^{1/3} = \boxed{1.5 \times 10^{-2} \text{ M}}$$

Note: The problem can be solved using an *ice* table:

$$\Rightarrow K_{sp} = (2s)^2s = 4s^3$$

	$\text{Ag}_2\text{SO}_4(\text{s}) \leftrightarrow 2\text{Ag}^+ + \text{SO}_4^{2-}$		
<i>i</i>	<i>excess</i>	0	0
<i>c</i>	-s	+2s	+s
<i>e</i>	<i>excess</i>	2s	s

➤ K_{sp} can be used as a guide in comparing molar solubilities of different ionic compounds (works only if the compounds have the same number of ions in the formula)

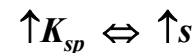


Table 19.3 Relationship Between K_{sp} and Solubility at 25°C

No. of Ions	Formula	Cation:Anion	K_{sp}	Solubility (M)
2	MgCO_3	1:1	3.5×10^{-8}	1.9×10^{-4}
2	PbSO_4	1:1	1.6×10^{-8}	1.3×10^{-4}
2	BaCrO_4	1:1	2.1×10^{-10}	1.4×10^{-5}
3	$\text{Ca}(\text{OH})_2$	1:2	6.5×10^{-6}	1.2×10^{-2}
3	BaF_2	1:2	1.5×10^{-6}	7.2×10^{-3}
3	CaF_2	1:2	3.2×10^{-11}	2.0×10^{-4}
3	Ag_2CrO_4	2:1	2.6×10^{-12}	8.7×10^{-5}

The Common Ion Effect

➤ For a slightly soluble ionic solid, MA



– If M^{n+} is added by means of the soluble salt (MB), the equilibrium shifts to the left toward formation of more MA(s)

– MA and MB have a **common ion** (M^{n+})

– Similarly, if A^{n-} is added to the solution, the equilibrium also shifts to the left toward formation of more MA(s)

⇒ **The molar solubility decreases in the presence of common ions**

Example: At a given temperature, K_{sp} of AgBr is 7.7×10^{-13} . Estimate the solubility of AgBr in:

a) Pure H_2O b) 0.10 M CaBr_2 solution

a) In pure H_2O

→ Express K_{sp} through the molar solubility, s

	$\text{AgBr}(\text{s}) \leftrightarrow \text{Ag}^+ + \text{Br}^-$		
<i>i</i>	<i>excess</i>	0	0
<i>c</i>	-s	+s	+s
<i>e</i>	<i>excess</i>	s	s

$$\Rightarrow [\text{Ag}^+] = s \quad \text{and} \quad [\text{Br}^-] = s$$

$$\Rightarrow K_{sp} = [\text{Ag}^+][\text{Br}^-] = s^2$$

$$\Rightarrow s = (K_{sp})^{1/2} = (7.7 \times 10^{-13})^{1/2} = \boxed{8.8 \times 10^{-7} \text{ M}}$$

b) In 0.10 M CaBr₂ solution

0.10 M CaBr₂ → 0.20 M Br⁻ (Br⁻ is the common ion)

→ Express K_{sp} through the molar solubility, s

	AgBr(s) ↔ Ag ⁺ + Br ⁻		
<i>i</i>	excess	0	0.20
<i>c</i>	- s	+ s	+ s
<i>e</i>	excess	s	0.20 + s

$$\Rightarrow K_{sp} = [\text{Ag}^+][\text{Br}^-] = s(0.20 + s)$$

→ Assume $s \ll 0.20 \Rightarrow K_{sp} = s(0.20)$

$$\Rightarrow s = K_{sp}/0.20 = 7.7 \times 10^{-13}/0.20 = \boxed{3.8 \times 10^{-12} \text{ M}}$$

→ Check assumption → OK

⇒ The solubility is much lower in 0.1 M CaBr₂

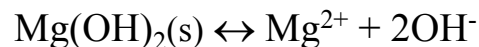
The Effect of pH on Solubility

➤ The solubility of some ionic solids in water is greatly affected by the **pH**

– **Metal hydroxides** (Fe(OH)₃, Mg(OH)₂, ...) – the anion (OH⁻) reacts with added H₃O⁺

⇒ The solubility can be improved by adding acids

Example: Mg(OH)₂



→ If acid (H₃O⁺) is added:

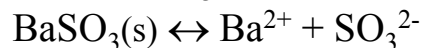
→ H₃O⁺ consumes OH⁻ (H₃O⁺ + OH⁻ → 2H₂O)

→ The equilibrium shifts to the right and the **solubility increases**

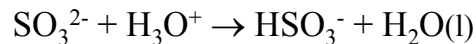
– **Salts of weak acids** (CaCO₃, BaSO₃, PbF₂, ZnS, ...) – the anion of the salt is a weak base which reacts with added H₃O⁺

⇒ The solubility can be improved by adding acids

Example: BaSO₃ (a salt of H₂SO₃)



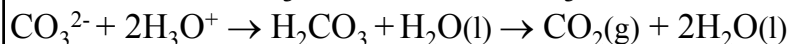
→ If acid (H₃O⁺) is added:



→ H₃O⁺ consumes SO₃²⁻

→ The equilibrium shifts to the right and the **solubility increases**

Example: CaCO₃(s) ↔ Ca²⁺ + CO₃²⁻



Predicting Precipitation – Q_{sp} versus K_{sp}

➤ The reaction quotient of the dissolution process (Q_{sp}) is defined in the same way as K_{sp} and at equilibrium $Q_{sp} = K_{sp}$

➤ To predict precipitation, compare Q_{sp} to K_{sp}

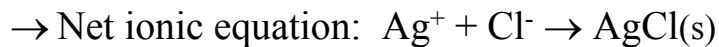
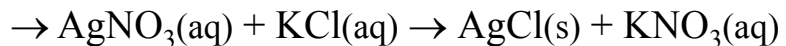
→ If $Q_{sp} > K_{sp}$, precipitation occurs

→ If $Q_{sp} < K_{sp}$, dissolution occurs (no precipitation)

→ If $Q_{sp} = K_{sp}$, no change occurs

Example: Does a precipitate form after mixing of 200. mL 1.0 × 10⁻⁴ M AgNO₃ with 900. mL 1.0 × 10⁻⁶ M KCl?

($K_{sp} = 1.8 \times 10^{-10}$ for AgCl)



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$V_{tot} = 0.200 + 0.900 = 1.100 \text{ L}$$

→ Initial concentrations after mixing:

$$[\text{Ag}^+] = \frac{1.0 \times 10^{-4} \frac{\text{mol}}{\text{L}} \times 0.200 \text{ L}}{1.100 \text{ L}} = 1.8 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

$$[\text{Cl}^-] = \frac{1.0 \times 10^{-6} \frac{\text{mol}}{\text{L}} \times 0.900 \text{ L}}{1.100 \text{ L}} = 8.2 \times 10^{-7} \frac{\text{mol}}{\text{L}}$$

→ Calculate Q_{sp} :

$$Q_{sp} = [\text{Ag}^+][\text{Cl}^-] = (1.8 \times 10^{-5}) \times (8.2 \times 10^{-7})$$

$$Q_{sp} = 1.5 \times 10^{-11}$$

$$K_{sp} = 1.8 \times 10^{-10}$$

$$\Rightarrow Q_{sp} < K_{sp}$$

⇒ No precipitation occurs