Chapter 16. Acid-Base Equilibria and Solubility Equilibria

What we will learn:

- Homogeneous and heterogeneous solution equilibria
- Common ion effect
- Buffer solutions
- Acid-base titrations
- Acid-base indicators
- Solubility equilibria
- Separation of ions by fractional precipitation
- Common ion effect and solubility
- pH and solubility
- Complex ion equilibria and solubility

Homogeneous solution equilibria

Solution equilibrium related to reactions in which all components are in the same phase

Heterogeneous solution equilibria

Solution equilibrium related to reactions in which the components are in more than one phase

The common ion effect

The shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance

Example

The solution of two different compounds having a common ion

$$CH_3COONa(s) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

$$CH_3COOH(aq) \leftrightarrows CH_3COO^-(aq) + H^+(aq)$$

Adding CH_3COONa to a solution of CH_3COOH increases a concentration of CH_3COO^-, which (Le Chatelier principle) decreases a concentration of H^+

$HA(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + A^-(aq)$

$HA(aq) \leftrightarrows H^+(aq) + A^-(aq)$

$K_a = [H^+]\,[A^-] / [HA]$

$[H^+] = K_a\,[HA] / [A^-]$

$-\log\,[H^+] = -\log K_a - \log\,([HA] / [A^-])$

$-\log\,[H^+] = -\log K_a + \log\,([A^-] / [HA])$

$pH = pK_a + \log([A^-] / [HA])$

$pK_a = -\log K_a$

$$pH = pKa + \log([base] / [acid])$$

Problem

Calculate the pH of a 0.2 *M* CH_3COOH solution. What is the pH of a solution containing both 0.2 *M* CH_3COOH and 0.3 *M* CH_3COONa. The K_a of CH_3COOH is 1.8×10^{-5}.

	$CH_3COOH(aq)$	$\leftrightarrows$	$H^+(aq)$	$+$	$CH_3COO^-(aq)$
Initial (*M*)	0.2		0		0
Change (*M*)	-x		+x		+x
Equilibrium (*M*)	0.2 - x		x		x

$$K_a = [H^+]\,[CH_3COO^-] / [CH_3COOH] = 1.8 \times 10^{-5}$$

$$1.8 \times 10^{-5} = x^2 / (0.2 - x)$$

$$x = 1.9 \times 10^{-3}\ M$$

$$pH = -\log(1.9 \times 10^{-3}) = 2.27$$

	$CH_3COONa(aq)$	$\rightarrow$	$Na^+(aq)$	+	$CH_3COO^-(aq)$
Initial (*M*)	0.3		0.0		0.0
Change (*M*)	-0.3		+0.3		+0.3
Final (*M*)	0		0.3		0.3

The initial concentration of the base will change

	$CH_3COOH(aq)$	$\leftrightarrows$	$H^+(aq)$	+	$CH_3COO^-(aq)$
Initial (*M*)	0.2		0		0.3
Change (*M*)	-x		+x		+x
Equilibrium (*M*)	0.2 - x		x		0.3 + x

$$K_a = [H^+]\,[CH_3COO^-] / [CH_3COOH]$$

$$1.8 \times 10^{-5} = (x)\,(0.3 + x) / (0.2 - x)$$

$x = 1.2 \times 10^{-5}\ M$

$\text{pH} = -\log[\text{H}^+]$

$= -\log(1.2 \times 10^{-5}) = 4.92$

Buffer solutions

The solution of a weak acid (or a weak base) and its salt

The buffer solution has the ability to resist changes in pH upon the addition of small amount of an acid or a base

Example

A solution of acetic acid (CH_3COOH) and sodium acetate (CH_3COONa)

$$CH_3COONa(s) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

If an acid is added the, H^+ will be consumed according to the reaction

$$CH_3COO^-(aq) + H^+(aq) \quad \leftrightarrows \quad CH_3COOH(aq)$$

If a base is added, the OH^- will be consumed according the the reaction

$$CH_3COOH(aq) + OH^-(aq) \quad \leftrightarrows \quad CH_3COO^-(aq) + H_2O(l)$$

Problem

Calculate the pH of a buffer system contining 1.0 *M* CH_3COOH and 1.0 *M* CH_3COONa. What is the pH of the buffer system after the addition of 0.10 mole of gaseous HCl to 1.0 L of the solution

