# CHEMICAL EQUILIBRIUM

Buffer solutions, salt hydrolysis& solubility product . Buffer solutions:

1. Solution whose p^H does not alter on the addition of small quantities of a strong acid or a strong base or any amount of water is called a buffer solution.Buffer solutions have reserve acidity and alkalinity

2. Acidic buffer solution can be prepared by mixing a weak acid and its salt with a strong base (or) excess of weak acid and strong base.

   Eg. $CH_3COOH + CH_3COONa$
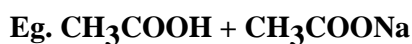
3. Basic buffer can be prepared by mixing weak base and its salt with a strong acid (or) excess of weak base with a strong acid.

   Eg. 1) $NH_4OH + NH_4Cl$

   2) $2M\ NH_4OH + 1M\ HCl$

4. Ammonium acetate$[CH_3COO\ NH_4]$ solution can act as a neutral buffer solution.

5. working of acid buffer;

   $CH_3COOH + CH_3COONa$ aq. solution containts CH_3COOH, H_3O^+ , CH_3COO^- and Na^+ ions.

   i. When some H^+ ions are added the reaction taking place is $CH_3COO^- + H^+ \rightleftharpoons$

   CH_3COOH, Hence the CH_3COO^- ion maintains P^H as constant and constant acidic nature.

   ii. When some OH^- ions are added, the reaction taking place is

   $OH^- + CH_3COOH \rightarrow CH_3COO^- + H_2O$. Hence CH_3COOH maintains the P^H as constant.

6. working of basic buffer;

   $NH_3 + NH_4Cl$ aq. solution contains NH_4OH, NH_4^+, OH^- and Cl^- ions.

   i. If some OH^- ions are added, then the reaction is $NH_4^+ + OH^- \rightleftharpoons NH_4OH$. NH_4^+

   removes OH^- ions and p^H remains constant.

   i. If some H^+ ions are added, then the reaction is $NH_4OH + H^+ \rightleftharpoons NH_4^+ + H_2O$.

Hence NH_4OH removes added H^+ ions as water and P^H remains constant.

7.   The P^H of an acidic buffer is given by Henderson equation

$$pH = pK_a + \log\frac{[salt]}{[acid]} \quad \textbf{(or)} \quad P^H = P^{K_a} + \log\left[\frac{N_{salt}.V_{salt}}{N_{acid}.V_{acid}}\right]$$

8.   The P^{OH} of a basic buffer is given by

$$pOH = pK_b + \log\frac{[salt]}{[base]} \quad \textbf{or} \quad P^{OH} = P^{K_b} + \log\left[\frac{N_{Salt}.V_{Salt}}{N_{base.}V_{base}}\right]$$

P^H of a basic buffer = $14 - P^H$

9.   Buffer capacity is defined as the number of moles of acid or base added per 1 litre of buffer solution to change its P^H by 1 unit.

$$\phi = \frac{\text{no of moles of Acid}(H^+)(\text{or})\ \text{Base}(OH^-)\text{added to one litre buffer solution}}{\text{Change in pH}(\Delta pH)}$$

10.   An acidic buffer solution has maximum buffer capacity when its $P^H = P^{Ka}$ or

when [salt]/[acid] = 1

For basic buffer, buffer capacity is maximum when $P^{OH} = P^{Kb}$ (or) $P^H = 14 - P^{Kb}$ (or)

[salt]/[base] = 1

11.   Buffer solutions are useful in Chemical analysis, Industrial synthetic reactions, enzyme catalysed reactions , biochemical processes and water softening.

12. $HCO_3^- + CO_3^{2-}$ maintains the pH of blood (7.36 to 7.42) as constant.

SALT HYDROLYSIS:

Salt hydrolysis is the phenomenon in which the cation (or) anion of the salt (or) both will react

with water to produce either OH^- ions (or) H^+ ions (or) both in aqueous solution. Salt

hydrolysis is the reverse of neutralisation.

i.Cations of strong bases & anions of strong acids are very weak and they are unable

to   dissociate water

ii.Cations of weak acids and anions of weak bases are strong and react with water.

$B^+ + HOH \rightleftharpoons BOH + H^+$ -Cationic   hydrolysis

$A^- + HOH \rightleftharpoons HA + OH^-$ -Anionic   hydrolysis
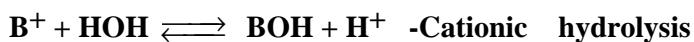
1. Salts of strong acids and strong bases like NaC*l*, KC*l* etc., do not undergo hydrolysis.

   Their aqueous solutions are neutral, with $p^H = 7$

   3.Salts of weak acids and strong bases like CH_3COONa,NaCN, Na_2CO_3, KCN, Na_2S etc.,

   undergo anionic hydrolysis. Their aqueous solutions are alkaline. The p^H of their solutions is

   greater than 7.

   For such salts, the hydrolysis constant, $K_h = K_w/K_a$

3. Salts of weak bases and strong acids like NH_4Cl, $CuSO_4$, $FeCl_3$, $MgCl_2$, $CaSO_4$ etc., undergo

   cationic hydrolysis. Their aqueous solutions are acidic. The p^H of the solution is less than 7.

