Class : Chemistry
Class : XI

Kannada

Ionic Equilibrium

- The equilibrium established between the unionised molecules and the ions in the solution of weak electrolytes is called ionic equilibrium e.g.
- $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Non-electrolytes

A solution of solute like urea, glucose, etc. does not contain any ion hence the solution is bad conductor of electricity. Such solutes art termed as non-electrolytes.

Electrolytes

Chemical substances which can conduct electricity in their aqueous state or in molten state are called electrolytes. The conduction of current through electrolyte is due to the movement of ions.

1. Strong Electrolytes

- Electrolytes which dissociate almost completely into constituent ions in aqueous solution are known as strong electrolytes, e.g. all salts (except $HgCl_2, CdBr_2$), mineral acids like HCl, H_2SO_4, HNO_3, etc., and bases like $NaOH, KOH$, etc.

2. Weak Electrolytes

- Electrolytes which dissociate to a lesser extent in aqueous solution are called weak electrolyte. All organic acids (except sulphonic acids), ant bases like NH_3, NH_4OH, amines, H_3BO_3, HCN etc.

Degree of Ionisation or Degree of Dissociation (α)

- It is the fraction of the total number of molecules which ionise (dissociate) into constituent ions.
- $\alpha = \frac{\text{number of molecules ionised or dissociated}}{\text{total number of molecules taken}}$
- for strong electrolytes,
- $\alpha = 1$
  $\alpha < 1$
- For weak electrolytes Values of the degree of dissociation (α) depends upon the following factors:
  (i) nature of solute
- (ii) nature of solvent
- (iii) concentration
- (iv) temperature
- (v) addition of other species.

Calculation of the Degree of Dissociation (α) from Density Measurement

- $\alpha = \frac{D-d}{d(y-1)}$
- where,
  $y =$ number of moles of product from one mole of reactant,
- $D =$ theoretical vapour density and
- $d =$ observed vapour density
- Now,
  molecular mass $= 2 \times VD$
- $\alpha = \frac{M_c - M_o}{M_o}$

- where, M_c = calculated molecular weight and
- M_o = observed molecular weight.

Ostwald's Dilution Law

- According to Ostwald, the degree of dissociation (α) of weak electrolyte is inversely proportional to the square root of the molar concentration of the solution.
- $K = \frac{C\alpha^2}{1-\alpha}$
- If α is very small $1 - \alpha = 1 \Rightarrow K = C\alpha^2$ or
- $\alpha = \sqrt{\frac{K}{C}} \Rightarrow \alpha \propto \frac{1}{\sqrt{C}}$
- Here, K is dissociation constant and C is molar concentration of the solution.

Acids and Bases

- Earlier definitions of acids and bases was given by Robert $B_{0y}l_e$, wh classified them on the basis of their properties. According to him, which? are the substances, which have sour taste, turns blue litmus acing liberate hydrogen with metals, conduct electricity in aqueous solution, and neutralise bases.
- Bases are the substance which have bitter taste, turns red litmus blue soapy to touch, conduct electricity in aqueous solution and neutralise, acids.

Arrhenius Concept of Acids and Bases

- Acid is a chemical substance which dissociates in aqueous solution to give hydrogen ions (H^+)or hydronium ions (H_3O^+).
  Base is a chemical substance which dissociates in aqueous solution to give hydroxyl ions (OH^-). Arrhenius theory fails to explain the acidic and basic behaviour in non-aqueous solutions. It cannot explain the acidic character of $AlCl_3$ BF_3 and basic character of NH_3, PH_3 and free $H^+$and OH^-ions do not exist in water:

Bronsted Concept of Acids and Bases

- Acid is a chemical substance that can donate a proton $(H^+)$to some other substance and a base is a chemical substance that can accept a proton from other substance. Thus, an acid is a proton donor (protogenic) and a base is proton acceptor (protophilic).
- [Strong acid has weak conjugate base and weak acid has strong conjugate base. Strong base has weak conjugate acid and weak base has strong conjugate acid.
- $HClO_4$ is the strongest while HCN is the weakest hydracid known. CsOH is the strongest base known.]
- Amphoteric or amphiprotic substance or ampholytes are the substances which act as an acid as well as a base, e.g. water acts as $^{\text{all}}$ acid with NH_3 and a base with acetic acid.
- The order of acidic strength of some acids is
- $HClO_4 > HI > HBr > H_2SO_4 > HCl > HNO_3$

