UNIT VI-Solubility Equilibria

Equilibrium between an insoluble substance and its solution:
Hetrogeneous equilibrium:
For a true equilibrium to exist between a solid and its solution, the solution must be saturated.

$BaSO_4 (s) \rightleftharpoons Ba^{2+} (aq) + SO_4^{2-} (aq)$

Equilibrium expression:

Example I : A saturated solution of $BaSO_4$ (s) has $[Ba^{2+}] = [SO_4^{2-}]$. Each is equal to 1.04×10^{-5} M.
What is K_{sp} ?

Example II: Write the expression for the solubility product constant for $Ca_3(PO_4)_2$ (s).

Example III: The value of K_{sp} for CaF_2 (s) is 3.4×10^{-11}. Determine the solubility of CaF_2(s).

Example IV: **COMMON ION EFFECT**
What is the solubility of CaF_2 (s) in a solution containing 0.010 M NaF?

Example V: **THE EFFECT OF pH ON THE SOLUBILITY**
a) What is the solubility of $Mg(OH)_2$(s) in a solution equilibrated at a pH equal to 9.00?
K_{sp} for $Mg(OH)_2$(s) is 1.2×10^{-11}

b) How would the solubility of $Mg(OH)_2$(s) be effected if we add some acid to the mixture above?
Ans: ________________

Example VI: What is the solubility of Ag_2CO_3 (s)? K_{sp} for Ag_2CO_3 (s) is 8.1×10^{-12}.

Example VII: Calculate the solubility of silver bromide in 0.0030 M NaBr. K_{sp} for AgBr is 5.0×10^{-13}

Example VIII: How many grams of PbI_2(s) will dissolve in 250 ml of 0.025 M $Pb(NO_3)_2$?
K_{sp} for PbI_2 is 7.1×10^{-9}.

Will a precipitate form?

The solubility product principle may be used to predict whether a precipitate will occur or not!

a) If under a given set of conditions, the ion product (Q_{sp}) is smaller than K_{sp}, the solution is unsaturated. No precipitate will form and any precipitate present will dissolve until equilibrium is reached. $Q_{sp} < K_{sp}$

b) If the ion product exceeds the value of Ksp, the solution is supersaturated and a precipitate will form.

$$Q_{sp} > K_{sp}$$

c) When the ion product is equal to Ksp, the solution is saturated and any precipitate present is in equilibrium with the solution.

$$Q_{sp} = K_{sp}$$

Example I: A 0.0010 mole of Bi^{2+} is added to a 1 liter solution of pH=10.00. Will a precipitate of $Bi(OH)_2$ occur? K_{sp} for $Bi(OH)_2$ is 1.0×10^{-12}

Example II: A 1.00 liter solution contains 0.25 mole CO_3^{2-} and 1.0×10^{-3} mole Mg^{2+} . Will a precipitate of $MgCO_3$ form? K_{sp} for $MgCO_3$ is 1.0×10^{-5}.

How could we increase the solubility of $MgCO_3$(s)?

Example III: A solution is 1.0×10^{-3} M in each of Cl^- and Br^-. Ag^+ ions are added slowly. Which halide will begin to precipitate first? At what Ag^+ ion concentration will this occur? K_{sp} for AgCl= 1.6×10^{-10} , K_{sp} for AgBr is 5.0×10^{-13}.

Ans: $[Ag^+]=5.3 \times 10^{-10}$ M

Example IV: 2.0×10^{-4} mole Tl_2SO_4 and 6.0×10^{-2} mole NaCl are combined in a 1 liter solution. Will TlCl(s) precipitate? K_{sp} for TlCl is 1.9×10^{-4}.

Example V: 50.0 ml of 0.20 M $Pb(NO_3)_2$(aq) is mixed with 50.0 ml of 1.5 M NaCl (aq). What is the concentration of Pb^{2+} in the solution? K_{sp} for $PbCl_2$(s) $=1.7 \times 10^{-4}$

Ans: $[Pb^{2+}]= 5.6 \times 10^{-4}$ M

Example VI: A solution of 0.010 M Fe^{2+} is saturated with 0.10M H_2S. The solution had acidity adjusted to pH=3.00 by adding HCl. Will a precipitate of FeS(s) form in this solution? K_{a1} for $H_2S=1.1 \times 10^{-7}$ and K_{a2} for $HS^-=1.0 \times 10^{-14}$. K_{sp} for FeS=3.7×10^{-19}

Example VII: A solution containing 0.0100 M Co^{2+} is kept saturated with H_2S ($[H_2S]=0.10M$). What range of hydrogen ion concentration will permit precipitation of this ion as its sulfide?
K_{sp} for $CoS=7.0x10^{-23}$

Ans: CoS(s) will be prevented from precipitation at $[H^+]=1.25M$. To ensure that CoS will precipitate the H^+ ion concentration should be less than 0.125 M.

Separation of ions by precipitation

Example: A 0.10 M solution in each of $Zn(NO_3)_2$ and $Hg(NO_3)_2$ is saturated with $H_2S(g)$,$[H_2S]= 0.10M$ after the concentration of H^+ is adjusted to 0.30M by adding HCl. Will sulfides of these ions precipitate under these conditions? K_{a1} for $H_2S=1.1x10^{-7}$,K_{a2} for HS^- $=1.0x10^{-14}$, K_{sp} for $ZnS=1.1x10^{-21}$ and K_{sp} for $HgS=1.0x10^{-50}$

THE RELATIONSHIP BETWEEN K_p and K_c:

$$K_p = K_c (RT)^{\Delta n}$$

$\Delta n = n_{\text{gaseous products}} - n_{\text{gaseous reactants}}$

It is most important to specify whether K_c or K_p is meant when discussing equilibrium of gases.

Only those instances where the same number of moles of gas appears on both sides of the equation will K_c and K_p have the same numerical value.

Deduce the relationship beyween K_c and Kp:

$$4\ HCl\ (g) + O_2\ (g) \rightleftharpoons 2\ Cl_2\ (g) + 2\ H_2O\ (g)$$

Example I: What is the value of K_p for the following equilibrium at 1273 °C ?

$$2\ CO(g) + O_2\ (g) \rightleftharpoons 2\ CO_2\ (g)$$

if K_c is 2.24×10^{-22} at the same temperature?

Ans: 1.77×10^{-24}

Example II: If K_p=266, calculate K_c for the reaction at 1050 °C:

$$CO_2\ (g) + C\ (s) \rightleftharpoons 2\ CO(g)$$

Ans: 2.45

Example III: If K_p for the reaction:

$$2\ NOBr(g) \rightleftharpoons 2\ NO\ (g) + Br_2\ (g)$$

Is 9.65×10^{-3} at 298 K, calculate K_c at the same temperature.

Ans: 3.94×10^{-4}