Ex.1

Calculate the amount of solubility in mole/liter of AgCl? $K_{sp} = 1.8\times10^{-10}$

Ex. 2

The amount of solubility of $BaSO_4$ is 1.14×10^{-5}M.Calculate the solubility product constant?

Dissociation Constant

Applying the Ion- Product for Water

Aqueous solutions contain small concentrations of hydronium and hydroxide ion as a consequence of the dissociation.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Or $$H_2O \rightleftharpoons H^+ + OH^-$$

$$K = \frac{[H_3O^+]\,[OH^-]}{[H_2O]^2}$$

$$K[H_2O]^2 = Kw = [H_3O^+][OH^-]$$

At: 25C°

$K_w = 1\times 10^{-14}$

At pure H_2O $[H^+] = [OH^-] = 10^{-7}$

$pK_w = pH + pOH = 14$

$-\log[H^+] = -\log[OH^-] = 7$

$pH = pOH = 7$

Example:

Calculate the hydrogen or hydronium ion concentration in solution contain [OH$^-$] (a). 0.01mole/L, (b) 0. 2× 10^{-9} mole/L, and describe the solution?

Dissociation of weak acid and weak base:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$pK_w = pH + pOH$

$pH = pKw - pOH$

$pH = \frac{1}{2}\, pKa - \frac{1}{2} \log C$

$pOH = \frac{1}{2}\, pKb - \frac{1}{2} \log C$

$pH = pKw - \frac{1}{2}\, pKb + \frac{1}{2} \log C$

$pOH = pKw - \frac{1}{2}\, pKa + \frac{1}{2} \log C$

Example

Calculate the pH value at 25C° of (0.1M) solution (of weak base) tri methyl amine $(CH_3)_3N$? Kb = 5.3×10^{-5}.

Buffer Solutions

A buffer is a mixture of a weak acid and its conjugate base its salt (acidic buffer solution) or a weak base and its conjugate acid its salt (basic buffer solution). That resists changes in pH of a solution, with dilution or with addition of acids or bases.

Example of buffer

Acetic acid / Sodium acetate	CH_3COOH / CH_3COONa	Acidic buffer solution
Formic acid / Sodium formate	$HCOOH$ / $HCOONa$	
Ammonium Chloride / Ammonia	NH_4Cl / NH_3	Basic buffer solution

Calculate the pH of Buffer Solution

A solution containing a weak acid, HA and its conjugates base, A^-, may be acidic, neutral, or basic, depending on the position of two competitive equilibria.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$ka = \frac{[H_3O^+]\,[A^-]}{[HA]} \text{ ----------------- } (1)$$

$[H_3O^+] = [H^+] = Ka \dfrac{[HA]\,acid}{[A^-]\,salt}$ take logarithm and multiply by (-).

$-\log [H^+] = -\log Ka - \log \dfrac{[acid]}{[salt]}$

$pH = pKa + \log \dfrac{[salt]}{[acid]}$

$$A^- + H_2O \rightleftharpoons OH^- + HA$$

$$kb = \frac{[OH^-]\,[HA]}{[A^-]} = \frac{Kw}{Ka} \text{ ---------------- } (2)$$

$[OH^-] = Kb \dfrac{[A^-]}{[HA]}$ take logarithm and multiply by (-).

$-\log [OH^-] = -\log Kb - \log \dfrac{[base]}{[salt]}$

$pOH = pKb + \log \dfrac{[salt]}{[base]}$

If the first equilibrium lies farther to the right than the second, the solution is acidic. If the second equilibrium is more favorable, the solution is basic.

These two equilibrium-constant expressions show that the relative concentrations of the hydronium and hydroxide ions depend not only on the magnitudes of Ka and Kb but also on the ratio between the concentrations of the acid and its conjugate base.

So that

The ***Hiderson-Hasselbalch Equations are:***

$$pH = pKa + \log \frac{[Salt]}{[Acid]}$$

$$pOH = pKb + \log \frac{[salt]}{[base]}$$

The effect of Added Acids or Bases

The following example illustrate resistance to pH change after addition of small amounts of strong acid or base.

a) Addition of HCl to converts part of the CH_3COO^- to CH_3COOH.

$$CH_3COO^- + H_3O^+ \rightleftharpoons CH_3COOH + H_2O$$

b) Addition of NaOH to converts part of the CH_3COOH in the solution to CH_3COO^-

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

The result of the above is the buffer don't maintain pH at an absolutely constant value, but changes in pH are relatively small when small amounts of acid and base are added.

