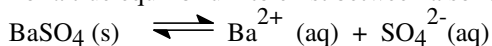


## UNIT VI-Solubility Equilibria

### Equilibrium between an insoluble substance and its solution:

#### Heterogeneous equilibrium:

For a true equilibrium to exist between a solid and its solution, the solution must be saturated.



Equilibrium expression:

Example I : A saturated solution of  $\text{BaSO}_4 (\text{s})$  has  $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}]$ . Each is equal to  $1.04 \times 10^{-5} \text{ M}$ .

What is  $K_{\text{sp}}$  ?

Example II: Write the expression for the solubility product constant for  $\text{Ca}_3(\text{PO}_4)_2 (\text{s})$ .

Example III: The value of  $K_{\text{sp}}$  for  $\text{CaF}_2 (\text{s})$  is  $3.4 \times 10^{-11}$ . Determine the solubility of  $\text{CaF}_2 (\text{s})$ .

#### Example IV: COMMON ION EFFECT

What is the solubility of  $\text{CaF}_2 (\text{s})$  in a solution containing 0.010 M NaF?

#### Example V: THE EFFECT OF pH ON THE SOLUBILITY

a) What is the solubility of  $\text{Mg}(\text{OH})_2 (\text{s})$  in a solution equilibrated at a pH equal to 9.00?

$K_{\text{sp}}$  for  $\text{Mg}(\text{OH})_2 (\text{s})$  is  $1.2 \times 10^{-11}$

b) How would the solubility of  $\text{Mg}(\text{OH})_2 (\text{s})$  be effected if we add some acid to the mixture above?

Ans: \_\_\_\_\_

Example VI: What is the solubility of  $\text{Ag}_2\text{CO}_3$  (s)?  $K_{\text{sp}}$  for  $\text{Ag}_2\text{CO}_3$  (s) is  $8.1 \times 10^{-12}$ .

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

Example VIII: How many grams of  $\text{PbI}_2$ (s) will dissolve in 250 ml of 0.025 M  $\text{Pb}(\text{NO}_3)_2$  ?  
 $K_{\text{sp}}$  for  $\text{PbI}_2$  is  $7.1 \times 10^{-9}$ .

### **Will a precipitate form?**

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

- If under a given set of conditions, the ion product ( $Q_{\text{sp}}$ ) is smaller than  $K_{\text{sp}}$ , the solution is unsaturated. No precipitate will form and any precipitate present will dissolve until equilibrium is reached.  
 $Q_{\text{sp}} < K_{\text{sp}}$
- If the ion product exceeds the value of  $K_{\text{sp}}$ , the solution is supersaturated and a precipitate will form.  
 $Q_{\text{sp}} > K_{\text{sp}}$
- When the ion product is equal to  $K_{\text{sp}}$ , the solution is saturated and any precipitate present is in equilibrium with the solution.

Example I: A 0.0010 mole of  $\text{Bi}^{2+}$  is added to a 1 liter solution of pH=10.00. Will a precipitate of  $\text{Bi}(\text{OH})_3$  occur?  
 $K_{\text{sp}}$  for  $\text{Bi}(\text{OH})_3$  is  $1.0 \times 10^{-12}$

Example II: A 1.00 liter solution contains 0.25 mole  $\text{CO}_3^{2-}$  and  $1.0 \times 10^{-3}$  mole  $\text{Mg}^{2+}$ . Will a precipitate of  $\text{MgCO}_3$  form?  $K_{\text{sp}}$  for  $\text{MgCO}_3$  is  $1.0 \times 10^{-5}$ .

How could we increase the solubility of  $\text{MgCO}_3$ (s)?

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

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

Example IV:  $2.0 \times 10^{-4}$  mole  $\text{Tl}_2\text{SO}_4$  and  $6.0 \times 10^{-2}$  mole  $\text{NaCl}$  are combined in a 1 liter solution. Will  $\text{TlCl}(s)$  precipitate?  $K_{\text{sp}}$  for  $\text{TlCl}$  is  $1.9 \times 10^{-4}$ .

Example V: 50.0 ml of 0.20 M  $\text{Pb}(\text{NO}_3)_2(\text{aq})$  is mixed with 50.0 ml of 1.5 M  $\text{NaCl}(\text{aq})$ . What is the concentration of  $\text{Pb}^{2+}$  in the solution?  $K_{\text{sp}}$  for  $\text{PbCl}_2(s) = 1.7 \times 10^{-4}$

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

Example VI: A solution of 0.010 M  $\text{Fe}^{2+}$  is saturated with 0.10M  $\text{H}_2\text{S}$ . The solution had acidity adjusted to  $\text{pH}=3.00$  by adding  $\text{HCl}$ . Will a precipitate of  $\text{FeS}(s)$  form in this solution?  $K_{\text{a}1}$  for  $\text{H}_2\text{S} = 1.1 \times 10^{-7}$  and  $K_{\text{a}2}$  for  $\text{HS}^- = 1.0 \times 10^{-14}$ .  $K_{\text{sp}}$  for  $\text{FeS} = 3.7 \times 10^{-19}$

Example VII: A solution containing 0.0100 M  $\text{Co}^{2+}$  is kept saturated with  $\text{H}_2\text{S}$  ( $[\text{H}_2\text{S}]=0.10\text{M}$ ). What range of hydrogen ion concentration will permit precipitation of this ion as its sulfide?  
 $K_{\text{sp}}$  for  $\text{CoS}=7.0 \times 10^{-23}$

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

### **Separation of ions by precipitation**

Example: A 0.10 M solution in each of  $\text{Zn}(\text{NO}_3)_2$  and  $\text{Hg}(\text{NO}_3)_2$  is saturated with  $\text{H}_2\text{S(g)}$ ,  $[\text{H}_2\text{S}]=0.10\text{M}$  after the concentration of  $\text{H}^+$  is adjusted to 0.30M by adding  $\text{HCl}$ . Will sulfides of these ions precipitate under these conditions?  $K_{\text{a}1}$  for  $\text{H}_2\text{S}=1.1 \times 10^{-7}$ ,  $K_{\text{a}2}$  for  $\text{HS}^- = 1.0 \times 10^{-14}$ ,  $K_{\text{sp}}$  for  $\text{ZnS}=1.1 \times 10^{-21}$  and  $K_{\text{sp}}$  for  $\text{HgS}=1.0 \times 10^{-50}$

**THE RELATIONSHIP BETWEEN  $K_p$  and  $K_c$ :**

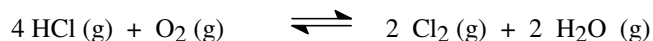
$$K_p = K_c (RT)^{\Delta n}$$

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

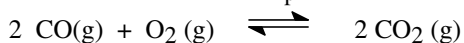
It is most important to specify whether  $K_c$  or  $K_p$  is meant when discussing equilibrium of gases.

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 between  $K_c$  and  $K_p$ :



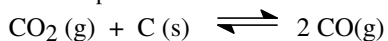
Example I: What is the value of  $K_p$  for the following equilibrium at 1273 °C ?



if  $K_c$  is  $2.24 \times 10^{-22}$  at the same temperature?

$$\text{Ans: } 1.77 \times 10^{-24}$$

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



$$\text{Ans: } 2.45$$

Example III: If  $K_p$  for the reaction:



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

$$\text{Ans: } 3.94 \times 10^{-4}$$

