

Topic 6I. Solubility Equilibria

- 6I.1 The Solubility Product
- 6I.2 The Common-Ion Effect
- 6I.3 Complex Ion Formation

The Solubility Product

- **Solubility Product** (K_{sp}): the equilibrium constant for the equilibrium between an undissolved salt and its ions in a saturated solution.
- Ex) $\text{Bi}_2\text{S}_3 (\text{s}) \leftrightarrow 2 \text{Bi}^{3+}(\text{aq}) + 3 \text{S}^{2-} (\text{aq})$

$$K_{sp} = (a_{\text{Bi}^{3+}})^2 (a_{\text{S}^{2-}})^3$$

For sparingly soluble salts, $K_{sp} = [\text{Bi}^{3+}] [\text{S}^{2-}]$

- A simple way to determine K_{sp} is to measure the **molar solubility** of the compound, the molar concentration of the compound in a saturated solution.

The Solubility Product

TABLE 6I.1 Solubility Products at 25 °C

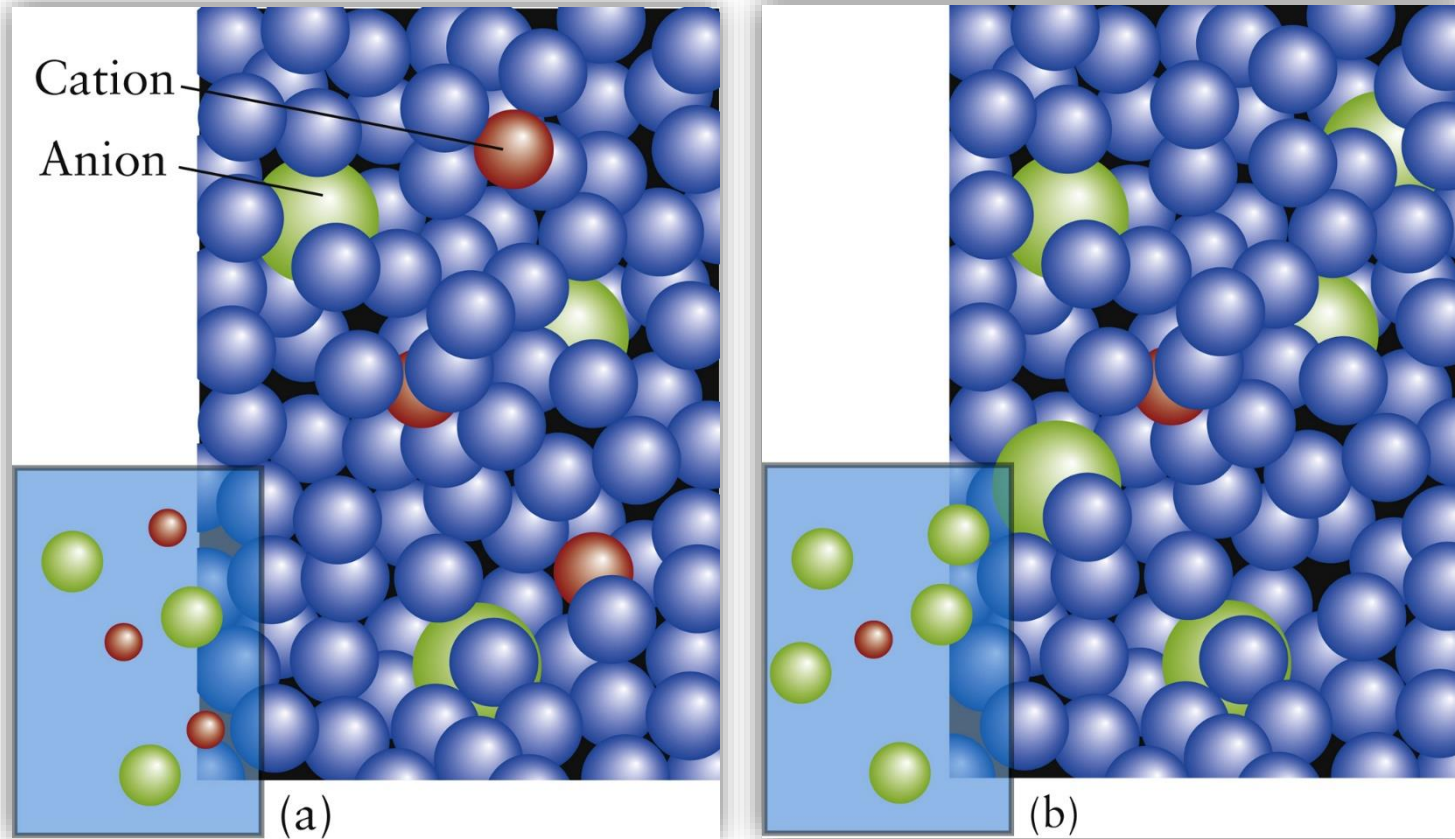
Compound	Formula	K_{sp}	Compound	Formula	K_{sp}
aluminum hydroxide	$\text{Al}(\text{OH})_3$	1.0×10^{-33}	lead(II) fluoride	PbF_2	3.7×10^{-8}
antimony sulfide	Sb_2S_3	1.7×10^{-93}	iodate	$\text{Pb}(\text{IO}_3)_2$	2.6×10^{-13}
barium carbonate	BaCO_3	8.1×10^{-9}	iodide	PbI_2	1.4×10^{-8}
fluoride	BaF_2	1.7×10^{-6}	sulfate	PbSO_4	1.6×10^{-8}
sulfate	BaSO_4	1.1×10^{-10}	sulfide	PbS	8.8×10^{-29}