	$CH_3COOH(aq)$	$\leftrightarrows$	$H^+(aq)$	+	$CH_3COO^-(aq)$
Initial (*M*)	1.0		0		1.0
Change (*M*)	-x		+x		+x
Equilibrium (*M*)	1.0 - x		x		1.0 + x

$$K_a = [H^+]\,[CH_3COO^-] / [CH_3COOH]$$

$$1.8 \times 10^{-5} = (x)\,(1.0 + x) / (1.0 - x)$$

$$x = 1.8 \times 10^{-5}\ M$$

$$pH = -\log(1.8 \times 10^{-5}) = 4.74$$

When the HCl is added, the initial concentration are

	$HCl(aq)$	$\rightarrow$	$H^+(aq)$	+	$Cl^-(aq)$
Initial (*M*)	0.1		0		0
Change (*M*)	-0.1		+0.1		+0.1
Final (*M*)	0		0.1		0.1

The H^+ ions provided by the strong HCl react completely with the CH_3COO^- base. At this point is more convinient work with number of moles rather than molarity. The change in volume will change of molarity but not the number of moles

	$CH_3COO^-(aq)$	+	$H^+(aq)$	→	$CH_3COOH(aq)$
Initial (mol)	1.0		0.1		1.0
Change (mol)	-0.1		-0.1		+0.1
Final (mol)	0.90		0		1.1

Finally, the we calculate the pH of the buffer after neutralization, taking the final concentrations of the species

	$CH_3COOH(aq)$	$\leftrightarrows$	$H^+(aq)$	+	$CH_3COO^-(aq)$
Initial (*M*)	1.1		0		0.9
Change (*M*)	-x		+x		+x
Equilibrium (*M*)	1.1 - x		x		0.9 + x

$K_a = [H^+] [CH_3COO^-] / [CH_3COOH]$

$1.8 \times 10^{-5} = (x) (0.9 + x) / (1.1 - x)$

$x = 2.2 \times 10^{-5}\ M$

$pH = -\log(2.2 \times 10^{-5}) = 4.66$

Making a buffer solution with specific pH

The molar concentrations of the acid and its conjugate base are approximately equal

$$pH \quad = \quad pKa \quad + \quad \log([base] / [acid])$$

$$\log([base] / [acid]) \quad =\sim \quad 0$$

$$pH =\sim pK_a$$

Example

Prepare a phosphate buffer solution with a pH of about 7

Solution

The concentration of the acid should be roughly equal to the concentration of its conjugate base

$\log([\text{base}] / [\text{acid}]) = 0$

$[\text{base}] / [\text{acid}] = 1$

The phosphoric acid is a triprotic acid

$H_3PO_4(aq) \leftrightarrows H^+(aq) + H_2PO_4^-(aq) \quad K_{a1} = 7.5 \times 10^{-3} \quad pK_{a1} = 2.12$
$H_2PO_4^-(aq) \leftrightarrows H^+(aq) + HPO_4^{2-}(aq) \quad K_{a2} = 6.2 \times 10^{-8} \quad pK_{a2} = 7.21$
$HPO_4^{2-}(aq) \leftrightarrows H^+(aq) + PO_4^{3-}(aq) \quad K_{a3} = 4.8 \times 10^{-13} \quad pK_{a3} = 12.32$

The most suitable of the three buffer systems is $HPO_4^{2-} / H_2PO_4^-$ because the pK_a is closest to the desired pH

$pH = K_a + \log([\text{base}] / [\text{acid}])$

$7.40 = 7.21 + \log([HPO_4^{2-}] / [H_2PO_4^-])$

$\log([HPO_4^{2-}] / [H_2PO_4^-]) = 0.19$

$[HPO_4^{2-}] / [H_2PO_4^-] = 10^{0.19} = 1.5$

Therefore we need to prepare a phosphate buffer with a pH of 7.40, by dissolving disodium hydrogen phosphate (Na_2HPO_4) and sodium dihydrogen phosphate (NaH_2PO_4) in a mole ratio 1.5/1.0 in water. For example we could dissolve 1.5 moles of Na_2HPO_4 and 1.0 mole NaH_2PO_4 in enough water to make up a 1 L solution

Acid base titrations

Neutralization of an acid by a base, or a base by an acid

- Titrations with a strong acid and a strong base
- Titrations with a weak acid and a strong base
- Titrations with a strong acid and a weak base

Strong acid and a strong base titrations

Example

$NaOH\ (aq) \quad + \quad HCl\ (aq) \rightarrow \quad NaCl\ (aq) \quad + \quad H_2O\ (l)$

