

Ionic Equilibrium

ARRHENIUS THEORY OF IONISATION : On the basis of colligative properties of solutions of salts, acids and bases, Arrhenius proposed the theory of ionisation i.e. splitting of these substances into ions in solution. It is reversible process, affects electrical conductivity, colligative properties like depression in freezing point, elevation in boiling point, lowering of vapour pressure, osmotic pressure.

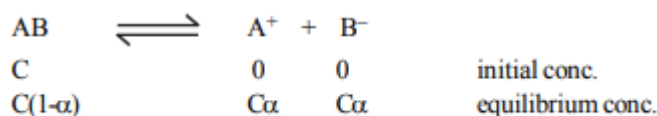
DEGREE OF IONISATION OR DISSOCIATION (α) : The fraction of the total number of molecules which is ionised at the equilibrium state is known as degree of ionisation or dissociation.

$$\alpha = \frac{\text{Number of moles ionised}}{\text{Total number of moles}}$$

FACTORS AFFECTING IONISATION OR DISSOCIATION :

1. **Nature of electrolytes** : The stronger the electrolyte, the more is the ionisation and vice versa.
2. **Nature of solvent** : The more the dielectric constant of solvent, the more is the ionisation.
3. **Concentration** : The lesser the concentration, the more is the ionisation.
4. **Temperature** : The higher the temperature, the more is the ionisation.
5. **Solvation** : The more the solvation, the more is the ionisation.
6. **Presence of the ions in the solution** : Ionisation decreases in presence of common ions.

OSTWALD'S DILUTION LAW : At a given temperature, the degree of ionisation or dissociation (α) of weak electrolytes increases with dilution and law of mass action can be applied to them.



$$\text{Ionisation constant } K = C\alpha^2$$

$$\therefore \alpha = \sqrt{\frac{K}{C}} \quad \alpha \propto \sqrt{\frac{1}{C}}$$

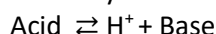
Concentration of A⁺ or B⁻ = C α

α approaches unity with dilution.

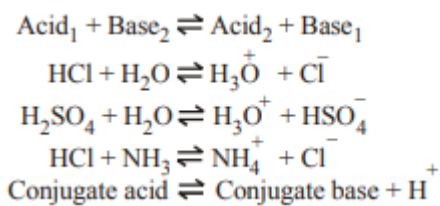
ACIDS AND BASES :

1. **Arrhenius concept** : An **acid** is a substance that dissociates to give hydrogen ions when dissolved in water eg. HCl, CH₃COOH, H₃PO₄. A **base** is a substance that dissociates to give hydroxyl ions when dissolved in water eg. NaOH, Ca(OH)₂.

2. **Lowry and bronsted concept** : An **acid** is a substance which has a tendency to donate a proton (H⁺) to any other substance. A **base** is a substance which has a tendency to accept a proton (H⁺) from any other substance.



Acid and base differing by a proton are known as **conjugate pair**. The weaker the acid, the stronger the base in conjugate pair and vice versa



3. Lewis concept : An **acid** is a substance which can accept a pair of electrons from any other substance e.g. BF_3 , AlCl_3 (incomplete octet), SnCl_4 , SF_4 (central atom has vacant d orbital) or cations Fe^{3+} , Cu^{2+} etc.

A **base** is a substance capable to donating a pair of electrons to any other substance eg. anions X^- , OH^- , CN^- or neutral molecules having lone pair(s) of electrons on one or more atom, e.g. ROH , NH_3 , H_2O . etc.

Lewis acid may be any of the following types of substances :

1. Molecules having an atom with incomplete octet
2. Simple cations
3. Molecules with central atom having empty d-orbitals
4. Molecules with a multiple bond between atoms of different electronegativities.

4. Hard and Soft acid-base:

Hard acids : Cations of lighter elements, smaller size, higher charge, not easily polarisable e.g. light alkali and alkaline metal ions of B, Al, Si, Ti^{4+} , Cr^{3+} , Co^{2+} , Fe^{3+} (lighter transition elements).