Relative Strength of Acids and Bases

- Are after the K_a value of an acid (or lesser the pK_a), stronger is the gad Similarly, greater the K_b (or lesser the pK_b) of a base, stronger is the base.
- $\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} = \frac{\text{strength of acid } (HA)_1}{\text{strength of acid } (HA)_2}$
  $\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}} = \frac{\text{strength of base } (BOH)_1}{\text{strength of base } (BOH)_2}$
- **Leveling effect** The acids like $HClO_4, H_2SO_4, HNO_3$, etc. react with water almost completely to form H_3O^+ions. Therefore, all the strong acids in aqueous solutions appear equally strong and their relative strengths in aqueous

solution cannot be compared. Since, $H_3O^+$is the strongest acid in water, the strength of above acids comedown to the level of H_3O^+strength in water. Similarly, strong bases like NaOH, KOH, $Ba(OH)_2$ come down to the strength of OH^-ion in water. This is called levelling effect.

- Bronsted concept fails to explain acidic nature of BF_3 and $AlCl_3$.

Lewis Concept of Acids and Bases

- Lewis acid is a chemical substance which can accept a pair of electrons, e.g.
  (i) Molecules with incomplete octet of central atom like BF_3, $AlCl_3$, $BeCl_2$, $MgCl_2$ etc.
  (ii) Simple cations like Ag^+, Na^+etc.
  (iii) Molecules in which the central atom has vacant d-orbital, e.g. SF_4, $SnCl_4$, PF_3, etc.
- Lewis base is a chemical substance which can donate a pair of electrons, e.g. etc.
- (i) Negatively charged species like CN, $\bar{C}$, OH, etc.
- (ii) In coordination complexes, the ligands act as Lewis base.

Limitations of Lewis Concept

- (i) It does not explain the behaviour of protonic acids such as HC H_2SO_4, HNO_3 etc.
- (ii) It does not predict the magnitude of relative strength of acids ant bases.
- All Bronsted-Lowry's acids are Lewis acids while all Lewis acids need not be Bronsted-Lowry's acids.

The Ionisation Constant of Water

- Ionic product is the product of the concentration of hydronium ions and hydroxyl ion in pure water, which remains constant at a particular temperature. It is symbolized by K_w. At 298 K, ionic product of wate (K_w) is given as $K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$ mol^2 L^{-2}.
  The value of K_w increases with increase in temperature.
- We can distinguish acidic, neutral and basic aqueous solutions by th relative value of the $H_3O^+$and OH^-concentration.
  Acidic : $[H_3O^+] > [OH^-]$
- Neutral : $[H_3O^+] = [OH^-]$
- Basic : $[H_3O^+] < [OH^-]$

The pH Scale

- pH is defined as the negative logarithm of hydrogen ion concentration
- the negative logarithm of had $[H^+] = 10^{-pH}$
- Total $[H^+]$or $[OH^-]$in a mixture of two strong acids or bases $= \frac{\Sigma NNV}{\Sigma V}$.
- Similarly, negative logarithm of hydroxyl ion concentration is pOH.
- $pOH = -\log [OH^-]$
- As we know $K_w = [H^+][OH^-] = 1 \times 10^{-14}$ (at 298 K)
- $-\log K_w = -\log [H^+] - \log [OH^-] = 14$
  $\Rightarrow pK_w = pH + pOH = 14$(at 298 K)

The pH scale (at 25°C)

H_3O^+	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{10}
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	11

Acidic character increases Neutral Basic character increases

- pH value of an acid having H^+concentration less than 10^{-7}, is always In between 6 and 7. For 10^{-8} NHCl solution, it is 6.958 . Similarly, for 10^{-8}NaOH solution, the pH is 7.04 (because basic solutions always have pH greater than 7.)
- pH of solution is accurately measured by pH meter or emf method or froughly by pH paper or indicator paper. ΓpH can be zero in 1 NHCl solution or it can be negative for more concentrated solution like $2\ \text{N}, 3\ \text{N}, 10\ \text{N}$ etc. pH range for some important substances are:
- Gastric juice $= 1 - 3$
  Vinegar $= 2.4 - 3.4$
  Tears $= 7.4$
  Human urine $= 4.8 - 8.4$
  Blood plasma $= 7.3 - 7.4$
  Boiled water $= 6.5625$