Net ionic charges

$H^+(aq) \quad + \quad OH^-(aq) \quad \rightarrow \quad H_2O(l)$

Calculations of pH at different steps of titrations

1. Addition of 10.0 mL 0.1 *M* NaOH to 25.0 mL of 0.1 *M* HCl

   Number of moles of NaOH in 10.0 mL

   10.0 mL x (0.1 mol NaOH)/(1 L NaOH) x (1 L)/(1000 mL) = 1 x 10^{-3} mol

Number of moles of HCl originally present in 25.0 mL of solution

25.0 mL x (0.1 mol HCl) /(1 L HCl) x (1 L) / (1000 mL) = 2.5 x 10^{-3} mol

Amount of HCl left after partial neutralization

(2.5 x 10^{-3}) - (1.0 x 10^{-3}) = 1.5 x 10^{-3} mol

The concentration of H^+ ions in 35.0 mL of solution

(1.5 x 10^{-3} mol HCl) / (35.0 mL) x (1000 mL) / (1 L) = 0.0429 *M* HCl

pH = -log (0.0429) = 1.37

2. Addition of 25.0 mL of 0.1 *M* NaOH to 25 mL of 0.1 *M* HCl
(NaCl does not undergo hydrolysis)

[H+] = [OH-] = 1.0 x 10^{-7} *M*

pH = 7.0

3. Addition of 35.0 mL of 0.1 *M* NaOH to 25.0 mL 0.1 *M* HCl

   35.0 mL x (0.1 mol NaOH) / (1 L NaOH) x (1 L) / 1000 mL) = 3.5×10^{-3}

   The number of moles of HCl in 25.0 mL solution is 2.5×10^{-3} mol. After complete neutralization of HCl, the number of moles of NaOH left is

   $(3.5 \times 10^{-3}) - (2.5 \times 10^{-3}) = 1 \times 10^{-3}$ mol

   The concentration of NaOH in 60.0 mL of solution is

   (1×10^{-3} mol NaCl) / (60.0 mL) x (1000 mL) / (1 L) = 0.0167 mol NaCl / L

   $[OH^-] = 0.0167$ *M*

   pOH = 1.78

   pH = 12.22

Weak acid and a strong base titrations

Example

$$CH_3COOH\,(aq) \quad + \quad NaOH\,(aq) \quad \rightarrow \quad CH_3COONa\,(aq) \quad + \quad H_2O\,(l)$$

Simplification

$$CH_3COOH\,(aq) \quad + \quad OH^-\,(aq) \rightarrow \quad CH_3COO^-\,(aq) \quad + \quad H_2O\,(l)$$

Weak acid reacts with water (hydrolysis)

$$CH_3COO^-\,(aq) \quad + \quad H_2O\,(l) \quad \leftrightarrows \quad CH_3COOH\,(aq) \quad + \quad OH^-\,(aq)$$

Calculate the pH in the titration of 25.0 mL of 0.1 *M* acetic acid (CH_3COOH) by sodium hydroxide (NaOH) after the addition

(a) 10.0 mL of 0.1 *M* NaOH

(b) 25.0 mL 0.1 *M* NaOH

(c) 35.0 mL of 0.1 *M* NaOH

a) Number of moles of NaOH present in 10.0 mL is

10.0 mL x (0.1 mol NaOH) / (1 L NaOH soln) x (1 L) / (1000 mL) =

= 1.0×10^{-3} mol

Number of moles of CH_3COOH originally present in 25.0 mL is

25.0 mL x (0.1 mol CH_3COOH) / (1 L CH_3COOH soln) x (1 L) / (1000 mL)

= 2.5×10^{-3} mol

We work with moles because two solutions are mixed and the volume of the final solution increases. The molarity will change however, the number of moles will remain the same

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

Initial (mol)	2.5×10^{-3}	1.0×10^{-3}	0
Change (mol)	-1.0×10^{-3}	-1.0×10^{-3}	1.0×10^{-3}
Final (mol)	1.5×10^{-3}	0	1.0×10^{-3}

We have a buffer made up of CH_3COOH and CH_3COO^- (from the salt). We can calculations of the pH solution

$$K_a = [H^+][CH_3COO^-] / [CH_3COOH] = 1.8 \times 10^{-5}$$

$$[H^+] = [CH_3COOH]\,K_a / [CH_3COO^-]$$

$$= (1.5 \times 10^{-3})(1.8 \times 10^{-5}) / (1.0 \times 10^{-3}) = 2.7 \times 10^{-5}\ \mathrm{M}$$

$$\mathrm{pH} = 4.57$$

b) 25.0 mL of 0.1 *M* NaOH reacting with 25.0 mL of 0.1 *M* CH_3COOH corresponds to the equivalence point. At the equivalence point the concentrations of both the base and the acid are zero. The number of moles of NaOH in 25.0 mL of the solution is