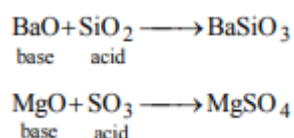
Soft acids : Cations of heavier elements, larger size, lower charge and easily polarisable e.g. heavy transition metal ions (second and third row) e.g. Hg^{2+} , Pd^{2+} , Cd^{2+} , Cu^+ , Ag^+ , Hg^+ etc.

Hard bases : Species having donor atoms of higher electronegativity and low polarisability e.g. N, O, F, Cl etc. Examples H_2O , NH_3 , ROH .

Soft bases : Species having donor atom of lower electronegativity and higher polarisability e.g. P, As, S, Se etc. Examples R_3P , R_2S , I^- .

5. Lux-flood concept of acids and bases :

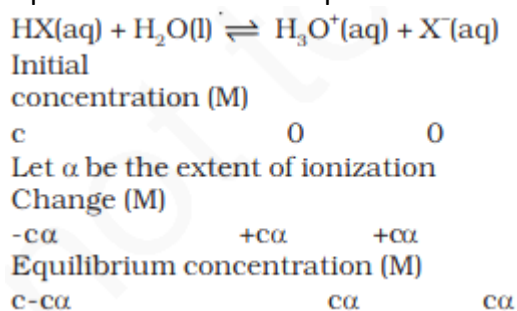
An oxide ion donor is a base and an oxide ion acceptor is an acid.



6. Ingold concept : All electrophiles are acids and nucleophiles are bases.

STRENGTH OF ACIDS AND BASES : The greater the value of K_a or K_b the stronger is the acid or base. the smaller the value of pK_a the stronger is the acid.

Ionization Constants of Weak Acids: Consider a weak acid HX that is partially ionized in the aqueous solution. The equilibrium can be expressed by:



Here, c = initial concentration of the undissociated acid, HX at time, $t = 0$. α = extent up to which HX is ionized into ions. Using these notations, we can derive the equilibrium constant for the above discussed acid dissociation equilibrium:

$$K_a = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

K_a is called the dissociation or ionization constant of acid HX. It can be represented alternatively in terms of molar concentration as follows,

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

At a given temperature T , K_a is a measure of the strength of the acid HX i.e., larger the value of K_a , the stronger is the acid. K_a is a dimensionless quantity with the understanding that the standard state concentration of all species is 1M.

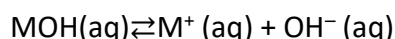
(i) **Relative strengths of acids:** For weak acid $K_a = C\alpha^2$. For two acids with dissociation constants

K_{a1} and K_{a2} at the same concentration C ,

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a1}}{K_{a2}}} = \frac{\text{Strength of acid HA}_1}{\text{Strength of acid HA}_2}$$

Ionization of Weak Bases:

The ionization of base MOH can be represented by equation:



In a weak base there is partial ionization of MOH into M^+ and OH^- , the case is similar to that of acid-dissociation equilibrium. The equilibrium constant for base ionization is called base ionization constant and is represented by K_b . It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation:

$$K_b = \frac{[M^+][OH^-]}{[MOH]}$$

Alternatively, if c = initial concentration of base and α = degree of ionization of base i.e. the extent to which the base ionizes. When equilibrium is reached, the equilibrium constant can be written as:

$$K_b = \frac{(c\alpha)^2}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

(ii) **Relative strengths of bases :** For weak base $K_b = C\alpha^2$. For two bases with dissociation constants K_{b1} and K_{b2} at the same concentration C .

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b1}}{K_{b2}}} = \frac{\text{Strength of base B}_1\text{OH}}{\text{Strength of base B}_2\text{OH}}$$

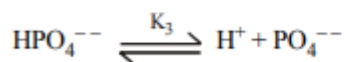
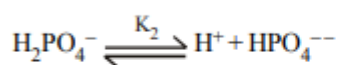
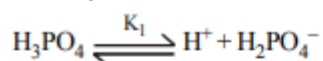
LEVELLING EFFECT : All the strong acids in aqueous, solution appear almost equally strong since water acts as strong base. For example HClO_4 , HBr , H_2SO_4 , HCl and HNO_3 appear equally strong.