Dissociation Constant of Weak Acid and Weak Base

- Let us consider the dissociation of weak acid (HA) as
  Initially at equilibrium
- ∵ Dissociation constant of an acid, of an acid
  $K_a = \frac{[\text{H}^+][A^-]}{[\text{H}A]} = \frac{C\alpha^2}{(1-\alpha)}$
- Similarly, for the dissociation of a weak base BOH as
- $\text{BOH} \rightleftharpoons B^+ + \text{OH}^-$
- Dissociation constant of the base
  $K_b = \frac{[\text{B}^+][OH^-]}{[\text{BOH}]} = \frac{C\alpha^2}{(1-\alpha)}$

Relation between Acid Dissociation (K_a) and Base Dissociation (K_b) Constants

- K_a and K_b are related to each other by the following formula,
- $K_a \times K_b = K_w$

Dissociation Constant for Polyprotic Acids and Bases

- For a tribasic acid,
  $\text{H}_3\text{PO}_4 \underset{\text{K}_{a_1}}{\rightleftharpoons} \text{H}^+ + \text{H}_2\text{PO}_4^-$
- $\text{H}_2\text{PO}_4^- \underset{\text{K}_{a_2}}{\rightleftharpoons} \text{H}^+ + \text{HPO}_4^{2-}$
  $\text{HPO}_4^{2-} \underset{\text{K}_{a_3}}{\rightleftharpoons} \text{H}^+ + \text{PO}_4^{3-}$
- The overall dissociation constant (K) is given as
- $K = K_1 \times K_2 \times K_3$
- where, $K_1 > K_2 > K_3$
- pH of H_2PO_4^-in aqueous medium $= \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2}$
  pH of HPO_4^{2-} in aqueous medium $= \frac{\text{p}K_{a_2} + \text{p}K_{a_3}}{2}$
- Similarly, for a dibasic acid like H_2CO_3, $\text{pH} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2}$
- Similarly, in case of a conjugate acid-base pair, $K_w = K_a \times K_b$ by taking negative logarithm of both sides of ths equation, then pK values of conjugate acid and base are related to eatit other by the equation

- $pK_a + pK_b = pK_w = 14$(at 298 K)
- The extent of dissociation of an acid depends on the strength and polarity of the H · A bond.
- (a) As the size of A increases down the group, H-A bond strength decreases and so the acid strength increases.
- e.g., → Size increases
- ⟶ Acid strength increases
- (b) As the electronegativity of A increases, the strength of the acid also increases.
- e.g., → Electronegativity of A increases

Common Ion Effect

- It is defined as the suppression of the dissociation of a weak electrolyte by the addition of a strong electrolyte having some common ion, e.g. degree of dissociation of ammonium hydroxide decreases in the presence of ammonium chloride.

  $NH_4OH \rightleftharpoons NH_4^+ + OH^-$
- $NH_4Cl \longrightarrow \underset{\text{Common ion}}{NH_4^+} + Cl^-$
- According to Le-Chatelier principle, because of the presence of common ion, degree of dissociation of NH_4OH decreases.

  Common ion effect is used in

  (i) purification of common salt.

  (ii) salting out of soap.

  (iii) qualitative analysis.
- Group II radicals are precipitated out in the presence of HCl which suppress the S^{2-} ion concentration; which is just sufficient to precipitate only group II radicals. Similarly in group III, NH_4OH is added in presence of NH_4Cl to avoid the precipitation of group V radicals.

Isohydric Solutions

- If the concentration of the common ions in the solution of two electrolytes, e.g. OH^-ion concentration in $Ca(OH)_2$ and $Ba(OH)_2$ solutions, is same then on mixing them there is no change in degree of dissociation of either of the electrolytes. Such solution are called isohydric solutions.

Salts

- These are the product of reaction between an acid and a base.
- This reaction is called neutralisation reaction.

Types of Salts

- (a) **Normal salts** These are obtained by complete neutralisation of an acid with a base, e.g. $NaCl, K_2SO_4$ etc.

  (b) **Acidic salts** These are formed by incomplete neutralisation of polybasic acids. e.g. $NaHCO_3, Na_2HPO_4$ etc.

  (c) **Basic salts** These are formed by incomplete neutralisation of polyacidic base, e.g. $Mg(OH)Cl, Bi(OH)_2Cl$, etc.