25.0 mL x (0.1 mol NaOH) / (1 L NaOH soln) x (1 L) / (1000 mL) =

= 2.5×10^{-3} mol

The changes in number of moles are

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

Initial (mol)	2.5×10^{-3}	2.5×10^{-3}	0
Change (mol)	-2.5×10^{-3}	-2.5×10^{-3}	2.5×10^{-3}
Final (mol)	0	0	2.5×10^{-3}

At the equivalence point, the concentration of the acid and the base are zero. The total volume is (25.0 + 25.0)mL. The concentration of the salt is

$[CH_3COONa]$ = (2.5 x 10^{-3} mol) / (50.0 mL) x (1000 mL) / (1 L)

= 0.05 M

The calculations of the pH of the solution that results from the hydrolysis of the CH_3COO^- ions

$$CH_3COO^-(aq) + H_2O(l) \quad \rightleftarrows \quad CH_3COOH(aq) + OH^-(aq)$$

	CH_3COO^-	$\rightleftarrows$	CH_3COOH	+	OH^-
Initial (*M*)	0.05		0.0		0.0
Change (*M*)	-x		+x		+x
Final (*M*)	0.05 - x		x		x

$$K_b = [CH_3COOH][OH^-] / [CH_3COO^-] = 5.6 \times 10^{-10}$$

$K_b = x^2 / (0.05 - x)$

$x = [OH^-] = 5.3 \times 10^{-6}\ M$ $\qquad$ $pOH = -\log(5.3 \times 10^{-6})$

pH = 8.72

c) Addition of 35.0 mL of NaOH. The number of moles of NaOH originally present is

35.0 mL x (0.1 mol NaOH) / (1 L NaOH soln) x (1 L) / (1000 mL) =

$= 3.5 \times 10^{-3}$ mol

The changes of moles

	$CH_3COOH(aq)$ +	$NaOH(aq) \leftrightarrows$	$CH_3COONa(aq) + H_2O(l)$
Initial (mol)	2.5×10^{-3}	3.5×10^{-3}	0
Change (mol)	-2.5×10^{-3}	-2.5×10^{-3}	2.5×10^{-3}
Final (mol)	0	1×10^{-3}	2.5×10^{-3}

Calculations of the pH solution using only the concentration of OH^- ions from the final concentration of NaOH

$[OH^-]$ = $(1.0 \times 10^{-3}\ \text{mol}) / (60.0\ \text{mL}) \times (1000\ \text{mL}) / (1\ \text{L})$

= $0.0167\ M$

pOH = $-\log(0.0167)$

pH = 12.22

Acid base indicators

A substance which changes its color when a titration is at the end point

Example

$$HIn(aq) \leftrightarrows H^{+}(aq) + In^{-}(aq)$$

$K_{in} = [In^{-}][H^{+}] / [HIn]$ $[HIn] / [In^{-}] = [H^{+}] / K_{in}$

$[HIn] / [In^{-}] > 10.0$ color of acid (HIn)

$[HIn] / [In^{-}] < 0.1$ color of base (In^{-})

between 0.1 and 10.0 the color is a combination of two colors

Phenolphtalein

In acid solution = colorless
In base solution = pink
pH range = 8.3 - 10

Solubility equilibria

Solubility product

A product of the molar concentration of the consituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation

Example

$$AgCl(s) \leftrightarrows Ag^{+}(aq) + Cl^{-}(aq)$$

The concentration of solid silver chloride (AgCl) is a constant (heterogeneous reaction)

$K_{sp} = [Ag^{+}]\,[Cl^{-}]$ $\quad$ K_{sp} - solubility product

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

$$K_{sp} = [Mg^{2+}]\,[F^{-}]^2$$

Molar solubility and solubility

Solubility - *the number of grams of a solute in 1 L of a saturated solution (g/L)*

Molar solubility - *the number of moles of a solute in 1 L of a saturated solution (mol/L)*

Example

The solubility of calcium sulfate ($CaSO_4$) is found to be 0.67 g/L. Calculate the value of K_{sp} for calcium sulfate

