Class 8.2

Aqueous Equilibrium

CHEM 102H

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Common Ion Effect

- Solubility product equilibria can operate even the original source of the ions involved is not the salt that is precipitated.

Example: How much $AgNO_3$ must be added to a 10 M NaCl solution before a precipitate forms (What is the precipitate? What information do we need?)

K_{sp} for AgCl is 1.6×10^{-10}.

Common Ions - Predicting Precipitation

- K_{sp} for $PbCl_2$ is 1.7×10^{-5}.

What are the concentrations of of all species in solution when 2.78 g of $PbCl_2$ is added to 1.0 L of water? (Neglect the volume change.)

What are the concentrations of of all species in solution when 2.92 g of NaCl is added to the solution above? (Neglect the volume change.)

Competing Equilibria can give Tricky Problems

- One of the two problems, (a) & (b), is easy and the other is not so easy. ($K_{sp}(MgF_2) = 6.4 \times 10^{-9}$)

Calculate the solubility of:

(a) MgF_2 in a 2.5×10^{-3} M solution of $Mg(NO_3)_2$.

(b) MgF_2 in a 1.0×10^{-1} M solution of KF.

- Which one is tricky?

The tricky problem

At first, it doesn't seem so bad:

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$$

$$x + (2.5 \times 10^{-3}) \quad 2x$$

Set-up and solve:

$$6.4 \times 10^{-9} = (x + 2.5 \times 10^{-3})(2x)^2$$

$$x = 1.09 \times 10^{-3} \text{ - solved graphically}$$

Bad News: This is wrong! Why?

(Hint: $K_a(HF) = 3.47 \times 10^{-4}$ — it gets messy!)

Selective Precipitation

- Differences in solubility can sometimes be used to separate mixtures of ions.
- Such differences are the basis of qualitative analysis schemes.
- Example: an acidic soln. contains 1.0×10^{-3} M of $Bi(NO_3)_3$, $Cr(NO_3)_3$, and $Co(NO_3)_3$. In what order do the hydroxides of each metal precipitate as solid NaOH is added? At what $[OH^-]$ and pH do each begin to precipitate?

K_{sp}'s:	$Bi(OH)_3$	3.2×10^{-40}
	$Cr(OH)_3$	6.7×10^{-31}
	$Co(OH)_3$	4.0×10^{-45}

Selective Precipitation

- Example, cont.: What % of Co^{3+} is still in solution when $Bi(OH)_3$ just begins to precipitate? What % of Bi^{3+} is still in solution when $Cr(OH)_3$ just begins to precipitate?

K_{sp}'s:

$Bi(OH)_3$ 3.2×10^{-40}

$Cr(OH)_3$ 6.7×10^{-31}

$Co(OH)_3$ 4.0×10^{-45}

Complex Ion Formation

- The complexation of metal ions can compete with other equilibria.
- Example: Ag^+ forms a cyanide complex

$$Ag^+ + 2\,CN^- \rightleftarrows [Ag(CN)_2]^- \quad K_f = 5.6 \times 10^8$$

  - What is the solubility of AgBr in a 0.10 M KCN solution? For AgBr, $K_{sp} = 7.7 \times 10^{-13}$

Solubility Rules (See Table I1)

1. The nitrates, chlorates and acetates of all metals are soluble in water. Silver acetate is sparingly soluble.
2. All sodium, potassium and ammonium salts are soluble in water.
3. The chlorides, bromides and iodides of all metals except lead, silver and mercury(I) are soluble in water. HgI_2 is insoluble in water. $PbCl_2$, $PbBr_2$, and PbI_2 are soluble in hot water. The water-insoluble chlorides, bromides and iodides are also insoluble in dilute acids.

Solubility Rules, cont.

4. The sulfates of all metals except lead, mercury(I), barium and calcium are soluble in water. Silver sulfate is slightly soluble. The water-insoluble sulfates are also insoluble in dilute acids.

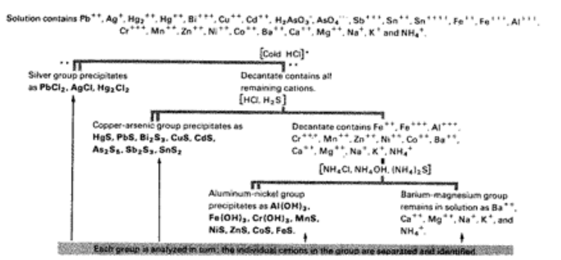
5. The carbonates, phosphates, borates, sulfites, chromates and arsenates of all metals except sodium, potassium and ammonium are insoluble in water but soluble in dilute acids. $MgCrO_4$ is soluble in water; $MgSO_3$ is slightly soluble in water.

Solubility Rules

6. The sulfides of all metals except barium, calcium, magnesium, sodium, potassium and ammonium are insoluble in water. BaS, CaS and MgS are sparingly soluble.

7. The hydroxides of sodium, potassium, and ammonium are very soluble in water. The hydroxides of calcium and barium are moderately soluble. The oxides and hydroxides of all other metals are insoluble.

Qualitative Analysis



*A bracketed formula [cold HCl] means that the substance (HCl in this case) is added as a reagent.

**The notation means separation by centrifuging and decanting. The double vertical parallel lines at the left refer to the precipitate and the one vertical line at the right refers to the decantate.

Qualitative Analysis