

Chapter 9

Ionic Equilibrium

In chemical equilibrium we studied reaction involving molecules only but in ionic equilibrium we will study reversible reactions involving formation of ions in water. When solute is polar covalent compound then it reacts with water to form ions.

Electrical conductors

Substances, which allow electric current to pass through them, are known as conductors or electrical conductors. Conductors can be divided into two types,

(1) Conductors which conduct electricity without undergoing any chemical change are known as metallic or electronic conductors.

(2) Conductors which undergo decomposition (a chemical change) when an electric current is passed through them are known as electrolytic conductors or electrolytes.

Electrolytes are further divided into two types on the basis of their strengths,

(i) Substances which almost completely ionize into ions in their aqueous solution are called strong electrolytes. Degree of ionization for this type of electrolyte is one i.e., $\alpha \approx 1$.

For example :

$HCl, H_2SO_4, NaCl, HNO_3, KOH, NaOH,$

$HNO_3, AgNO_3, CuSO_4$ etc. means all strong acids, bases and all types of salts.

(ii) Substances which ionize to a small extent in their aqueous solution are known as weak electrolytes.

Degree of ionization for this types of electrolytes is $\alpha \ll 1$.

For example : $H_2O, CH_3COOH, NH_4OH, HCN,$
 $Liq. SO_2, HCOOH$ etc. means all weak acids and bases.

Arrhenius theory of electrolytic dissociation

(1) Postulates of Arrhenius theory

(i) In aqueous solution, the molecules of an electrolyte undergo spontaneous dissociation to form positive and negative ions.

(ii) Degree of ionization (α)

$$= \frac{\text{Number of dissociated molecules}}{\text{Total number of molecules of electrolyte before dissociation}}$$

(iii) At moderate concentrations, there exists an equilibrium between the ions and undissociated molecules, such as, $NaOH \rightleftharpoons Na^+ + OH^-$; $KCl \rightleftharpoons K^+ + Cl^-$

This equilibrium state is called *ionic equilibrium*.

(iv) Each ion behaves osmotically as a molecule.

(2) Factors affecting degree of ionisation

(i) At normal dilution, value of α is nearly 1 for strong electrolytes, while it is very less than 1 for weak electrolytes.

(ii) Higher the dielectric constant of a solvent more is its ionising power. Water is the most powerful ionising solvent as its dielectric constant is highest.

$$(iii) \alpha \propto \frac{1}{\text{Con. of solution}} \propto \frac{1}{\text{wt. of solution}}$$

\propto Dilution of solution \propto Amount of solvent

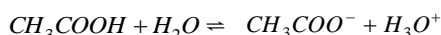
(iv) Degree of ionisation of an electrolyte in solution increases with rise in temperature.

(v) **Presence of common ion** : The degree of ionisation of an electrolyte decreases in the presence of a strong electrolyte having a common ion.

Ostwald's dilution law

The strength of an acid or a base is experimentally measured by determining its dissociation or ionisation constant.

When acetic acid (a weak electrolyte) is dissolved in water, it dissociates partially into H^+ or H_3O^+ and CH_3COO^- ions and the following equilibrium is obtained,



Applying law of chemical equilibrium,

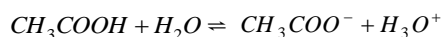
$$K = \frac{[CH_3COO^-] \times [H_3O^+]}{[CH_3COOH] \times [H_2O]}$$

In dilute solution, $[H_2O]$ is constant. The product of K and constant $[H_2O]$ is denoted as K_a , the ionization constant or dissociation constant of the acid is,

$$K_a = \frac{[CH_3COO^-] \times [H_3O^+]}{[CH_3COOH]} \quad \dots(i)$$

The fraction of total number of molecules of an electrolyte which ionise into ions is known as degree of dissociation/ionisation α .

If 'C' represents the initial concentration of the acid in moles L^{-1} and α the degree of dissociation, then equilibrium concentration of the ions (CH_3COO^- and H_3O^+) is equal to $C\alpha$ and that of the undissociated acetic acid = $C(1 - \alpha)$ i.e., we have



Initial conc	C	O	O
Conc. at eqb.	$C(1 - \alpha)$	$C\alpha$	$C\alpha$

Substituting the values of the equilibrium concentrations in equation (i), we get

$$K_a = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = \frac{C^2\alpha^2}{C(1 - \alpha)} = \frac{C\alpha^2}{1 - \alpha} \quad \dots(ii)$$

In case of weak electrolytes, the value of α is very small and can be neglected in comparison to 1 i.e., $1 - \alpha = 1$.

Hence, we get

$$K_a = C\alpha^2 \text{ or } \alpha = \sqrt{\frac{K_a}{C}} \quad \dots(iii)$$

The degree of dissociation, α can therefore be calculated at a given concentration, C if K_a is known. Further, if V is the volume of the solution in litres containing 1 mole of the electrolyte, $C = 1/V$. Hence we have

$$\alpha = \sqrt{K_a V} \quad \dots(iv)$$

Similarly, for a weak base like NH_4OH , we have

$$\alpha = \sqrt{K_b / C} = \sqrt{K_b V} \quad \dots(v)$$

The above equations lead to the following result

“For a weak electrolyte, the degree of ionisation is inversely proportional to the square root of molar concentration or directly proportional to the square root of volume containing one mole of the solute.”

This is called **Ostwald's dilution law**.

Dissociation constants of acids and Bases

(1) **Dissociation constant for weak acid** :

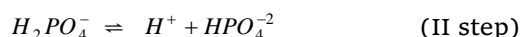
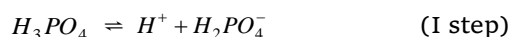
Consider an acid HA which, when dissolved in water ionizes as,



Applying the law of mass action, $K_a = \frac{[H^+][A^-]}{[HA]}$

Where, K_a is the dissociation constant of the acid, HA . It has constant value at definite temperature and does not change with the change of concentration.

Dissociation Constant for polybasic acid : Polybasic acids ionise stepwise as, for example, orthophosphoric acid ionises in three steps and each step has its own ionisation constant.