	$CaSO_4(s) \leftrightarrows$	$Ca^{2+}(aq)$ +	$SO_4^{2-}(aq)$
Initial (*M*)		0	0
Change (*M*)	-s	+s	+s
Equilibrium (*M*)		s	s

The solubility product

$$K_{sp} = [Ca^{2+}][SO_4^{2-}] = s^2$$

The number of moles of $CaSO_4$ dissolved in 1 L of solution

$$(0.67 \text{ g } CaSO_4) / (1 \text{ L soln}) \times (1 \text{ mol } CaSO_4) / (136.2 \text{ g } CaSO_4) =$$

$$= 4.9 \times 10^{-3} \text{ mol/L} = s$$

Calculations of K_{sp}

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

$$= (4.9 \times 10^{-3})(4.9 \times 10^{-3})$$

$$= 2.4 \times 10^{-5}$$

Separation of ions by fractional precipitation

Removing of one type of ion from solution by precipitation, leaving other ions in solution

Precipitation - *to separate a substance in solid form from a solution*

Example

Addition of sulfate ions to a solution containing both potasion (K) and barium (Ba) ions causes $BaSO_4$ to precipitate out

Problem

A solution contains 0.02 *M* Cl^- ions and 0.02 *M* Br^- ions. What concentration of Ag^+ is needed to precipitate AgBr (silver bromide) and AgCl (silver chloride).

Solution

$$AgBr(s) \leftrightarrows Ag^{+}(aq) + Br^{-}(aq)$$

The concentration of Ag^{+} must be exceeded to initiate the precipitation of AgBr

$$K_{sp} = [Ag^{+}][Br^{-}] = 7.7 \times 10^{-13}$$

$$[Ag^{+}] = K_{sp} / [Br^{-}]$$

$$= (7.7 \times 10^{-13}) / (0.02)$$

$$= 3.9 \times 10^{-11}\ \mathrm{M}$$

Thus $[Ag^{+}] > 3.9 \times 10^{-11}$ *M* is required to start the precipitation of AgBr

Similarly, the solubility equilibrium of AgCl is

$$AgCl(s) \leftrightarrows Ag^{+}(aq) + Cl^{-}(aq)$$

The concentration of Ag^+ must be exceeded to initiate the precipitation of AgCl

$$K_{sp} = [Ag^{+}][Cl^{-}] = 1.6 \times 10^{-10}$$

$$[Ag^{+}] = K_{sp} / [Cl^{-}]$$

$$= (1.6 \times 10^{-10}) / (0.02)$$

$$= 8 \times 10^{-9}\ M$$

Therefore $[Ag^+] > 8 \times 10^{-9}\ M$ is needed to initiate the precipitation of AgCl

Common ion effect and solubility

The solubility product is an equilibrium constant, and precipitation of an ionic substance from solution occurs whenever the ion product constant exceeds K_{sp}

Example

$$AgNO_3\,(s) \quad \leftrightarrows \quad Ag^+(aq) \;+\; NO_3^-(aq)$$

The solubility equilibrium of AgCl is

$$AgCl\,(s) \quad \leftrightarrows \quad Ag^+(aq) \;+\; Cl^-(aq)$$

If $AgNO_3$ is added to a saturated AgCl, the increase in $[Ag^+]$ will make the ion product greater than the solubility product

$$Q \quad = \quad [Ag^+]_0\,[Cl^-]_0$$

The effect of adding a common Ag ion, is a decrease in soublility of the AgCl salt in solution

Problem

Calculate the solubility of silver chloride (AgCl) (g/L) in a 6.5×10^{-3} *M* silver nitrate ($AgNO_3$) solution.

$AgNO_3$ is a soluble strong electrolyte (it dissociates completely)

$$\mathit{AgNO_3(s)} \quad \leftrightarrows \quad \mathit{Ag^+(aq)} \quad + \quad \mathit{NO_3^-(aq)}$$

$$6.5 \times 10^{-3}\mathit{M} \qquad\qquad 6.5 \times 10^{-3}\mathit{M}$$

	$\mathit{AgCl(s)}$ $\leftrightarrows$	$\mathit{Ag^+(aq)}$ +	$\mathit{Cl^-(aq)}$
Initial (*M*)		6.5×10^{-3}	0
Change (*M*)	-s	+s	+s
Equilibrium (*M*)		$s + 6.5 \times 10^{-3}$	s

$$K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$$

$$1.6 \times 10^{-10} = (6.5 \times 10^{-3} + s)(s)$$

s = 2.5×10^{-8} *M*

At equilibrium

$[Ag^+]$ = $(6.5 \times 10^{-3} + 2.5 \times 10^{-8})$ = 6.5×10^{-3} *M*

$[Cl^-]$ = 2.5×10^{-8} *M*

Because all the Cl^- ions must come from AgCl, the amount of AgCl dissolved in $AgNO_3$ solution also is 2.5×10^{-8} M. The calculation of the solubility of AgCl

