IONIC EQUILIBRIA

ACIDS AND BASES

1. The Arrhenius Concept :

Arrhenius classified a substance into an acid or a base in terms of the characteristics ions of water which it produces in aqueous solution. Thus an acid is a substance which ionizes in water to produce H^+ (aq) or the hydronium ion; a base is a substance which produces OH^-(aq)

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

- The strength of an acid is defined in terms of concentration of H^+(aq) that is present in the aqueous solution of a given concentration of the acid. Likewise, the strength of a base depends upon the relative concentration of OH^-(aq) in an aqueous solution of the base.
- A neutralisation reaction involves the combination of H^+ and OH^- ions to form water.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

- By Arthenius concept NH_3 should not be a base. It was proposed that in aqueous solution NH_3 forms the compound NH_4OH, which then dissociate as a weak base into NH_4^+ and OH^- ions

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+(aq) + OH^-_{(aq)}$$

2. Bronsted–Lowry concept of Acids and Bases

According to this concept, any hydrogen containing species (a molecule, a cation or an anion), which is capable of donating one or more protons to any other substance, is called an **acid.**

Any species (molecule, cations or anions) which is capable of accepting one or more protons from an acid, is called a **base.**

Thus, according to the Bronsted-Lowry concept, an acid is proton-donor, and a base is proton-acceptor.

The reaction of an acid with a base involves transfer of a proton from the acid to the base. So, an acid and a base should be present simultaneously in any system. The extent of an acid-base reaction is governed not only by the proton-donating ability of the acid, but also by the proton-accepting tendency of the base. Acids and bases classified on the basis of this concept are termed as Bronsted acids and bases.

$$HCl_{(aq)} + H_2O(l) \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$

In this reaction, HCl donates its one proton to become Cl^-, and H_2O accepts one proton to become H_3O^+. Thus, HCl is Bronsted acid and H_2O is a Bronsted base. For the reverse reaction., H_3O^+ is able to transfer its proton to Cl^-. So, H_3O^+ is a Bronsted acid and Cl^- is a Bronsted base.

Every acid must form a base on donating its proton, and every base must form an acid on accepting a proton. The base that is produced when an acid donates its proton is called **the conjugate base of the** acid. The acid that is produced when a base accepts a proton is called the **conjugate acid of the base.** The above reaction can be written as

$$\underset{\text{acid}_1}{HCl} + \underset{\text{base}_2}{H_2O} \rightleftharpoons \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{Cl^-}$$

In this Cl^- is the conjugate base of the acid HCl and H_2O is the conjugate base of the acid H_3O^+. The conjugate acid differs from conjugate base by one proton. A pair of an acid and a base which differ from one another by a proton constitute a conjugate acid base pair. Thus,

$$\overbrace{\underset{\text{acid}_1}{HCl} + \underbrace{\underset{\text{base}_2}{H_2O} \rightleftharpoons \underset{\text{acid}_2}{H_3O^+}}_{\text{Conjugate acid-base pair}} + \underset{\text{base}_1}{Cl^-}}^{\text{Conjugate acid-base pair}}$$

$$\text{Bronsted acid} \longrightarrow \text{Conjugate base of the acid} + H^+$$

$$\text{Bronsted base} + H^+ \longrightarrow \text{Conjugate acid}$$

Although the Bronsted-Lowry concept of acids and bases is better than the Arrhenius concept, it cannot account for the acidic and basic character of compound not containing hydrogen. For example, acidic nature of oxides such as CO_2, SO_2 etc., and the basic nature of the compounds of the type CaO, Na_2O etc.

Relative Strengths of Conjugate Acid–Base Pairs

A stronger Bronsted acid will have a higher tendency for donating proton to the base, hence would tend to exist as its conjugate base. The conjugate base so formed will have very little tendency to pick up a proton, hence would act as a weak base. Thus, there exists an interdependent relationship between the strengths of an acid and its conjugate base.

The stronger an acid, weaker is its conjugatte base, and stronger a base, weaker is its conjugate acid.

In water, HCl acts as a strong acid. As the reverse reaction occurs to a very small extent Cl^- ion acts as a weak base. So, the anion of a strong acid is a weak base. Similarly, the cation of a weak base acts as a strong acid. e.g., NH_4^+ ion in water is a strong acid.