Let K_1 , K_2 and K_3 be the ionization constants of first, second and third steps respectively. Thus,

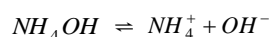
$$K_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}; K_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}; K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

In general, $K_1 > K_2 > K_3$

The overall dissociation constant (K) is given by the relation,

$$K = K_1 \times K_2 \times K_3$$

(2) **Dissociation constant for weak base** : The equilibrium of NH_4OH (a weak base) can be represented as,

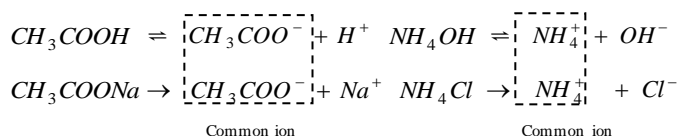


Applying the law of mass action, $K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$

K_b is constant at a definite temperature and does not change with the change of concentration.

Common ion effect

The degree of dissociation of an electrolyte (weak) is suppressed by the addition of another electrolyte (strong) containing a common ion, this is termed as *common ion effect*. Acetic acid is a weak electrolyte and its ionisation is suppressed in presence of a strong acid (H^+ ion as common ion) or a strong salt like sodium acetate (acetate ion is a common ion). Similarly, the addition of NH_4Cl or $NaOH$ to NH_4OH solution will suppress the dissociation of NH_4OH due to common ion either NH_4^+ or OH^- .



As a result of common ion effect, the concentration of the ion of weak electrolyte which is not common in two electrolytes, is decreased. The use of this phenomenon is made in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group.

Isohydric solution

If the concentration of the common ions in the solution of two electrolytes, for example H^+ ion concentration in HCl and HNO_3 or OH^- ion concentration in $Ca(OH)_2$ and $Ba(OH)_2$ is same, then on mixing them there is no change in the degree of dissociation of either of the electrolytes. Such solutions are called *isohydric solutions*.

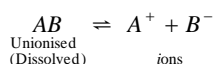
Consider two isohydric solutions of acids HA_1 and HA_2 . Let V_1 and V_2 be their dilutions and α_1 and α_2 be their degree of dissociation at the respective dilution. Then,

$$\frac{\alpha_1}{V_1} = \frac{\alpha_2}{V_2}$$

Above equation is useful for calculating the relative dilution of two acids at which they would be isohydric.

Solubility product

In a saturated solution of sparingly soluble electrolyte two equilibria exist and can be represented as, $\underbrace{AB}_{\text{Solid}} \rightleftharpoons$



Applying the law of mass action, $\frac{[A^+][B^-]}{[AB]} = K$

Since the solution is saturated, the concentration of unionised molecules of the electrolyte is constant at a particular temperature, i.e., $[AB] = K' = \text{constant}$.

Hence, $[A^+][B^-] = K[AB] = KK' = K_{sp}$ (constant)

K_{sp} is termed as the solubility product. It is defined as *the product of the concentration of ions in a saturated solution of an electrolyte at a given temperature*.

Consider, in general, the electrolyte of the type A_xB_y which dissociates as, $A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$

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

When the solution is saturated, $[A_xB_y] = K'$ (constant) or

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

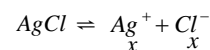
Thus, solubility product is defined as the product of concentrations of the ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte at a given temperature when the solution is saturated.

(1) **Difference between solubility product and ionic product** : Both ionic product and solubility product represent the product of the concentrations of the ions in the solution. The term ionic product has a broad meaning since, it is applicable to all types of solutions, either unsaturated or saturated and varies accordingly.

On the other hand, the term solubility product is applied only to a saturated solution in which there exists a dynamic equilibrium between the undissolved salt and the ions present in solution. Thus the solubility product is in fact the ionic product for a saturated solution at a constant temperature.

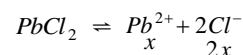
(2) Different expression for solubility products

(i) Electrolyte of type AB (1 : 1 type salt) e.g., $AgCl$, $BaSO_4$



$$K_{sp} = [Ag^+][Cl^-] ; K_{sp} = x^2 ; x = \sqrt{K_{sp}}$$

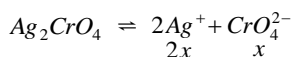
(ii) Electrolytes of type AB_2 (1:2 type salt) e.g., $PbCl_2$, CaF_2



$$K_{sp} = [Pb^{2+}][Cl^-]^2 ; K_{sp} = [x][2x]^2 ; K_{sp} = 4x^3$$

$$x = \sqrt[3]{K_{sp}/4}$$

(iii) Electrolyte of type A_2B (2 : 1 type salt)
e.g., Ag_2CrO_4 , H_2S

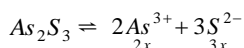


$$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]; K_{sp} = [2x]^2 [x]; K_{sp} = 4x^3$$

$$x = \sqrt[3]{\frac{K_{sp}}{4}}$$

(iv) Electrolyte of type A_2B_3 (2 : 3 type salt)

e.g., As_2S_3 , Sb_2S_3

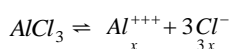


$$K_{sp} = [As^{3+}]^2 [S^{2-}]^3; K_{sp} = [2x]^2 [3x]^3; K_{sp} = 4x^2 \times 27x^3$$

$$K_{sp} = 108x^5; x = \sqrt[5]{\frac{K_{sp}}{108}}$$

(v) Electrolyte of type AB_3 (1 : 3 type salt)

e.g., $AlCl_3$, $Fe(OH)_3$



$$K_{sp} = [Al^{+++}] [3Cl^-]^3; K_{sp} = [x] [3x]^3$$

$$K_{sp} = 27x^4; x = \sqrt[4]{\frac{K_{sp}}{27}}$$

(3) **Criteria of precipitation of an electrolyte :**

When Ionic product of an electrolyte is greater than its solubility product, precipitation occurs.

(4) **Applications of solubility product**

(i) **In predicting the formation of a precipitate**

Case I : When $K_{ip} < K_{sp}$, then solution is unsaturated in which more solute can be dissolved. i.e., no precipitation.

Case II : When $K_{ip} = K_{sp}$, then solution is saturated in which no more solute can be dissolved but no ppt. is formed.

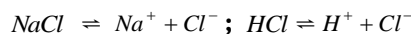
Case III : When $K_{ip} > K_{sp}$, then solution is supersaturated and precipitation takes place.

When the ionic product exceeds the solubility product, the equilibrium shifts towards left-hand side, i.e., increasing the concentration of undissociated molecules of the electrolyte. As the solvent can hold a fixed amount of electrolyte at a definite temperature, the excess of the electrolyte is thrown out from the solutions as precipitate.

(ii) **In predicting the solubility of sparingly soluble salts** Knowing the solubility product of a sparingly soluble salt at any given temperature, we can predict its solubility.