Solibility of AgCl in $AgNO_3$ solution =

= $(2.5 \times 10^{-8}$ mol AgCl) / (1 L soln) x (143.4 g AgCl) / (1 mol AgCl)

= 3.6×10^{-6} g/L

pH and Solubility

The solubility of many substances depends on the pH of the solution

Example

$$Mg(OH)_2(s) \leftrightarrows Mg^{2+}(aq) + 2\ OH^-(aq)$$

Adding OH^- ions shifts the equilibrium from right to left, decreasing the solubility of $Mg(OH)_2$

	$Mg(OH)_2(s) \leftrightarrows$	$Mg^{2+}(aq)$ +	$2\ OH^-(aq)$
Initial (*M*)		0	0
Change (*M*)	-s	+s	+2s
Equilibrium (*M*)		s	2s

$K_{sp} = [Mg^{2+}][OH^-]^2 = 1.2 \times 10^{-11}$

$K_{sp} = (s)(2s)^2 = 4s^3$

$s = 1.4 \times 10^{-4}\ M$

At equilibrium

$[OH^-] = 2 \times 1.4 \times 10^{-4}\ M = 2.8 \times 10^{-4}\ M$

$pOH = -\log(2.8 \times 10^{-4}) = 3.55$

$pH = 14.0 - 3.55 = 10.45$

The dissolution process and the effect of extra H^+ can be summarized as

$$\begin{array}{lrcrcrcl} & & & Mg(OH)_2(s) & \leftrightarrows & Mg^{2+}(aq) & + & 2OH^-(aq) \\ & 2H^+(aq) & + & 2OH^-(aq) & \leftrightarrows & 2H_2O(l) & & \\ \hline \text{Overall} & Mg(OH)_2(s) & + & 2\,H^+(aq) & \leftrightarrows & Mg^{2+}(aq) & + & 2H_2O(aq) \end{array}$$

Complex ion equilibria and solubility

Complex ion

An ion containing a central metal cation bonded to one or more molecules or ions

Transition metals have a particular tendency to form complex ions because they have incompletely filled *d* electronic subshell

Example

$$Co^{2+}(aq) + 4Cl^{-}(aq) \leftrightarrows CoCl_4^{2-}(aq)$$

Formation constant

The equilibrium constant for the complex formation

Example

$$Cu^{2+}(aq) + 4NH_3(aq) \leftrightarrows Cu(NH_3)_4^{2+}(aq)$$

$$K_f = [Cu(NH_3)_4^{2+}] / ([Cu^{2+}] [NH_3]^4)$$

$$= 5.0 \times 10^{13}$$

The very large value of K_f indicates that the complex ion is very stable

Problem

Calculate the molar solubility of AgCl in a 1.0 *M* NH_3 solution.

$$AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq)$$

The Ag^+ ions form a complex ion with NH_3

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

$AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$

$Ag^+(aq) + 2NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq) \qquad K_f = [Ag(NH_3)_2^+] / ([Ag^+][NH_3]^2) = 1.5 \times 10^7$

$AgCl(s) + 2NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq) + Cl^-(aq)$

The equilibrium constant K is the product of the equilibrium constants of individual reactions

$$K = K_{sp}K_f = [Ag(NH_3)_2^+][Cl^-] / [NH_3]^2$$

$$= (1.6 \times 10^{-10})(1.5 \times 10^7)$$

$$= 2.4 \times 10^{-3}$$

Changes in concentrations that result from formation of the complex ion

	$AgCl(s)$	+	$2NH_3(aq)$	$\leftrightarrows$	$Ag(NH_3)_2^+(aq)$	+	$Cl^-(aq)$
Initial (*M*)			1.0		0.0		0.0
Change (*M*)	-s		-2s		+s		+s
Equilibrium (*M*)			(1.0 - 2s)		s		s

After formation a complex ion

$$K = (s)\,(s) / (1.0 - 2s)^2$$

$$2.4 \times 10^{-3} = s^2 / (1.0 - 2s)^2$$

$$s = 0.045\ M$$

$$[Ag(NH_3)_2^+] = 0.045\ M$$