bismuth sulfide	Bi_2S_3	1.0×10^{-97}	magnesium ammonium phosphate	MgNH_4PO_4	2.5×10^{-13}
calcium carbonate	CaCO_3	8.7×10^{-9}	carbonate	MgCO_3	1.0×10^{-5}
fluoride	CaF_2	4.0×10^{-11}	fluoride	MgF_2	6.4×10^{-9}
hydroxide	$\text{Ca}(\text{OH})_2$	5.5×10^{-6}	hydroxide	$\text{Mg}(\text{OH})_2$	1.1×10^{-11}
sulfate	CaSO_4	2.4×10^{-5}	mercury(I) chloride	Hg_2Cl_2	2.6×10^{-18}
chromium(III) iodate	$\text{Cr}(\text{IO}_3)_3$	5.0×10^{-6}	iodide	Hg_2I_2	1.2×10^{-28}
copper(I) bromide	CuBr	4.2×10^{-8}	mercury(II) sulfide, black	HgS	1.6×10^{-52}
chloride	CuCl	1.0×10^{-6}	sulfide, red	HgS	1.4×10^{-53}
iodide	CuI	5.1×10^{-12}	nickel(II) hydroxide	$\text{Ni}(\text{OH})_2$	6.5×10^{-18}
sulfide	Cu_2S	2.0×10^{-47}	silver bromide	AgBr	7.7×10^{-13}
copper(II) iodate	$\text{Cu}(\text{IO}_3)_2$	1.4×10^{-7}	carbonate	Ag_2CO_3	6.2×10^{-12}
oxalate	CuC_2O_4	2.9×10^{-8}	chloride	AgCl	1.6×10^{-10}
sulfide	CuS	1.3×10^{-36}	hydroxide	AgOH	1.5×10^{-8}
iron(II) hydroxide	$\text{Fe}(\text{OH})_2$	1.6×10^{-14}	iodide	AgI	8×10^{-17}
sulfide	FeS	6.3×10^{-18}	sulfide	Ag_2S	6.3×10^{-51}
iron(III) hydroxide	$\text{Fe}(\text{OH})_3$	2.0×10^{-39}	zinc hydroxide	$\text{Zn}(\text{OH})_2$	2.0×10^{-17}
lead(II) bromide	PbBr_2	7.9×10^{-5}	sulfide	ZnS	1.6×10^{-24}
chloride	PbCl_2	1.6×10^{-5}			