  (d) **Double salts** These are formed by the combination of simple salts and exist only in solid state, e.g. Mohr salt or format ammonium sulphate $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$, alum etc. 4,

  (e) **Complex salts** These are formed by the combination of simple salts or molecular compounds. These are stable in solid state al well as in solutions.

  The properties of their solutions are different from the properties of substances from which they have been constituted.

  (f) **Mixed salts** These salts furnish more than one cation or more than one anion when dissolved in water, e.g. $Ca(OCl)Cl, NaKSO_4$ etc.

Salt Hydrolysis

- Salts are strong electrolytes and on dissolution in water split up into ions which react with H^+or OH^-ions furnished by water yielding acidic or basic solution. The process is known as salt hydrolysis.

Salt of	Example	Kh Hydrolysis of Solution	Degre of Hydrolysis	pH of solution
Weak acid and strong base	CH_3COONa	$\frac{K_w}{k_a}$	$\sqrt{\frac{K_w}{K_a \cdot C}}$	$\frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log\ C$
Strong acid and weak base	NH_4Cl	$\frac{K_w}{K_b}$	$\sqrt{\frac{K_w}{K_b \cdot C}}$	$\frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log\ C$
Weak acid and weak base	CH_3COONH_4	$\frac{K_w}{K_s \cdot K_b}$	$\sqrt{\frac{K_w}{K_a \cdot K_b}}$	$\frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$
Strong acid and strong base	NaCl	Does not undergoes hydrolysis		

- Aqueous solution of salt of strong acid and strong base is neutral. Aqueous solution of salt of a weak acid and a strong base is alkaline due to anionic hydrolysis, and aqueous solution of salt of strong acid and a weak base is acidic due to cationic hydrolysis.
- With dilution degree of hydrolysis increases. Hydrolysis is a reverse process of neutralisation.

Buffer Solution

- Solution which resists the change in its pH value by addition of a small amount of acid or a base, is called buffer solution.

  (a) **Acidic buffer** They have pH value < 7, e.g. CH_3COOH/CH_3COONa, boric acid/borax.
- (b) **Basic buffer** They have pH value > 7
- e.g. NH_4OH/NH_4Cl
- Buffer system present in blood is $H_2CO_3 + NaHCO_3$.

Henderson-Hesselbalch Equation

This equation is used to calculate the pH of a buffer solution.

(i) For acidic buffer,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{ salt }]}{[\text{ acid}]}$$

(ii) For basic buffer,

- $\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$

  and $\text{pH} = 14 - \text{pOH}$
- Here, $\text{p}K_a = -\log\ K_a, \text{p}K_b = -\log\ K_b$ and K_a and K_b are dissociation constants of acid and base. [salt], [acid] and [base] represent molar concentrations of salt, acid and base respectively.

If addition of a strong acid or base changes the pH of a buffer by/unit, the buffer solution is assumed to be destroyed, i.e.

- New pH $= \mathrm{p}K_a \pm 1$
- This means the ratio,
- $\frac{[\text{ salt }]}{[\text{ acid}]}$ or $\frac{[\text{ salt }]}{[\text{ base}]} = 10$ or $\frac{1}{10}$

Buffer Capacity

- It is defined as the number of moles of acid or base added in 1 L of solution to change the pH by unity. Buffer capacity (ϕ)
- capacity (ϕ)
  $= \frac{\text{number of moles of acids or base added to 1 L of buffer}}{\text{change in pH}}$

Solubility Product

- It is defined as the product of the concentrations of the ions of the the ions produced by the dissociation of one mole of the salt if denoted by $K_{\text{sp.}}$. Consider the dissociation of an electrolyte A_xB,
- $A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$
  $K_{\text{sp}} = [A^{y+}]^x[B^{x-}]^y$

Application of Solubility Product

1. The concept of K_{sp} helps in predicting the formation th precipitate. In general if

(i) Ionic product $< K_{\text{sp}}$, no ppt is formed.

(ii) Ionic product $> K_{\text{sp}}$, ppt is formed.

(iii) Ionic product $= K_{\text{sp}}$, the reaction is at equilibrium.