   For such salts the hydrolysis constant $K_h = K_w/K_b$

4. Salts of weak acids and weak bases like CH_3COONH_4 ,$(NH4)_2CO_3$ etc., undergo both cationic

   and anionic hydrolysis . In the case of ammonium acetate ,the acid and base are equally strong.

   Hence ammonium acetate solution is neutral.

   I .If the acid is weaker as in the case of $(NH_4)_2CO_3$ and NH_4CN, then the solution is slightly

   alkaline.

   ii If the base is weaker, the solution is slightly acidic. In Ammonium phosphate, the solution

   is slightly acidic.

   iii.The nature of such a solution depends on relative values of Ka and Kb.

   If $K_a = K_b$ ------------ Neutral

   If $K_a > K_b$ ------------ Acidic

   If $K_a < K_b$ ------------ Basic

   iv.For salts of weak acids and weak bases $K_h = K_w/K_aK_b$

COMMON ION EFFECT & SOLUBILITY PRODUCT:

1. **The supression of the dissociation of weak electrolyte by the addition of a strong electrolyte having some common ion is called common ion effect.**

   Eg..The dissociation of week acid CH_3COOH is decreased by the addition of HCl (H^+ ion is common) or by the addition of CH_3COONa (CH_3COO^- is the common ion) .
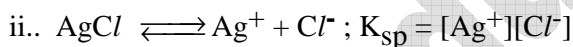
2. **The product of the concentration of ions in a saturated solution of an electrolyte at a given temperature is called as Solubility product.**

3. **Solubility product is not ionic product under all conditions but only when the solution is saturated. It is denoted by K_{sp}. The expression of K_{sp} for some electrolytes are given below:**

   i.Consider the dissociation of an electrolyte, $A_x B_y$ as : $A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$

   Applying law of mass action, $K = \dfrac{[A^{y+}]^x[B^{x-}]^y}{[A_xB_y]}$

   In saturated solution, $[A_xB_y] = K^1$ (constant)

   Thus $[A^{y+}]^x[B^{x-}]^y = K[A_xB_y] = KK^1 = K_{sp}$ (constant)

   ii.. $AgCl \rightleftharpoons Ag^+ + Cl^-$; $K_{sp} = [Ag^+][Cl^-]$

   iii. $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$; $K_{sp} = [Mg^{2+}][OH^-]^2$

   iv.$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$; $K_{sp} = [Al^{3+}][OH^-]^3$

4. Solubility product of the electrolyte has a constant value at a particular temperature and it is the highest limit of ionic product of the electrolyte in solutions.

5. **For electrolyte of the type AB: If solubility of salt is 'S' its Ksp = S^2 (or) S = $\sqrt{Ksp}$**

   eg : $AgCl$, AgI, $BaSO_4$, $PbSO_4$

6. **For Electrolytes of the type AB_2 (or) A_2B :If the solubility of the salt is S mole /lit, then**

   $K_{SP} = 4S^3$ & $S = \sqrt[3]{\dfrac{K_{SP}}{4}}$. **Eg. Ag_2CO_3, Ag_2CrO_4 ,$PbCl_2$ etc**

7. **For Electrolyte of the type AB_3 : If solubility of the salt in saturated solution is S mole/lit**

   Ksp = $S(3S)^3 = 27S^4$ or S = $\sqrt[4]{Ksp/27}$

8. **Electrolyte of the type A_2B_3 : If the solubility is S mole / lit , Ksp = $(2s)^2 (3s)^3 = 108 s^5$**

   Eg : Ag_2S_3, Sb_2S_3, $Ca_3(PO_4)_2$

9. **The concept of solubility product helps in predicting the formation of a precipitate. In general, if**

   i. ionic product < K_{sp}, no precipitate is formed and the solution is unsaturated.

   ii.If ionic product > K_{sp}, a precipitate is formed and the solution is supersaturated.

   iii.If Ksp = ionic product then the solution saturated and that is the point where ppt just starts.

10. Soaps are sodium or potassium salts of higher fatty acids. As the solubility of soap is not much, any soap present in the solution is salted out by the addition of sodium chloride, which increase the conc. of Na^+ ions. Thus, the ionic product $[RCOO^-]$ $[Na^+]$ exceeds the solubility product of soap and, therefore, soap precipitates out from the solution. This is called salting out of soap

11. In Qualitative Analysis, the separation and identification of various basic radicals into different groups is based on (a) solubility product principle and (b) common ion effect.

    Eg. The Ksp values of sulphides of IIA is lower than that of IVA group. Hence low ion concentration of S^{-2} is sufficiant for the ppt of IIA group sulphides. The low conc of S^{-2} can be achieved in acidic medium where ionisation of H_2S is suppressed.

    But to get ppt of IVA group sulphides, high concentration of S^{-2} ions is required which can be done by changing the medium from acidic to alkaline.

12. Purification of common salt. Saturated solution of impure common salt is prepared and insoluble impurities are filtered off. HC*l* gas is passed through this solution.

    $NaCl \rightleftharpoons Na^+ + Cl^-$, $\qquad$ $HCl \rightleftharpoons H^+ + Cl^-$

    The concentration of Cl^- ions increases due to ionization of HC*l*. Thus, the ionic product $[Na^+]$ $[Cl^-]$ exceeds the solubility product and pure sodium chloride precipitates out from the solution.