Hence relative strengths in aqueous solution cannot be compared. This phenomenon is known as levelling effect.

RELATION BETWEEN K_a AND K_b :

$$K_a \times K_b = K_w \text{ or } pK_a + pK_b = pK_w = 14 \text{ at } 25^\circ\text{C}.$$

Ionisation of polybasic acids : Polybasic acids ionise in various steps e.g. Orthophosphoric acid H_3PO_4 .



$K_1 > K_2 > K_3$ and overall dissociation const. $K = K_1 \times K_2 \times K_3$

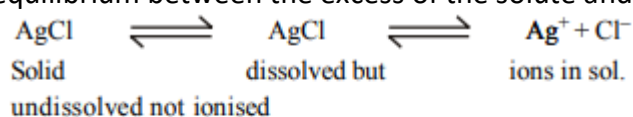
AMPHOTERIC OR AMPHIPROTIC SUBSTANCE OR AMPHOLYTES : A substance acting as an acid as well as a base, eg. water acts as an acid with ammonia and as base with acetic acid. A substance acting as proton donor and proton acceptor.

COMMON ION EFFECT : The degree of ionisation of an electrolyte is suppressed by the addition of another electrolyte having a common ion. This is known as **common ion effect** e.g. ionisation of CH_3COOH is suppressed by the addition of HCl or CH_3COONa .

- (i) It helps in controlling the concentration of ions furnished by weak electrolytes.
- (ii) It effects the solubility of salts.

SOLUBILITY PRODUCT (K_{sp}) :

At constant temperature and pressure the saturated solution of a sparingly soluble salt has an equilibrium between the excess of the solute and the ions furnished by it. e.g



Applying law of mass action, $K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$

or $K[\text{AgCl}] = [\text{Ag}^+][\text{Cl}^-]$, $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$

The constant K_{sp} is known as solubility product. It is equal to the product of the concentration of ions in saturated solution.

When $K_{sp} > [\text{Ag}^+][\text{Cl}^-]$ Solution is not saturated

When $K_{sp} < [\text{Ag}^+][\text{Cl}^-]$ Solution is supersaturated and precipitation takes place

When $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$ Solution is saturated

Relation between solubility product (K_{sp}) and solubility (S).

1. For binary electrolyte e.g. AgCl , BaSO_4

$$S = \sqrt{K_{sp}}$$

2. For ternary electrolyte e.g. CaF_2 , PbI_2

$$S = \left(\frac{K_{sp}}{4} \right)^{\frac{1}{3}}$$

DISSOCIATION CONSTANT OF WATER / IONIC PRODUCT OF WATER (K_w) :

Water being weak electrolyte is slightly ionised as follows :



$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \quad \text{or} \quad K[\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\text{or} \quad K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

K_w is known as ionic product of water or dissociation constant of water. It is equal to the product of concentration of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ ions in water. At constant temperature of 25°C , the value of K_w is 1.0×10^{-14} .

In pure water $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ (M)}$ at 298 K

Molar concentration of water is 55.55 mol/lit $K[\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-] K \times 55.5 = K_w$. Hence ionic product of water is 55.5 times greater than K . K_w increases with temperature.

EXPRESSING HYDROGEN ION CONCENTRATION : pH SCALE: Any aqueous solution of some electrolyte or non-electrolyte having equal concentrations of H^+ and OH^- ions, is neutral. It has been observed that H^+ ion concentrations can usually vary from 0 to 10^{-14} moles/l. Sorensen represented the acidic or basic character of an aqueous solution in terms of pH. The pH of a solution is the numerical value of the negative power to which ten must be raised to express the H^+ ion concentration.

$$[\text{H}^+] = 10^{-\text{pH}}$$

In pure water $[\text{H}^+] = 10^{-7} = 10^{-\text{pH}}$ at 25°C or 298 K

Hence pH of pure water is 7.