2. In predicting the solubility of a sparingly soluble salt

$$\underset{s \text{ mol/L}}{A_xB_y} \rightleftharpoons \underset{xs}{xA^{y+}} + \underset{ys}{yB^{x-}}$$

$$K_{\text{sp}} = x^x \cdot y^y \cdot s^{x+y}$$

- Knowing the values of K_{sp}, x and y, the solubility of the salt can be computed.
- For salts of the type AB: $K_{\text{sp}} = s^2$ or $s = K_{\text{sp}}$
- For salts of the type AB_2: $K_{\text{sp}} = 4s^3$ or $s = \left(\frac{K_{\text{sp}}}{4}\right)^{\frac{1}{3}}$
- For salts of the type AB_3: $K_{\text{sp}} = 27s^4$ or $s = \left(\frac{K_{\text{sp}}}{27}\right)^{\frac{1}{4}}$
- K_{sp} of AgI is lower than that of AgCl. So, the former gets precipitated in preference to later. Distinction Between Solubility Product and Ionic Product

Solubility product	**Ionic product**
1. It is the product of the ionic any concentration of the solution. It is applicable only to the saturated solutions	It is the product of the ionic concentration at concentration of the solution It is applicable to all types of solutions

Acid-Base Indicator

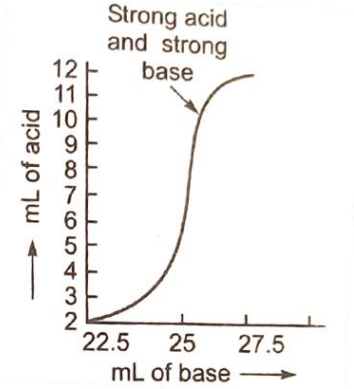
- An acid-base indicator is a substance which possesses one colour acid solution and altogether different colour in alkaline medium or th: substance which shows colour change with change in pH. The poin where the indicator

shows a sudden change in colour during the titration is called end point. End point is the point at which the reaction is observed to be complete.

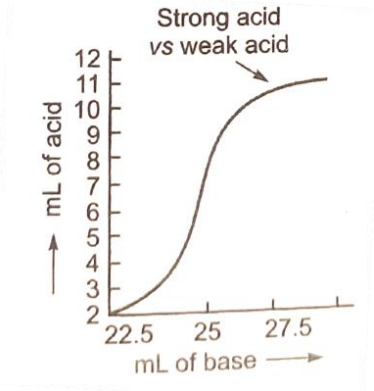
- Theory of indicators
  (i) Ostwald theory
  (ii) Quinonoid theory

Titration Curves and Indicator Used

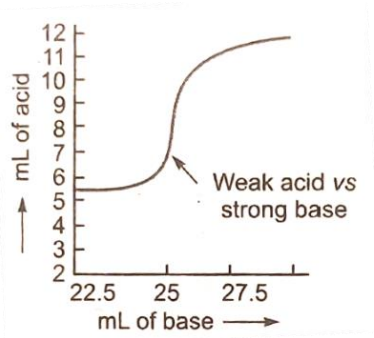
(a) Titration curve for the neutralisation of strong acid vs strong base pH curve of strong acid (say HCl) and strong base (say NaOH) is vertical over almost the pH range 4-10. So, the indicators phenolphthalein (pH range 8.3 to 10.5), methyl red (pH range 4.4-6.5 and methyl orange (pH range $3.2-4.5$) are suitable for such a titration.



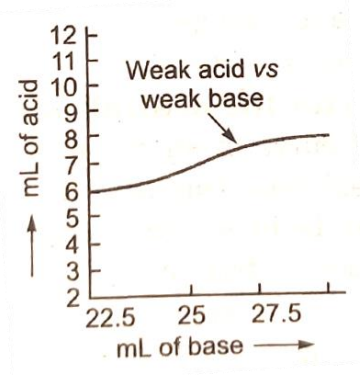
(b) Titration curve for the neutralisation of strong acid *vs* weak base pH curve of strong acid (say HCl or H_2SO_4 or HNO_3) with a weak base (say NH_4OH) is vertical over the pH range of 4 to 7 . So the indicators methyl red and methyl orange are suitable for such a titration.



(c) Titration curve for the neutralisation of weak acid strong base pH curve of weak acid (say CH_3COOH_{or} oxalic acid) and strong base (say NaOH) is vertical over the approximate pH range 7 to 11 . So, phenolphthalein is the suitable indicator for such a titration.



(d) Titration curve for the neutralisation of weak acid vs weak base pH curve of weak acid and weak base indicates that there is no vertical part and hence, no suitable indicator can be used for such a titration.



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