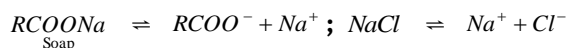
(iii) **Purification of common salt :** HCl gas is circulated through the saturated solution of common

salt. HCl and $NaCl$ dissociate into their respective ions as,



The concentration of Cl^- ions increases considerably in solution due to ionisation of HCl and due to common ion effect, dissociation of $NaCl$ is decreased. Hence, the ionic product $[Na^+][Cl^-]$ exceeds the solubility product of $NaCl$ and therefore pure $NaCl$ precipitates out from the solution.

(iv) **Salting out of soap :** From the solution, soap is precipitated by the addition of concentrated solution of $NaCl$.



Hence, the ionic product $[RCOO^-][Na^+]$ exceeds the solubility product of soap and therefore, soap precipitates out from the solution.

(v) **In qualitative analysis :** The separation and identification of various basic radicals into different groups is based upon solubility product principle and common ion effect.

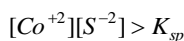
(a) **Precipitation of group first radicals (Pb^{+2} , Ag^+ , Hg^{+2})** The group reagent is dilute HCl . $[Ag^+][Cl^-] > K_{sp}$ for $AgCl$.

(b) **Precipitation of group second radicals (Hg^{+2} , Pb^{+2} , Bi^{+3} , Cu^{+2} , Cd^{+2} , As^{+3} , Sb^{+3} and Sn^{+2})** : The group reagent is H_2S in presence of dilute HCl . $[Pb^{+2}][S^{2-}] > K_{sp}$ for PbS .

(c) **Precipitation of group third radicals (Fe^{+3} , Al^{+3} and Cr^{+3})** The group reagent is NH_4OH in presence of NH_4Cl .



(d) **Precipitation of group fourth radicals (Co^{+2} , Ni^{+2} , Mn^{+2} and Zn^{+2})** : The group reagent is H_2S in presence of NH_4OH .



(e) **Precipitation of group fifth radicals (Ba^{+2} , Sr^{+2} , Ca^{+2})** The group reagent is ammonium carbonate in presence of NH_4Cl and NH_4OH . $[Ba^{+2}][CO_3^{2-}] > K_{sp}$

(vi) **Calculation of remaining concentration after precipitation :** Sometimes an ion remains after precipitation if it is in excess. Remaining concentration can be determined,

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$$\text{Example : } [A^+]_{\text{left}} = \frac{K_{sp}[AB]}{[B^-]} ;$$

$$[Ca^{2+}]_{\text{left}} = \frac{K_{sp}[Ca(OH)_2]}{[OH^-]^2}$$

$$\text{In general } [A^{n+}]_{\text{left}}^m = \frac{K_{sp}[A_m B_n]}{[B^{m-}]^n}$$

$$\begin{aligned} & \text{\% precipitation of ion} \\ &= \left[\frac{\text{Initial conc.} - \text{Remaining conc.}}{\text{Initial conc.}} \right] \times 100 \end{aligned}$$

(vii) **Calculation of simultaneous solubility** : Solubility of two electrolytes having common ion; when they are dissolved in the same solution, is called *simultaneous solubility*.

Calculation of simultaneous solubility is divided into two cases.

Case I : When the two electrolytes are almost equally strong (having close solubility product).

e.g., $AgBr$ ($K_{sp} = 5 \times 10^{-13}$); $AgSCN$ ($K_{sp} = 10^{-12}$)

Here, charge balancing concept is applied.

Charge of Ag^+ = Charge of Br^- + Charge of SCN^-

$$\begin{array}{rclcl} [Ag^+] & = & [Br^-] & + & [SCN^-] \\ (a+b) & = & a & & b \end{array}$$

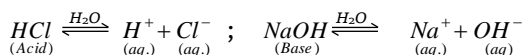
Case II : When solubility products of two electrolytes are not close, i.e., they are not equally strong.

e.g., CaF_2 ($K_{sp} = 3.4 \times 10^{-11}$); SrF_2 ($K_{sp} = 2.9 \times 10^{-9}$)

Most of fluoride ions come of stronger electrolyte.

Acid and Bases

(1) **Arrhenius concept** : According to Arrhenius concept all substances which give H^+ ions when dissolved in water are called acids while those which ionise in water to furnish OH^- ions are called bases.



Some acids and bases ionise almost completely in solutions and are called *strong acids and bases*. Others are dissociated to a limited extent in solutions and are termed *weak acids and bases*. HCl , HNO_3 , H_2SO_4 , $HClO_4$, etc., are examples of strong acids and $NaOH$, KOH , $(CH_3)_4NOH$ are strong bases. Every hydrogen compound cannot be regarded as an acid, e.g., CH_4 is not an acid. Similarly, CH_3OH , C_2H_5OH , etc., have OH groups but they are not bases.

(i) **Utility of Arrhenius concept** : The Arrhenius concept of acids and bases was able to explain a number of phenomenon like neutralization, salt hydrolysis, strength of acids and bases etc.

(ii) **Limitations of Arrhenius concept**

(a) For the acidic or basic properties, the presence of water is absolutely necessary. Dry HCl shall not act as an acid. HCl is regarded as an acid only when dissolved in water and not in any other solvent.

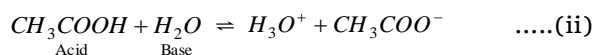
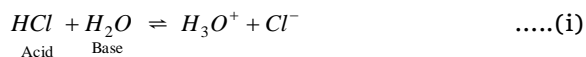
(b) The concept does not explain acidic and basic character of substances in non-aqueous solvents.

(c) The neutralisation process is limited to those reactions which can occur in aqueous solutions only, although reactions involving salt formation do occur in absence of solvent.

(d) It cannot explain the acidic character of certain salts such as $AlCl_3$ in aqueous solution.

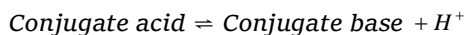
(2) **Bronsted-Lowry concept** : According to this concept,

"An acid is defined as a substance which has the tendency to give a proton (H^+) and a base is defined as a substance which has a tendency to accept a proton. In other words, an acid is a proton donor whereas a base is a proton acceptor."



(i) HCl and CH_3COOH are acids because they donate a proton to H_2O . (ii) NH_3 and CO_3^{2-} are bases because they accept a proton from water.