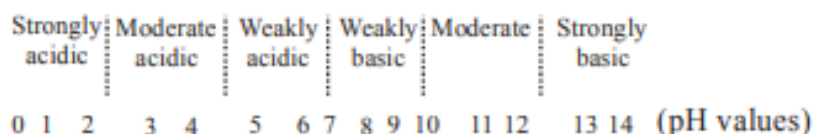
$$\log [\text{H}^+] = -\text{pH} \log 10$$

$$\therefore \text{pH} = -\log (\text{H}^+) = \log \frac{1}{[\text{H}^+]}$$

Thus pH of a solution is the negative logarithm of hydrogen ion concentration. Similarly, negative logarithm of hydroxyl ion concentration is known as pOH.

$$\text{pOH} = -\log [\text{OH}^-]$$

An aqueous solution having pH value less than 7, is acidic and more than 7 is basic at 298 K.



$$\text{pH} + \text{pOH} = 14$$

The pH changes with temperature. It decreases with rise in temperature.

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

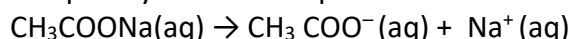
We now consider the hydrolysis of the salts of the following types :

(i) salts of strong acid and strong base e.g NaCl, KNO₃ etc.

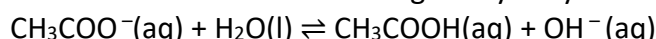
The cations (e.g., Na⁺, K⁺, Ca²⁺, Ba²⁺, etc.) of strong bases and anions (e.g., Cl⁻, Br⁻, NO₃⁻, ClO₄⁻ etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7.

(ii) salts of weak acid and strong base e.g., CH₃COONa :

In the first case, CH₃COONa being a salt of weak acid, CH₃COOH and strong base, NaOH gets completely ionised in aqueous solution.



Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and OH⁻ ions



Acetic acid being a weak acid ($K_a = 1.8 \times 10^{-5}$) remains mainly unionised in solution. This results in increase of OH⁻ ion concentration in solution making it alkaline. The pH of such a solution is more than 7

Important parameters:

$$\text{Salt hydrolysis constant } K_h = \frac{K_w}{K_a}$$

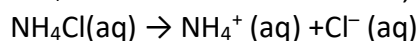
$$\text{Degree of hydrolysis } \alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

$$[\text{H}^+] = \sqrt{\frac{K_w \times K_a}{C}}$$

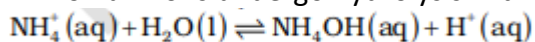
$$\text{pH} = 7 + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log C$$

(iii) salts of strong acid and weak base e.g., NH₄Cl :

NH₄Cl formed from weak base, NH₄OH and strong acid, HCl, in water dissociates completely



Ammonium ions undergo hydrolysis with water to form NH₄OH and H⁺ ions



Ammonium hydroxide is a weak base ($K_b = 1.77 \times 10^{-5}$) and therefore remains almost unionized in solution. This results in increased of H⁺ ion concentration in solution making the solution acidic. Thus, the pH of NH₄Cl solution in water is less than 7.

Important parameters:

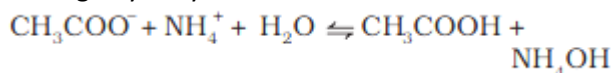
$$\text{Degree of hydrolysis } \alpha = \sqrt{\frac{K_w}{K_b \times C}}$$

$$[\text{H}^+] = \sqrt{\frac{K_w \cdot C}{K_b}}$$

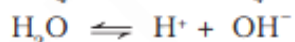
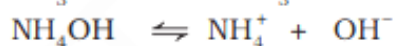
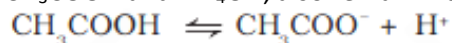
$$\text{pH} = 7 - \frac{1}{2}\text{p}K_b - \frac{1}{2}\log C$$

(vi) salts of weak acid and weak base, e.g., CH₃COONH₄ .

Consider the hydrolysis of CH₃COONH₄ salt formed from weak acid and weak base. The ions formed undergo hydrolysis as follow:



CH₃COOH and NH₄OH, also remain into partially dissociated form:



Without going into detailed calculation, it can be said that degree of hydrolysis is independent of concentration of solution, and pH of such solutions is determined by their pK values:

$$\text{pH} = 7 + \frac{1}{2} (\text{p}K_a - \text{p}K_b)$$

The pH of solution can be greater than 7, if the difference is positive and it will be less than 7, if the difference is negative.