The Common Ion Effect

- **Common ion effect:** the reduction in solubility of a sparingly soluble salt by the addition of a soluble salt that has an ion in common with it.
- Ex) The addition of a solution of Cl^- to a saturated solution of AgCl
- Qualitatively, the Le Chatelier's principle
- Quantitatively, the decrease in cation's concentration.

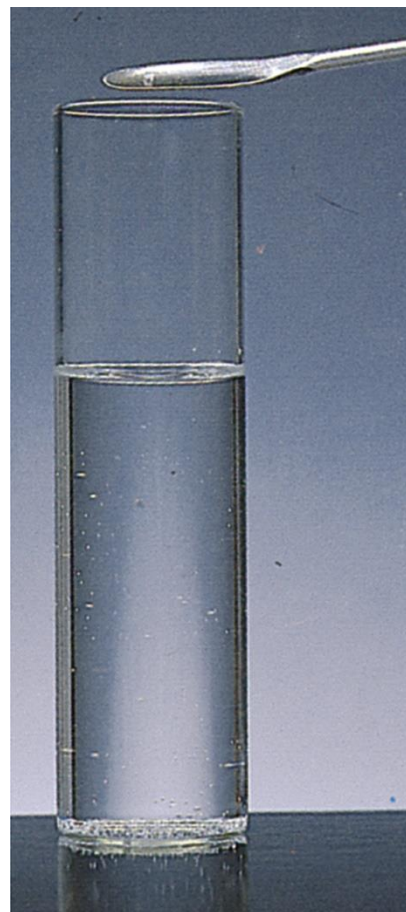
The Common Ion Effect

Before and after the addition of a salt

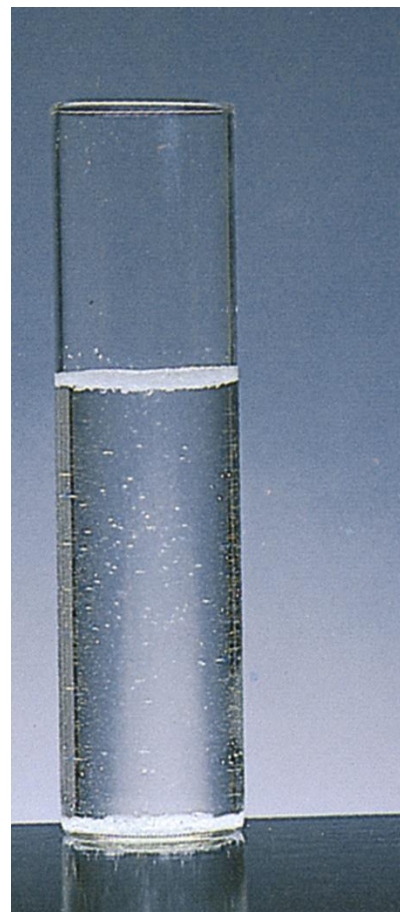


The Common Ion Effect

Zn acetate



Zn acetate +
Na acetate



Complex Ion Formation

- How can we increase the solubility of a salt?
→ Finding a way to conceal the ions in solution, because then the dissolution process continues in a vain attempt to reach equilibrium.
- Ion can be concealed by making use of the fact that many metal cations are Lewis acids. When a Lewis acid and a Lewis base react, they form a **coordination complex**.
- Ex) $\text{AgCl (s)} \leftrightarrow \text{Ag}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$ $K_{\text{sp}} = [\text{Ag}^+] [\text{Cl}^-]$
 $\text{Ag}^+ \text{ (aq)} + 2 \text{ NH}_3 \text{ (aq)} \leftrightarrow \text{Ag(NH}_3)_2^+ \text{ (aq)}$ $K_{\text{f}} = [\text{Ag(NH}_3)_2] / [\text{Ag}^+][\text{NH}_3]^2$
 $\text{AgCl(s)} + 2 \text{ NH}_3 \text{ (aq)} \leftrightarrow 2 \text{ Ag(NH}_3)_2^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$ $K = K_{\text{sp}} \times K_{\text{f}}$