In reaction (i), in the reverse process, H_3O^+ can give a proton and hence is an acid while Cl^- can accept the proton and hence is a base. Thus there are two acid-base pairs in reaction (i). These are $HCl - Cl^-$ and $H_3O^+ - H_2O$. These acid-base pairs are called *conjugate acid-base pairs*.



Conjugate base of a strong acid is a weak base and vice a versa. Weak acid has a strong conjugate base and vice a versa.

Levelling effect and classification of solvents

In acid-base strength series, all acids above H_3O^+ in aqueous solution fall to the strength of H_3O^+ . Similarly the basic strength of bases above OH^- fall to the strength of OH^- in aqueous solution. This is known as *levelling effect*. Levelling effect of water is due to its high dielectric constant and strong proton accepting tendency.

On the basis of proton interaction, solvents are of four types,

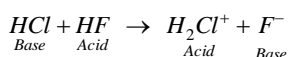
(i) **Protophilic solvents** : Solvents which have greater tendency to accept protons, *i.e.*, water, alcohol, liquid ammonia, etc.

(ii) **Protogenic solvents** : Solvents which have the tendency to produce protons, *i.e.*, water, liquid hydrogen chloride, glacial acetic acid, etc.

(iii) **Amphiprotic solvents** : Solvents which act both as protophilic or protogenic, *e.g.*, water, ammonia, ethyl alcohol, etc.

(iv) **Aprotic solvents** : Solvents which neither donate nor accept protons, *e.g.*, benzene, carbon tetrachloride, carbon disulphide, etc.

HCl acts as acid in H_2O , stronger acid in NH_3 , weak acid in CH_3COOH , neutral in C_6H_6 and a weak base in HF .



Utility of Bronsted – Lowry concept

(i) Bronsted – Lowry concept is not limited to molecules but includes even the ionic species to act as acids or bases.

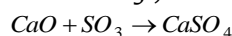
(ii) It can explain the basic character of the substances like Na_2CO_3 , NH_3 etc.

(iii) It can explain the acid-base reactions in the non-aqueous medium or even in the absence of a solvent (*e.g.*, between HCl and NH_3).

Limitations of Bronsted lowry concept

(i) The protonic definition cannot be used to explain the reactions occurring in non-protonic solvents such as $COCl_2$, SO_2 , N_2O_4 , etc.

(ii) It cannot explain the reactions between acidic oxides like CO_2 , SO_2 , SO_3 etc and the basic oxides like CaO , BaO , MgO etc which take place even in the absence of the solvent *e.g.*,



There is no proton transfer in the above example.

(iii) Substances like BF_3 , $AlCl_3$ etc, do not have any hydrogen and hence cannot give a proton but are known to behave as acids.

Table: 9.1 Conjugate acid-base pairs

Acid		Conjugate base	
$HClO_4$	(Perchloric acid)	ClO_4^-	(Perchlorate ion)
H_2SO_4	(Sulphuric acid)	HSO_4^-	(Hydrogen sulphate ion)
HCl	(Hydrogen chloride)	Cl^-	(Chloride ion)
HNO_3	(Nitric acid)	NO_3^-	(Nitrate ion)
H_3O^+	(Hydronium ion)	H_2O	(Water)
HSO_4^-	(Hydrogen sulphate ion)	SO_4^{2-}	(Sulphate ion)
H_3PO_4	(Ortho phosphoric acid)	$H_2PO_4^-$	(Dihydrogen phosphate ion)
CH_3COOH	(Acetic acid)	CH_3COO^-	(Acetate ion)
H_2CO_3	(Carbonic acid)	HCO_3^-	(Hydrogen carbonate ion)
H_2S	(Hydrogen sulphide)	HS^-	(Hydrogen sulphide ion)
NH_4^+	(Ammonium ion)	NH_3	(Ammonia)
HCN	(Hydrogen cyanide)	CN^-	(Cyanide ion)
C_6H_5OH	(Phenol)	$C_6H_5O^-$	(Phenoxide ion)
H_2O	(Water)	OH^-	(Hydroxide ion)
C_2H_5OH	(Ethyl alcohol)	$C_2H_5O^-$	(Ethoxide ion)
NH_3	(Ammonia)	NH_2^-	(Amide ion)
CH_4	(Methane)	CH_3^-	(Methyl carbanion)

Increasing order of acidic strength

Increasing order of basic strength

(3) **Lewis concept** : This concept was proposed by G.N. Lewis, in 1939. According to this concept, “a base is defined as a substance which can furnish a pair of electrons to form a coordinate bond whereas an acid is a substance which can accept a pair of electrons.” The acid is also known as electron pair acceptor or *electrophile* while the base is electron pair donor or *nucleophile*.

A simple example of an acid-base is the reaction of a proton with hydroxyl ion, $\underset{\text{Acid}}{H^+} + \underset{\text{Base}}{OH^-} \rightarrow HOH$

Lewis concept is more general than the Bronsted Lowry concept. *All Bronsted bases are also Lewis bases but all Bronsted acids are not Lewis acids.* [*e.g.*, HCl , H_2SO_4 as they are not capable of accepting a pair of electrons]

(i) **Types of Lewis acids** : According to Lewis concept, the following species can act as Lewis acids.

(a) Molecules in which the central atom has incomplete octet BF_3 , BCl_3 , $AlCl_3$, $BeCl_2$, etc.

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(b) All cations are expected to act as Lewis acids since they are deficient in electrons.

(c) *Molecules in which the central atom has empty d-orbitals.* e.g., $\text{SiF}_4, \text{SnCl}_4, \text{PF}_5$ etc.

(d) *Molecules having a multiple bond between atoms of dissimilar electronegativity* e.g., CO_2, SO_2 .

(ii) **Types of Lewis bases** : The following species can act as Lewis bases.

(a) Neutral species having at least one lone pair of electrons : $\text{NH}_3, \ddot{\text{N}}\text{H}_2, \text{R}-\ddot{\text{O}}-\text{H}$

(b) Negatively charged species or anions

(iii) **Hard and Soft principle of acids and bases** : Lewis acids and bases are classified as hard and soft acids and bases. Hardness is defined as the property of retaining valence electrons very strongly. Thus a hard acid is that in which electron-accepting atom is small, has a high positive charge and has no electron which can be easily polarised or removed e.g., $\text{Li}^+, \text{Na}^+, \text{Be}^{2+}, \text{Mg}^{+2}, \text{Al}^{+3}, \text{BF}_3, \text{SO}_3$ etc.. On the contrary, a soft acid is that in which the acceptor atom is large, carries a low positive charge or it has electrons in orbitals which are easily polarised or distorted e.g., $\text{Pb}^{+2}, \text{Cd}^{+2}, \text{Pt}^{+2}, \text{Hg}^{+2}, \text{Rn}^+, \text{Rn}^+, \text{I}_2$ etc..

