EQUILIBRIUM OF COMPLEX IONS

COMPLEX IONS:

Metal ions, particularly transition metals, combine with one or more ligands to produce more complex species that are called ***complex ions.***

There are two ways of dealing with the equilibria involving complex ions:

- One, is to consider their **dissociation** equilibria:

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+(aq) + 2\ NH_3(aq)$$

$$K_{instability} = K_{dissociation} = \frac{[Ag^+]\ [NH3]^2}{[Ag(NH_3)_2^+]}$$

The larger the value of K_{inst}, the less stable the complex. For the above reaction,

$K_{inst} = 6.0 \times 10^{-8}$

The above complex is quite stable.

- Another, is to consider the **formation** of the complex:

$$Ag^+(aq) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+$$

$$K_{form} = K_{stability} = \frac{[Ag(NH_3)_2^+]}{[Ag^+]\ [NH3]^2}$$

What is the relationship between K_{inst} and K_{form} ?_____

CALCULATIONS INVOLVING COMPLEX IONS:

In actual practice complex ions are almost always formed in the presence of an **excess** of the complexing agent. Therefore, certain assumptions can be made to simplify the calculations:

1) Most of the metal ions are tied up in the coordinated complex. The free metal ions have a small concentration compared to the fully coordinated complex.

2) The concentration of the free ligand is assumed to be equal to the concentration of the excess complexing agent. That is, neglect the contribution from the dissociation of the complex.

Example 1:

Calculate the concentration of [Zn^{2+}] ion in a solution prepared by adding 0.118 mole $Zn(NO_3)_2$ to a 1.00 liter of 0.90 M NaOH. K_{inst} for $Zn(OH)_4^{2-}$ = 3.60 x 10^{-16} .

Setup:

Answer: 1.2 x 10^{-15} M

Example 2:

Calculate the concentration of Cd^{2+} in a solution prepared by dissolving 0.010 mole $Cd(NO_3)_2$ in a 1.00 liter solution that is 2.00 M in NH_3 . K_{inst} for $Cd(NH_3)_2^{2+}$ = 7.5 x 10^{-8} .

Setup:

Answer_____

Example 3:
A quantity of 0.20 mole of $CuSO_4$ is added to a 1.00 liter of 1.2 M NH_3 solution. What is the concentration of Cu^{2+} ions at equilibrium? K_{form} for $Cu(NH_3)_4^{2+}$ is 5.0×10^{13}.
Setup:

Answer_____

Example 4:
Calculate the concentration of Ag^+ in a solution prepared by dissolving 0.010 mole of $AgNO_3$ in a 1.00 liter of a solution that is 2.00 M in NH_3. K_{inst} for $Ag(NH_3)_2^+ = 6.0 \times 10^{-8}$.
Setup:

Answer_____

Example 5:

Calculate the concentration of Ag^+ in a solution which is prepared by dissolving 5.88×10^{-3} mole $AgNO_3$ and 9.60×10^{-2} mole KCN in sufficient water to make 1.00 liter solution.

K_{form} for $Ag(CN)_2^-$ = 1.0×10^{22} .

Setup:

Answer: _____

Example 6:

What is the concentration of Ag^+ in a 0.10 M solution of $Na[Ag(CN)_2]$?

K_{inst} for $Ag(CN)_2^-$ = 1.0×10^{-22} .

Setup:

Answer _____

Example 7:

a) What is the concentration of Cd^{2+} in a solution of 0.10 M $Cd(NO_3)_2$ if 1.00 liter is treated with 0.50 mol KCN? K_{inst} for $Cd(CN)_4^{2-} = 1.4 \times 10^{-19}$.

Setup:

Answer_____

b) Determine whether any CdS(s) will precipitate from the mixture if it is made 1.0×10^{-3} M in S^{2-} by the addition of soluble sulfide. K_{sp} for CdS(s)= 1.0×10^{-28}.

Setup:

Answer_____

COMPLEX IONS AND SOLUBILITY:

When a complex ion is formed in a solution of an insoluble salt, it reduces the concentration of the free metal ion. As a result more solid must dissolve in order to make up for the amount of metal ion lost, until the concentration required by the K_{sp} of the salt is achieved. Thus the solubility of an insoluble salt generally increases when complex ions are formed.