Complex Ion Formation

TABLE 6I.2 Formation Constants of Complexes in Water at 25 °C

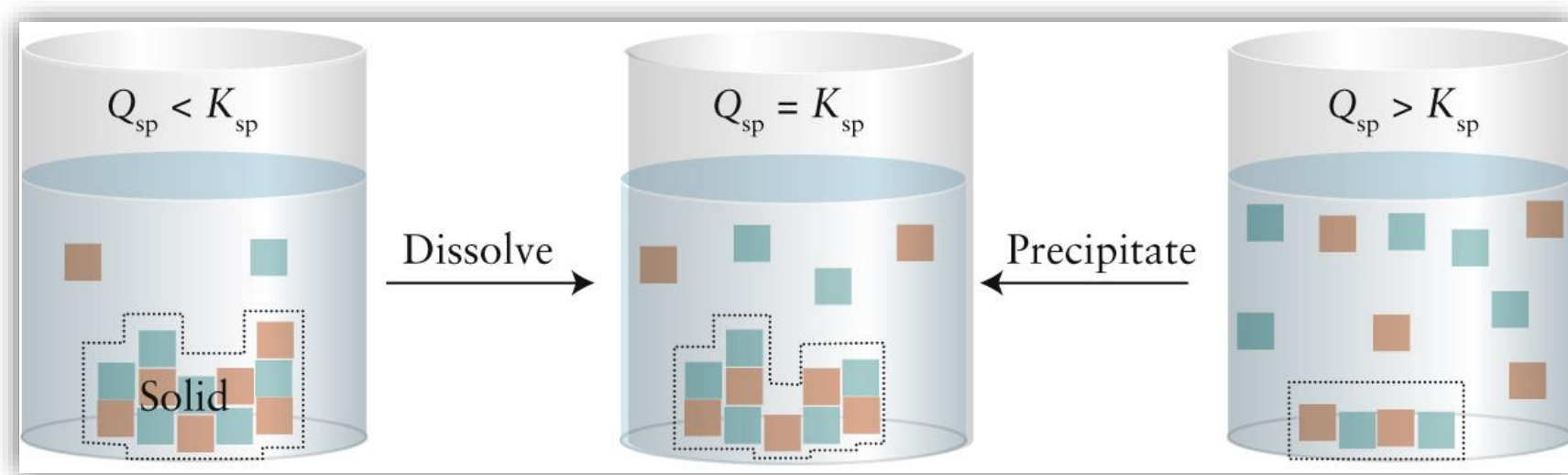
Equilibrium	K_f
$\text{Ag}^+(\text{aq}) + 2 \text{CN}^-(\text{aq}) \rightleftharpoons \text{Ag}(\text{CN})_2^-(\text{aq})$	5.6×10^8
$\text{Ag}^+(\text{aq}) + 2 \text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(\text{aq})$	1.6×10^7
$\text{Au}^+(\text{aq}) + 2 \text{CN}^-(\text{aq}) \rightleftharpoons \text{Au}(\text{CN})_2^-(\text{aq})$	2.0×10^{38}
$\text{Cu}^{2+}(\text{aq}) + 4 \text{NH}_3(\text{aq}) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$	1.2×10^{13}
$\text{Hg}^{2+}(\text{aq}) + 4 \text{Cl}^-(\text{aq}) \rightleftharpoons \text{HgCl}_4^{2-}(\text{aq})$	1.2×10^5
$\text{Fe}^{2+}(\text{aq}) + 6 \text{CN}^-(\text{aq}) \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}(\text{aq})$	7.7×10^{36}
$\text{Ni}^{2+}(\text{aq}) + 6 \text{NH}_3(\text{aq}) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}(\text{aq})$	5.6×10^8

Topic 6J. Precipitation

- 6J.1 Predicting Precipitation
- 6J.2 Selective Precipitation
- 6J.3 Dissolving Precipitates
- 6J.4 Qualitative Analysis

Predicting Precipitation

- Q_{sp} vs K_{sp}
 - $Q_{sp} > K_{sp}$: precipitation
 - $Q_{sp} < K_{sp}$: dissolution



Selective Precipitation

- For selective precipitation

A mixture of ions in solution can be separated by adding oppositely charged ions with which they form salts with very different solubilities..

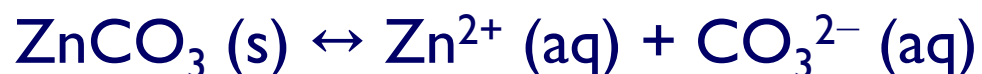
- A sample of seawater contains 0.050 mol/L Mg^{2+} (aq) and 0.010 mol/L Ca^{2+} (aq).

(a) Determine the order in which ion precipitates as solid NaOH is added, and give the concentration of OH^- when precipitation of each begins.

(b) Calculate the concentration of the first ion when the second one starts to precipitate. $K_{sp} = 1.1 \times 10^{-11}$ ($\text{Mg}(\text{OH})_2$) and $K_{sp} = 5.5 \times 10^{-6}$ ($\text{Ca}(\text{OH})_2$)

Dissolving Precipitates

- The solubility of a solid can be increased by removing one of its ions from solution.
- I) Acid can be used to dissolve a hydroxide, sulfide, sulfite, or carbonate precipitate.