A Lewis base which holds its electrons strongly is called hard base, e.g., $\text{OH}^-, \text{F}^-, \text{H}_2\text{O}, \text{NH}_3, \text{CH}_3\text{OCH}_3$, etc. on the other hand, a Lewis base in which the position of electrons is easily polarised or removed is called a soft base e.g., $\text{I}^-, \text{CO}, \text{CH}_3\text{S}^-, (\text{CH}_3)_3\text{P}$, etc.

In general, hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases. The bonding between hard acids and hard bases is chiefly ionic and that between soft bases and soft acids is mainly covalent.

(iv) **Utility of Lewis concept** : Lewis concept is the most general of all the concepts and can explain the acidic and basic nature of all those substances which could not be explained by the earlier concepts. Similarly, it can explain even those acid-base reactions which could not be explained by the other concepts.

(v) **Limitations of Lewis concept** : It does not explain behaviour of well known protonic acids, as $\text{HCl}, \text{H}_2\text{SO}_4$ etc, as which do not form coordinate bonds with bases.

It does not explain relative strengths of acids and bases. Many Lewis acids do not possess catalytic property.

Relative strength of acids and Bases

In practice K_a is used to define the strength only of those acids that are weaker than H_3O^+ and K_b is used to define the strength of only those bases that are weaker than OH^- . For two weak acids HA_1 and HA_2

of ionisation constant K_{a1} and K_{a2} respectively at the same concentration C , we have,

$$\frac{\text{Acid strength of } \text{HA}_1}{\text{Acid strength of } \text{HA}_2} = \sqrt{\frac{K_{a1}}{K_{a2}}}$$

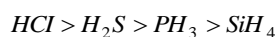
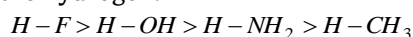
Similarly, relative strengths of any two weak bases at the same concentration are given by the ratio of the square-roots of their dissociation constants. i.e.,

$$\frac{\text{Basic strength of } \text{BOH}_1}{\text{Basic strength of } \text{BOH}_2} = \sqrt{\frac{K_{b1}}{K_{b2}}}$$

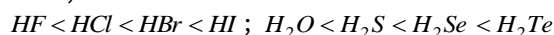
(1) Relative strength of Inorganic acids

(i) Hydrides

(a) The acidic strength increases with the increase in the electronegativity of the element directly attached with the hydrogen.

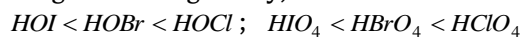


(b) The acidic strength increases with the increase in atomic size,

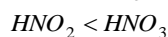
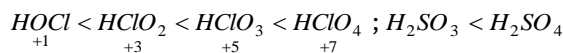


(ii) Oxyacids

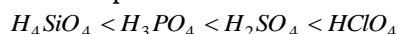
(a) Among oxyacids of the same type formed by different elements, acidic nature increases with increasing electronegativity,



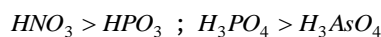
(b) In oxyacids of the same element, acidic nature increases with its oxidation number



(c) The strength of oxyacids increases from left to right across a period



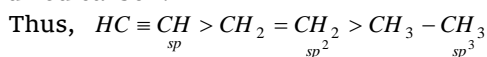
(d) For the same oxidation state and configuration of the elements, acid strength decreases with increase in size of the atom.



(2) Relative strength of organic acids

(i) A compound is acidic in nature, if its conjugate base can stabilize through resonance. Thus phenol is acidic while ethanol is neutral because the conjugate base of phenol ($\text{C}_6\text{H}_5\text{O}^-$) can be stabilized through resonance while that of alcohol ($\text{C}_2\text{H}_5\text{O}^-$) can not.

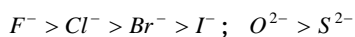
(ii) Hydrogen atom attached to sp -hybridized carbon is more acidic than that on sp^2 hybridized carbon which in turn is more acidic than that on sp^3 hybridized carbon.



(3) Relative strength of Inorganic bases

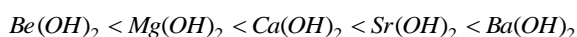
(i) The basicity of a compound decreases with increase in electronegativity of the atom holding the electron pair, $NH_3 > H_2O > HF$:

(ii) The larger the size of the atom holding the unshared electrons, the lesser is the availability of electrons.



(iii) Presence of negative charge on the atom holding the electron pair increases the basicity, while the presence of positive charge on the atom holding the electron pair decreases the basicity. $OH^- > H_2O > H_3O^+$

(iv) Among alkali and alkaline earth hydroxides (oxides) the basic nature increases with electropositivity



$CsOH$ is the strongest known base

(v) On going down the group; basic nature decreases with size of the central atom due to decrease in the ability to donate the lone pair. $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

(4) Relative strength of Organic bases

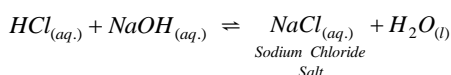
(i) Higher the electron density on nitrogen, more is the basic character of amine.

(ii) A compound is basic in nature, if its conjugate acid can be stabilized through resonance. Thus

guanidine ($NH_3 - \overset{NH_2}{\underset{|}{C}} = NH$) is as strong alkali as metal hydroxides because its conjugate acid ($H_3N^+ - \overset{NH_2}{\underset{|}{C}} = NH$) is very much stabilised through resonance.

The acid-base neutralisation and Salt

The reaction between an acid and a base to form salt and water is termed *neutralisation*



The process of neutralisation does not produce the resulting solution always neutral; no doubt it involves the interaction of H^+ and OH^- ions. The nature of the resulting solution depends on the particular acid and the particular base involved in the reaction.

Salts : Salts are regarded as compounds made up of positive and negative ions. *The positive part comes from a base while negative part from an acid.* Salts are ionic compounds. The salts can be classified into following classes,

(1) **Simple salts :** The salt formed by the interaction between acid and base, is termed as simple salt. These are of three types,

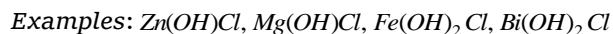
(i) **Normal salts :** the salts formed by the loss of all possible protons (replaceable hydrogen atoms as H^+) are called normal salts. Such a salt does not contain either replaceable hydrogen or a hydroxyl group.