Important parameters:

$$\text{Salt hydrolysis Const., } K_h = \frac{K_w}{K_a \times K_b}$$

pH of the solution may be 7, > 7 or < 7

$$\text{Degree of hydrolysis, } \alpha = \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$\text{H}^+ = \sqrt{\frac{K_w \times K_a}{K_b}}$$

$$\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

BUFFERS : Solutions which resist the change in the value of pH when small amount of acid or base is added to them are known as buffers.

Types **(I) Simple buffers** : Solution of salt of weak acid and weak base CH₃COONH₄ , NH₄CN.

(II) Mixed buffers :

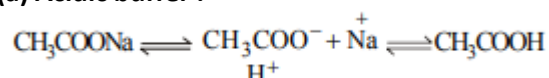
(a) Acidic buffers : Solution of equimolar mixture of a weak acid and its salt with a strong base e.g. (CH₃COOH + CH₃COONa); (H₂CO₃ + NaHCO₃); (Boric acid + borax); (H₃ PO₄ + NaH₂ PO₄)

(b) Basic buffers : Solution of equimolar mixture of a weak base and its salt with a strong acid e.g. (NH₄OH + NH₄Cl)

Buffer action of simple buffer : CH₃COONH₄ exist as ions CH₃COO⁻ and NH₄⁺ in solution. Added acid (H⁺) combine with CH₃COO⁻ to give feebly ionised CH₃COOH and added base (OH⁻) combine with NH₄⁺ to give feebly ionized NH₄OH. Thus pH remains unchanged.

Buffer action of mixed buffers :

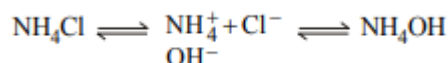
(a) Acidic buffer :



When small amount of an acid is added to the buffer the added H⁺ ions combine with CH₃COO⁻ to form feebly ionised CH₃COOH and when small amount of a base is added to the buffer the added OH⁻ ions combine with H⁺ to form feebly ionised H₂O. In the latter case more CH₃COOH ionises to

keep K_a of acid constant and hence constant concentration of H^+ ions. Thus whether we add acid or a base, the H^+ concentration remain constant and pH of solution does not change.

(b) Basic buffer :



When small amount of an acid is added to the buffer the added H^+ ions combine with OH^- to form feebly ionised H_2O , equilibrium is disturbed. More NH_4OH ionises to keep $[OH^-]$ fixed. When small amount of a base is added to the buffer the added OH^- ions combine with NH_4^+ to form feebly ionised NH_4OH to keep $[OH^-]$ fixed. Hence there is no change of pH in both cases.

$$\text{Buffer capacity} = \frac{\text{Moles of acid or a base added to 1 litre of buffer}}{\text{Change in pH}}$$

Calculation of pH value of buffers : Acidic buffer contains weak acid and its salt with strong base. The H^+ ion concentration is given by

$$[H^+] = \frac{K_a [ACID]}{[SALT]}$$

$$-\log[H^+] = -\log K_a + \log \frac{[SALT]}{[ACID]}$$

$$pH = pK_a + \log \frac{[SALT]}{[ACID]}$$

This is known as **Henderson's equation**.

Basic buffer contains a weak base and its salt with strong acid. The OH^- ion concentration is given by

$$[OH^-] = \frac{K_b [BASE]}{[SALT]}$$

$$-\log[OH^-] = -\log K_b + \log \frac{[SALT]}{[BASE]}$$

$$pOH = pK_b + \log \frac{[SALT]}{[BASE]}$$

Note : $pH + pOH = 14 = pK_w$.

A buffer has maximum buffer capacity when

$$\frac{[SALT]}{[ACID]} \text{ or } \frac{[SALT]}{[BASE]} = 1$$

In such case $pH = pK_a$ for acid buffer and $pOH = pK_b$ for basic buffer. For a buffer the ratio of concentration of salt to acid or base must lie between 0.1 and 10. Thus pH range for acid buffer is from $(pK_a - 1)$ to $(pK_a + 1)$. For basic buffer the pOH range is $(pK_b - 1)$ to $(pK_b + 1)$.