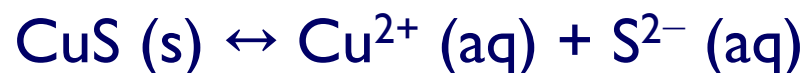


Dissolving Precipitates



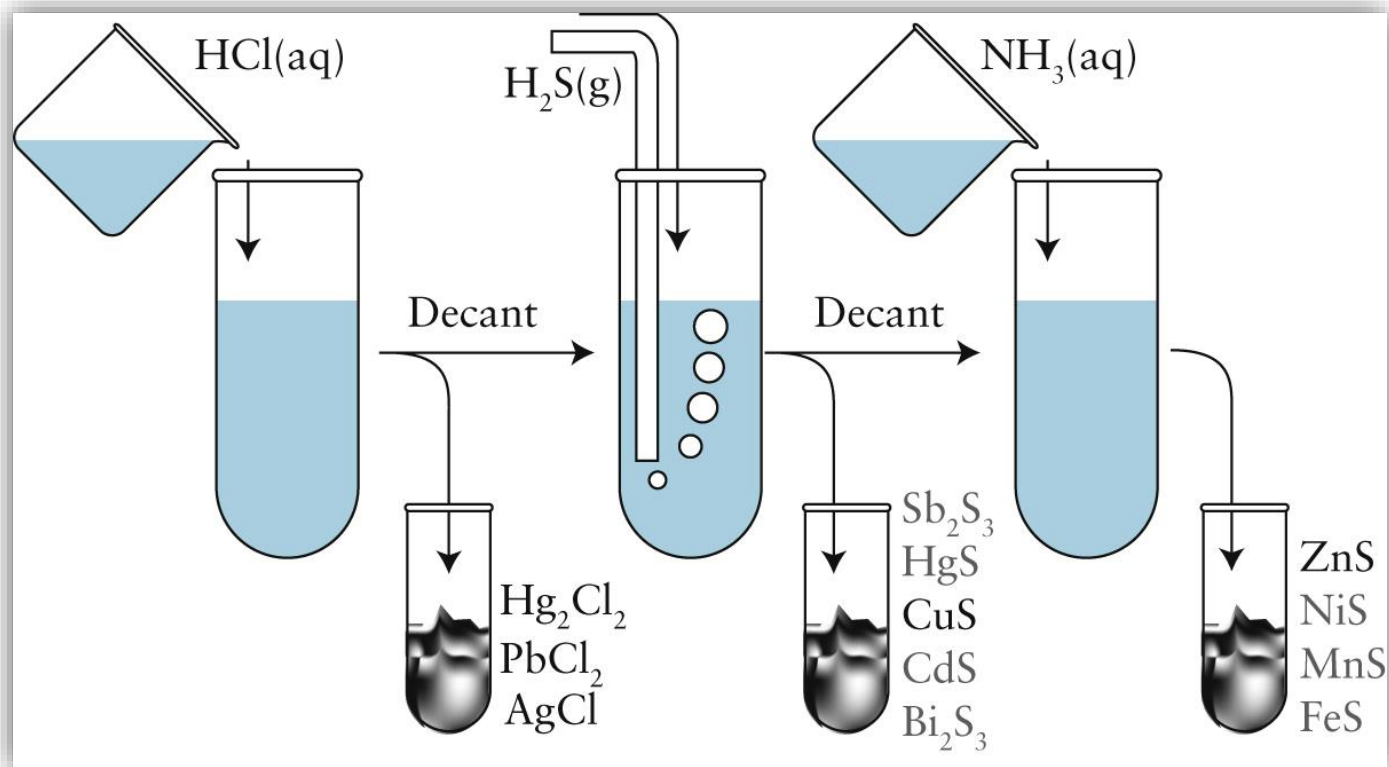
Dissolving Precipitates

- 2) Nitric acid can be used to oxidize metal sulfides to sulfur and a soluble salt.



- 3) Some solids can be dissolved by changing the temperature or by forming a complex ion.

Qualitative Analysis



- $\text{Pb}^{2+}(\text{aq}) + \text{CrO}_4^{4-}(\text{aq}) \rightarrow \text{PbCrO}_4(\text{s})$
- $\text{Ag}^+(\text{aq}) + 2 \text{NH}_3(\text{aq}) \rightarrow \text{Ag}(\text{NH}_3)_2^+(\text{aq})$
 $\text{Hg}_2\text{Cl}_2(\text{s}) + 2 \text{NH}_3(\text{aq}) \rightarrow \text{Hg}(\text{l}) + \text{HgNH}_2\text{Cl}(\text{s}) + \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- $\text{Ag}(\text{NH}_3)_2^+(\text{aq}) + \text{Cl}^-(\text{aq}) + 2 \text{H}_3\text{O}^+(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + 2 \text{NH}_4^+(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$

Dissolving Precipitates



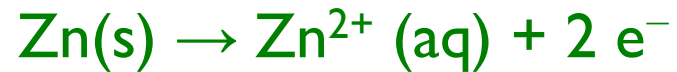
Topic 6K. Representing Redox Reactions

6K.1 Half-Reactions

6K.2 Balancing Redox Equations

Half-Reactions

- **Redox reaction**: the joint process of electron loss and gain.
- **Half-reaction** is the oxidation or reduction part of a reaction considered alone.



- **Redox couple** (Ox/Red)

The redox couple consisting of Zn^{2+} and Zn: Zn^{2+}/Zn .

Balancing Redox Equations

- Balance the net ionic equation for this skeletal reaction in an acidic aqueous solution.



- Balance the net ionic equation for this skeletal reaction in a basic aqueous solution.