Examples : $NaCl, NaNO_3, K_2SO_4, Ca_3(PO_4)_2, Na_3BO_3, Na_2HPO_3$ (one H atom is not replaceable as H_3PO_2 is a dibasic acid) NaH_2PO_2 (both H atoms are not replaceable as H_3PO_2 is a monobasic acid) etc.

(ii) **Acidic salts :** Salts formed by incomplete neutralisation of poly-basic acids are called acidic salts. Such salts still contain one or more replaceable hydrogen atoms. These salts when neutralised by bases form normal salts.

Examples : $NaHCO_3, NaHSO_4, NaH_2PO_4, Na_2HPO_4$, etc.

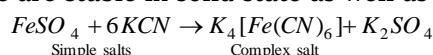
(iii) **Basic salts :** Salts formed by incomplete neutralisation of poly acidic bases are called basic salts. Such salts still contain one or more hydroxyl groups. These salts when neutralised by acids form normal salts.



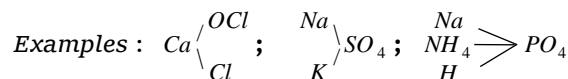
(2) **Double salts :** The addition compounds formed by the combination of two simple salts are termed double salts. Such salts are stable in solid state only.

Examples : Ferrous ammonium sulphate, Potash alum and other alums.

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



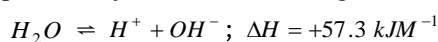
(4) **Mixed salts :** The salt which furnishes more than one cation or more than one anion when dissolved in water is called a mixed salt.



Ionic product of water

Water is a weak electrolyte and undergoes self-ionisation to a small extent.

“The product of concentrations of H^+ and OH^- ions in water at a particular temperature is known as ionic product of water.” It is designated as K_w .



$$K = \frac{[H^+][OH^-]}{[H_2O]} ; K[H_2O] = [H^+][OH^-] ; K_w = [H^+][OH^-]$$

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The value of K_w increases with the increase of temperature, i.e., the concentration H^+ and OH^- ions increases with increase in temperature.

The value of K_w at $25^\circ C$ is 1×10^{-14} mole/litre. Since pure water is neutral in nature, H^+ ion concentration must be equal to OH^- ion concentration.

$$[H^+] = [OH^-] = x \quad \text{or} \quad [H^+][OH^-] = x^2 = 1 \times 10^{-14} \quad \text{or} \\ x = 1 \times 10^{-7} M \quad \text{or} \quad [H^+] = [OH^-] = 1 \times 10^{-7} \text{ mole litre}^{-1}$$

This shows that at $25^\circ C$, in 1 litre only 10^{-7} mole of water is in ionic form out of a total of approximately 55.5 moles.

Thus when, $[H^+] = [OH^-]$; the solution is neutral

$[H^+] > [OH^-]$; the solution is acidic

$[H^+] < [OH^-]$; the solution is basic

Hydrogen ion concentration – pH scale

Sorensen, a Danish biochemist developed a scale to measure the acidity in terms of concentrations of H^+ in a solution. As defined by him, “pH of a solution is the negative logarithm to the base 10 of the concentration of H^+ ions which it contains.”

$$pH = -\log[H^+] \quad \text{or} \quad pH = \log \frac{1}{[H^+]}$$

Just as pH indicates the hydrogen ion concentration, the pOH represents the hydroxyl ion concentration, i.e.,

$$pOH = -\log[OH^-]$$

Considering the relationship,

$$[H^+][OH^-] = K_w = 1 \times 10^{-14}$$

Taking log on both sides, we have

$$\log[H^+] + \log[OH^-] = \log K_w = \log(1 \times 10^{-14}) \quad \text{or}$$

$$-\log[H^+] - \log[OH^-] = -\log K_w = -\log(1 \times 10^{-14})$$

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

	$[H^+]$	$[OH^-]$	pH	pOH
Acidic solution	$> 10^{-7}$	$< 10^{-7}$	< 7	> 7
Neutral solution	10^{-7}	10^{-7}	7	7
Basic solution	$< 10^{-7}$	$> 10^{-7}$	> 7	< 7

pH of some materials

Material	pH	Material	pH
Gastric juice	1.4	Rain water	6.5
Lemon juice	2.1	Pure water	7.0
Vinegar	2.9	Human saliva	7.0
Soft drinks	3.0	Blood plasma	7.4
Beer	4.5	Tears	7.4
Black coffee	5.0	Egg	7.8
Cow's milk	6.5	Household ammonia	11.9

Limitations of pH scale

(i) pH values of the solutions do not give us immediate idea of the relative strengths of the solutions. A solution of pH = 1 has a hydrogen ion concentration 100 times that of a solution pH = 3 (not three times). A $4 \times 10^{-5} N HCl$ is twice concentrated of a $2 \times 10^{-5} N HCl$ solution, but the pH values of these solutions are 4.40 and 4.70 (not double).

(ii) pH value zero is obtained in 1N solution of strong acid. If the concentration is 2N, 3N, 10N, etc. the respective pH values will be negative.

(iii) A solution of an acid having very low concentration, say $10^{-8} N$, can not have pH 8, as shown by pH formula but the actual pH value will be less than 7.

pK value : p stands for negative logarithm. Just as H^+ and OH^- ion concentrations range over many negative powers of 10, it is convenient to express them as pH or pOH, the dissociation constant (K) values also range over many negative powers of 10 and it is convenient to write them as pK. Thus, pK is the negative logarithm of dissociation constant.

$$pK_a = -\log K_a \quad \text{and} \quad pK_b = -\log K_b$$

Weak acids have higher pK_a values. Similarly weak bases have higher pK_b values

For any conjugate acid-base pair in aqueous solution, $K_a \times K_b = K_w$

$$pK_a + pK_b = pK_w = 14 \quad (\text{at } 298^\circ K)$$

Calculation of the pH of $10^{-8} M HCl$ & $10^{-8} M NaOH$

If we use the relation $pH = -\log[H_3O^+]$ we get pH equal to 8, but this is not correct because an acidic solution cannot have pH greater than 7. In this condition H^+ concentration of water cannot be neglected.