Let us see the effect of adding NH_3 to a saturated solution of AgCl(s):

a) Before any NH_3 is added:

$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq)$ $\quad \mathbf{K_{sp} = [Ag+]\ [Cl^-]}$

b) Because NH_3 forms such a stable complex with free Ag^+ ions, when NH_3 is added to this system a second equilibrium is established:

$Ag^+\ (aq) + 2\ NH_3\ (aq) \rightleftharpoons Ag(NH_3)_2^+\ (aq)$ $\quad \mathbf{K_{form} = \dfrac{[Ag(NH_3)_2^+]}{[Ag^+]\ [NH3]^2}}$

The above **two** equilibria can be combined in one overall equilibrium by **adding** them together:

$AgCl\ (s) + \cancel{Ag^+\ (aq)} + 2\ NH_3\ (aq) \rightleftharpoons \cancel{Ag^+\ (aq)} + Cl^-\ (aq) + Ag(NH_3)_2^+\ (aq)$

This is simplified into:

$AgCl\ (s) + 2\ NH_3\ (aq) \rightleftharpoons Cl^-\ (aq) + Ag(NH_3)_2^+\ (aq)$ $\quad \mathbf{K_{overall} = \dfrac{[Cl^-]\ [Ag(NH_3)_2^+]}{[NH3]^2}}$

We can obtain the same expression by multiplying the $\mathbf{K_{sp}}$ of AgCl(s) by the $\mathbf{K_{form}}$ of the complex ion.

$$\mathbf{K_{sp} \cdot K_{form} = [Ag+]\ [Cl^-] \cdot \frac{[Ag(NH_3)_2^+]}{[Ag^+]\ [NH3]^2} = K_{overall}}$$

Example 1:

What is the molar solubility of AgCl in 1.00 liter of 1.0 M NH_3 at 25 ° C?

K_{sp} for AgCl (s) = 1.6×10^{-10} and K_{form} for $Ag(NH_3)_2^+$ = 1.7×10^7

Setup:

Answer _____

Example 2:

Calculate the molar solubility of AgCl in 0.800 M KCN. K_{sp} for AgCl (s) is 1.7×10^{-10}, K_{inst} for $Ag(CN)_2^-$ = 1.8×10^{-19} .

Setup:

Answer_____

Example 3:

a) What is the molar solubility of AgBr (s) in 1.00 liter of 2.00 M NH_3 at 25 ° C?

K_{sp} for AgBr= 4.9×10^{-13} and K_{form} for $Ag(NH_3)_2^+ = 2.5 \times 10^7$.

Setup:

Answer_____

b) How many grams of AgBr (s) will dissolve in 500. ml of 2.00 M NH_3(aq)?

Setup:

Answer _____

Example 4:

a) What must be the NH_3 concentration in order to assure the formation of 0.010 M $Cd(NH_3)_4^{2+}$ complex ion by dissolving $Cd(OH)_2$ (s)? K_{sp} for $Cd(OH)_2$ (s)= 8.1×10^{-15}, K_{inst} for $Cd(NH_3)_4^{2+} = 1.0 \times 10^{-7}$.

Setup:

Answer _____

b) How many moles of NH_3 must be added to 1.0 liter containing $Cd(OH)_2$(s) to achieve the above condition?

Setup:

Answer_____

Example 5:
Unexposed silver halides are removed from photographic plate film when they react with a solution of $Na_2S_2O_3$ and form the complex ion, $Ag(S_2O_3)_2^{3-}$. K_{form} for $Ag(S_2O_3)_2^{3-}$ is 4.7×10^{13}.

a) What must be the concentration of $S_2O_3^{2-}$ present after 1.00 g AgBr (s) is dissolved in 1.00 liter by the formation of $Ag(S_2O_3)_2^{3-}$? K_{sp} for AgBr= 4.7×10^{-13} (molar mass of AgBr is 187.8 g/mole).
Setup:

Answer _____

b) How many moles of $Na_2S_2O_3$ must be added to a 1.00 liter solution to dissolve 1.00 g AgBr?
Setup:

Answer _____