The resistance to pH change depends on the buffer capacity.

Buffer capacity: Is the number of moles of strong acid or strong base that 1L of the buffer can absorb without changing pH by more than 1.

The capacity of a buffer depends not only on the total concentration of the two buffer components but also on their concentration ratio.

Buffer capacity decreases fairly rapidly as the concentration ratio of acid to conjugate base becomes larger or smaller than unity. For this reason the pKa of the acid chosen for a given application should lie within ±1 unite of the desired pH for the buffer to have a reasonable capacity.

So, the higher value of buffer capacity when the salt concentration is equal to the acid or base concentration in this value become:

$$pH = pKa$$

$$pOH = pKb$$

Eample1.

Calculate the pH value of buffer solution which prepare from acetic acid and conjugated salt in 0.1M? Ka = 1.8 $\times 10^{-5}$.

Example 2.

Calculate the pH value of buffer solution contain 10 mL acetic acid in 0.1N and 20 mL sodium acetate in 0.1N? pKa = 4.74.

The common ion effect:

The ion which present in both the crystalline precipitate and its solution is known as the common ion. The solubility(s) of precipitate (ppt) is decrease if sufficient amount of a common ion added to the solution.

e.g. $AgCl_{(S)} \rightleftharpoons Ag^+ + Cl^-$ ---------------- (1)

$AgNO_3 \longrightarrow Ag^+ + NO_3^-$ ---------------(2)

Common ion

Revers word ←

e.g: . $AgCl_{(S)} \rightleftharpoons Ag^+ + Cl^-$ ---------------- (3)

$KCl \longrightarrow K^+ + Cl^-$ -----------------(4)

Common ion

According to Le Chatelier principle the reaction (1) & (3) are forced to the left .

Example: Calculate the molar solubility of CaF_2 in : (a) water

(b) 0.01M $CaCl_2$, (c) 0.01M NaF solutions, since the

Ksp of $CaF_2 = 4\times10^{-11}$.

(a) In water . $CaF_{2\,(S)} \rightleftharpoons Ca^{+2} + 2F^-$

S 2S Solute : S

$Ksp = [Ca^{+2}]\,[2F^-]^2$

$4\times10^{-11} = S \times (2S)^2 4\times10^{-11} = 4S^3$

$S = \sqrt[3]{\frac{4\times10^{-11}}{4}} = 2.1\times10^{-4}$ mol/L

(b) . In the presence of 0.01M $CaCl_2$

$$CaF_{2\,(S)} \rightleftharpoons Ca^{+2} + 2F^{-}$$

$$S \qquad 2S$$

$$CaCl_2 \longrightarrow Ca^{+2} + 2Cl^{-}$$

$$0.01 \qquad 2\times 0.01$$

$$\therefore Ksp = [\,\underset{CaCl_2}{\underset{\downarrow}{Ca^{+2}}} + \underset{CaF_2}{\underset{\downarrow}{Ca^{+2}}}]\,[\,F^{-}]^2$$

Neglect → very small

$$4\times10^{-11} = (0.01 + \underset{\text{neglect}}{\underline{S}})\,(2S)^2$$

$$4S^2 = 4\times 10^{-9}$$

$$S = 3.2\times 10^{-5}\ \text{mol}/L$$

(C) 0.01 M NaF

$$CaF_{2\,(S)} \rightleftharpoons Ca^{+2} + 2F^{-}$$

$$S \qquad 2S$$

$$NaF \longrightarrow Na^{+} + F^{-}$$

$$0.01 \qquad 0.01$$

$$Ksp = [Ca^{+2}]\,[(2F^{-})^2 + F^{-}]$$

$$4\times 10^{-11} = (S)\,[\,\underset{\text{neglect}}{(2S)^2} + 0.01] \qquad 2S << 0.01$$

$$\therefore\ 4\times 10^{-11} = S\times (0.01)$$

$$4\times 10^{-11} = S\times 0.01$$

$$S = 4\times 10^{-9}\ \text{mol}/L$$