$$\text{Therefore, } [H^+]_{total} = H^+_{Acid} + H^+_{water}$$

Since HCl is strong acid and completely ionised,

$$[H^+]_{HCl} = 1 \times 10^{-8}, \quad [H^+]_{H_2O} = 10^{-7}$$

$$[H^+]_{total} = [H^+]_{HCl} + [H^+]_{H_2O} = 10^{-8} + 10^{-7} = 10^{-8} [1 + 10] \\ = 10^{-8} \times 11$$

$$pH = -\log 10^{-8} + \log 11 = 6.958$$

Similarly if NaOH concentration is $10^{-8} M$

$$\text{Then, } [OH^-]_{total} = [10^{-8}]_{NaOH} + [10^{-7}]_{H_2O}$$

$$[OH^-] = 10^{-8} \times 11; \quad pOH = 6.96 \quad pH = 7.04$$

Buffer solutions

A solution whose pH is not altered to any great extent by the addition of small quantities of either strong acid (H^+ ions) or a strong base (OH^- ions) is called the buffer solution. It can also be defined as a solution of reserve acidity or alkalinity which resists change of pH upon the addition of small amount of acid or alkali.

(1) **Types of buffer solutions** : There are two types of buffer solutions,

(i) **Solutions of single substances** : The solution of the salt of a weak acid and a weak base.

Example : ammonium acetate (CH_3COONH_4), NH_4CN act as a buffer.

(ii) **Solutions of Mixtures** : These are further of two types,

(a) **Acidic buffer** : It is the solution of a mixture of a weak acid and a salt of this weak acid with a strong base.

Example : $CH_3COOH + CH_3COONa$

(b) **Basic buffer** : It is the solution of a mixture of a weak base and a salt of this weak base with a strong acid.

Example : $NH_4OH + NH_4Cl$

(2) **Buffer action** : Buffer action is the mechanism by which added H^+ ions or OH^- ions are almost neutralised; so that pH practically remains constant. Reserved base of buffer neutralises the added H^+ ions while the reserved acid of buffer neutralises the added OH^- ions.

(3) Examples of buffer solutions

(i) Phthalic acid + potassium hydrogen phthalate

(ii) Citric acid + sodium citrate.

(iii) Boric acid + borax (sodium tetraborate).

(iv) Carbonic acid (H_2CO_3) + sodium hydrogen carbonate ($NaHCO_3$). This system is found in blood and helps in maintaining pH of the blood close to 7.4 (pH value of human blood lies between 7.36 – 7.42; a change in pH by 0.2 units may cause death).

(v) $NaH_2PO_4 + Na_3PO_4$

(vi) $NaH_2PO_4 + Na_2HPO_4$

(vii) Glycerine + HCl

(viii) The pH value of gastric juice is maintained between 1.6 and 1.7 due to buffer system.

(4) **Henderson - Hasselbalch equation** : pH of an acidic or a basic buffer can be calculated by Henderson- Hasselbalch equation.

For acidic buffers, $pH = pK_a + \log \frac{[salt]}{[acid]}$

When $\frac{[salt]}{[acid]} = 10$, then, $pH = 1 + pK_a$ and

when $\frac{[salt]}{[acid]} = \frac{1}{10}$, then, $pH = pK_a - 1$

So weak acid may be used for preparing buffer solutions having pH values lying within the ranges $pK_a + 1$ and $pK_a - 1$. The acetic acid has a pK_a of about 4.8; it may, therefore, be used for making buffer solutions with pH values lying roughly within the range 3.8 to 5.8.

For basic Buffers, $pOH = pK_b + \log \frac{[salt]}{[base]}$

Knowing pOH , pH can be calculated by the application of formula, $pH + pOH = 14$

pH of a buffer solution does not change with dilution but it varies with temperature because value of K_w changes with temperature.

(5) **Buffer capacity** : The property of a buffer solution to resist alteration in its pH value is known as *buffer capacity*. It has been found that if the ratio $\frac{[salt]}{[acid]}$

or $\frac{[salt]}{[base]}$ is unity, the pH of a particular buffer does

not change at all. Buffer capacity is defined quantitatively as number of moles of acid or base added in one litre of solution as to change the pH by unity, i.e.,

Buffer capacity

$$(\phi) = \frac{\text{Number of moles of acid or base added to 1 litre}}{\text{Change in pH}}$$

Thus greater the buffer capacity, the greater is its capacity to resist change in pH value. Buffer capacity is greatest when the concentration of salt and weak acid/base are equal, or when $pH = pK_a$ or $pOH = pK_b$.

(6) Significance of buffer solutions

(i) Buffer solutions are used for comparing colorimetrically the hydrogen ion concentration of unknown solutions.

(ii) Acetic acid-sodium acetate is used in the removal of phosphate radical during the qualitative analysis of the mixture.

(iii) NH_4Cl / NH_4OH buffer is used for the precipitation of hydroxides of third group of qualitative analysis.

(iv) In industries, buffer solutions are used in the alcoholic fermentation (pH 5 to 6.5), tanning of leather,

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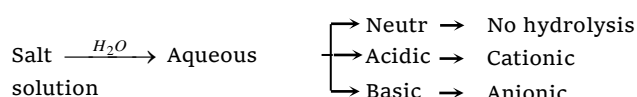
electroplating, manufacture of sugar, paper manufacturing etc.,

(v) In bacteriological research culture media are generally buffered to maintain the pH required for the growth of the bacteria being studied.

(vi) In biological systems buffer system of carbonic acid and sodium bicarbonate is found in our blood. It maintains the pH of blood to a constant value (about 7.4) inspite of various acid and base-producing reactions going on in our body.

Salt hydrolysis

It is the reaction of the cation or the anion or both the ions of the salt with water to produce either acidic or basic solution. Hydrolysis is the reverse of neutralization.



(1) **Hydrolysis constant** : The general equation for the hydrolysis of a salt (BA), $BA + H_2O \rightleftharpoons HA + BOH$

Applying the law of chemical equilibrium, we get $\frac{[HA][BOH]}{[BA][H_2O]} = K$, where K is the equilibrium constant.

Since water is present in very large excess in the aqueous solution, its concentration $[H_2O]$ may be regarded as constant so,

$$\frac{[HA][BOH]}{[BA]} = K[H_2O] = K_h$$

where K_h is called the hydrolysis constant.

(2) **Degree of hydrolysis** : It is defined as the fraction (or percentage) of the total salt which is hydrolysed at equilibrium. For example, if 90% of a salt solution is hydrolysed, its degree of hydrolysis is 0.90 or as 90%. It is generally represented by ' h '.

$$h = \frac{\text{Number of moles of the salt hydrolysed}}{\text{Total number of moles of the salt taken}}$$

Types of salt	Exp. for K_h	Exp. for h	Exp. for pH
(i) Salt of weak acid and strong base	$K_h = K_w / K_a$	$h = \sqrt{\left(\frac{K_h}{C}\right)}$	$pH = -\frac{1}{2} [\log K_w + \log K_a - \log C]$
(ii) Salt of strong acid and weak base	$K_h = K_w / K_b$	$h = \sqrt{\left(\frac{K_h}{C}\right)}$	$pH = -\frac{1}{2} [\log K_w - \log K_b + \log C]$
(iii) Salt of weak acid and weak base	$K_h = \frac{K_w}{K_a K_b}$	$h = \sqrt{K_h}$	$pH = -\frac{1}{2} [\log K_a + \log K_w - \log K_b]$

(iv) Salts of strong acids and strong bases do not undergo hydrolysis (they undergo only ionization) hence the resulting aqueous solution is neutral.

Indicators

An indicator is a substance, which is used to determine the end point in a titration. In acid-base titrations, organic substance (weak acids or weak bases) are generally used as indicators. They change their colour within a certain pH range. The colour change and the pH range of some common indicators are tabulated below

Table : 9.2 Colour changes of indicators with pH

Indicator	pH range	Colour	
		Acid solution	Base solution
Cresol red	1.2 – 1.8	Red	Yellow
Thymol blue	1.2 – 2.8	Red	Yellow
Methyl yellow	2.9 – 4.0	Red	Yellow
Methyl orange	3.1 – 4.4	Pink	Yellow
Methyl red	4.2 – 6.3	Red	Yellow
Litmus	5.0 – 8.0	Red	Blue
Bromothymol blue	6.0 – 7.6	Yellow	Blue
Phenol red	6.4 – 8.2	Yellow	Red
Thymol blue (base)	8.1 – 9.6	Yellow	Blue
Phenolphthalein	8.3 – 10.0	Colourless	Pink
Thymolphthalein	8.3 – 10.5	Colourless	Blue
Alizarin yellow R	10.1 – 12.0	Blue	Yellow
Nitramine	10.8 – 13.0	Colourless	Orange, Brown

Two theories have been proposed to explain the change of colour of acid-base indicators with change in pH .

(i) *Ostwald's Theory* (ii) *Quinonoid theory*

(1) **Selection of suitable indicator or choice of indicator** : In order to choose a suitable indicator, it is necessary to understand the pH changes in the titrations. The change in pH in the vicinity of the equivalence point is most important for this purpose. The curve obtained by plotting pH as ordinate against the volume of alkali added as abscissa is known as neutralisation or titration curve. The suitable indicators for the following titrations are,

(i) **Strong acid Vs strong base** : Phenolphthalein (pH range 8.3 to 10.5), methyl red (pH range 4.4 – 6.5) and methyl orange (pH range 3.2 to 4.5).

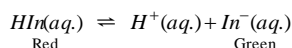
(ii) **Weak acid Vs strong base** : Phenolphthalein.

(iii) **Strong acid Vs weak base** : Methyl red and methyl orange.

(iv) **Weak acid vs. weak base** : No suitable indicator can be used for such a titration.

Reason for use of different indicators for different systems : Indicators are either weak acids or weak bases and when dissolved in water their dissociated form acquires a colour different from that

of the undissociated form. Consider a weak acid indicator of the general formula HIn , where In^- represents indicator. The equilibrium established in aqueous solution will be



Let K_{In} be the equilibrium constant

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \quad \text{or} \quad \frac{[HIn]}{[In^-]} = \frac{[H^+]}{K_{In}}$$

The human eye can detect the change in colour if the ratio of the two forms of indicator ranges between 0.1 to 10.

If, $\frac{[HIn]}{[In^-]} = 1.0$, the colour visible will be yellow

$\frac{[HIn]}{[In^-]} = 10$, the colour visible will be red.

$\frac{[HIn]}{[In^-]} = 0.1$, the colour visible will be green.

In other words,

The colour visible will be red, when $pH = pK_{In} - 1$

The colour visible will be yellow, when $pH = pK_{In}$

The colour visible will be green, when $pH = pK_{In} + 1$

Thus, our imaginary indicator will be red at any pH which just falls below $pK_{In} - 1$ and green at any pH which just exceeds $pK_{In} + 1$. The indicator changes its colour in the narrow pH range $pK_{In} - 1$ to $pK_{In} + 1$ from red to (red-yellow, yellow, yellow-green) green. We can therefore use this indicator to locate this narrow pH range. In other words, in order to use the indicator effectively in this range, we should have a solution for which pH is very near to pK_{In} of the indicator. The colour change of an indicator can, therefore, be summarised as,

	First change of colour	Mid point of change	Colour change complete
$[H^+]$	$10 K_{In}$	K_{In}	$0.1 K_{In}$
pH	$pK_{In} - 1$	pK_{In}	$pK_{In} + 1$

It is for this reason that we use different indicators for different systems.

Tips & Tricks

not 3 times. (ii) A $4 \times 10^{-5} M$ HCl solution is twice concentrated as compared to $2 \times 10^{-5} M$ HCl solution but pH values of these solutions are 4.4 and 4.7 respectively and not double.

- ✍ pH can be zero in $1M$ HCl or it can be negative for more concentrated solutions like $2M$, $3M$, $10M$ etc.
- ✍ At the temperature of the human body which is nearly $37^\circ C$, pH of neutral solution is 6.8.
- ✍ Buffer solutions have reserve acidity and reserve alkalinity.
- ✍ The greater the buffer capacity, the greater is its capacity to resist change in pH value.
- ✍ Buffers cannot withstand the addition of large amounts of acids or alkalies. The addition of $0.1mol$ per litre of $[H^+]$ or OH^- is about the maximum that any buffer can be expected to withstand.

✍ pH of boiling water is 6.5625. It does not mean that boiling water is not neutral. It is due to greater dissociation of H_2O into H^+ and OH^- .

✍ pH values of solutions do not give the exact idea of their relative strengths e.g., (i) A solution with $pH = 1$ had $[H^+]$ 100 times than that with $pH = 3$ and