Relative strengths of common conjugate acid-base pairs

Bronsted acid $\rightleftharpoons$ Conjugate base of the acid + H^+	
$HClO_4$	ClO_4^-
H_2SO_4	HSO_4^-
HI	I^-
HBr	Br^-
HCl	Cl^-
HNO_3	NO_3^-
CH_3COOH	CH_3COO^-
H_2CO_3	HCO_3^-
H_2S	HS^-
NH_4^+	NH_3
HCN	CN^-
H_2O	OH^-
NH_3	NH_2^-

Amphoteric substances

Substances which can act as an acid as well as a base are called **amphoteric substances.** For example, $Al(OH)_3$, $Zn(OH)_2$ behave both as acids and as bases in their reactions. The substance, which can donate or accept a proton to act as an acid or a base is termed **amphiprotic**. For example, the species such as HSO_4 and HCO_3 are amphiprotic, because of the following reactions.

$$HSO_4^- + H_2O \longrightarrow H_3O + SO_4^{2-} \text{ (}HSO_4^-\text{ acting as an acid)}$$

$$HSO_4^- + H_2O \longrightarrow OH^- + H_2SO_4 \text{ (}HSO_4^-\text{ acting as base)}$$

$$HCO_3^- + H_2O \longrightarrow H_3O^+ + CO_3^{2-} \text{ (}HCO_3^-\text{ acting as an acid)}$$

$$HCO_3^- + H_2O \longrightarrow OH^- + H_2CO_3 \text{ (}HCO_3^-\text{ acting as an acid)}$$

Water is the most common solvent showing a unique behaviour. It can act as an acid as well as a base. In reactions like,

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{NH_3} \rightleftharpoons NH_4^+ + OH^-$$

it acts as an acid, while it behaves like a base in a reaction of the type,

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

The dual role of water molecule may thus be represented by the equation,

$$\underset{\text{acid}_1}{H_2O} + \underset{\text{base}_2}{H_2O} \rightleftharpoons \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{OH^-}$$

Water is thus known as an amphiprotic solvent. Solvents which neither donate nor accept protons are called **aprotic solvents.**

Relative Strength of Bronsted Acids and Bases

According to Bronsted-Lowry theory, an acid is a proton donor and base is a proton acceptor. Therefore the strength of an acid or a base is determined by its tendency to lose or gain protons. A strong acid is a substance which loses a proton easily to a base.

Relative strength of acids

The relative tendency of acids to transfer a proton to a common base, generally water is expressed as the relative strength of bronsted acids. For example, HCl has a higher tendency to transfer a proton to H_2O than CH_3COOH. This means HCl is a stronger acid than acetic acid. Thus,

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

(higher tendency for forward reaction)

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

(small tendency for forward reaction)

Similarly, a base having a higher tendency to accept a proton is stronger. For example, ammonia accepts a proton more readily from water molecule than a water molecule from another water molecule, and hence ammonia is more basic than water.

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

(very little tendency for the forward reaction)

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

(little tendency for the forward reaction)

The ability of an acid to lose a proton (acid strength) is described by its acid ionization constant. The larger the value of the acid ionization constant K_a, higher is the concentration of H_3O^+ in the solution, stronger is the acid. Knowing the ionization constants of acids one can get the relative strengths of different acids at a particular temperature.

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

$$\text{Acetic acid, } (CH_3COOH)\ K_a = 1.85 \times 10^{-5}$$

$$K_a = \frac{\left[H_3O^+\right]\left[CH_3COO^-\right]}{[CH_3COOH]}$$

$$HF + H_2O \rightleftharpoons F^- + H_3O^+$$

$$\text{Hydrofluoric acid, } (HF)\ Ka = 6.7 \times 10^{-4} \quad Ka = \frac{\left[H_3O^+\right]\left[F^-\right]}{[HF]}$$

Since the ionization constant of HF is larger than the ionization constant of CH_3COOH, hydrofluoric acid (HF) is a stronger acid than acetic acid, (CH_3COOH).

Relative strength of bases

The ability of a base to accept a proton (basic strength) is described by its base ionization constant (K_b). The larger the value of K_b, higher is the concentration of OH^-, stronger is the base.

For example,

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{[NH_3]} = 1.8 \times 10^{-5}$$

$$H_2O + C_6H_5NH_2 \rightleftharpoons C_6H_5NH_3^+ + OH^-,$$

Since the value of K_b for aniline is much less than that of ammonia, hence aniline ($C_6H_5NH_2$) is a weaker base than ammonia (NH_3).

Example 1

Give the conjugate acids of the following :

(a) **OH^-, HCO_3^-, HPO_{4}^{-2}, CH_3NH_2, CO_3^{-2}, NH_3, CH_3COOH**

(b) **Give the conjugate bases of the following : HS^-, H_3O^+, $H_2PO_4^-$, HSO_4^-, HF, CH_3COOH, $[Al(H_2O)_6]^{3+}$.**

Solution :

(a) OH^- : H_2O

HCO_3^- : H_2CO_3

HPO_4^{2-} : $H_2PO_4^-$

CH_3NH_2 : $CH_3NH_3^+$

CO_3^{2-} : HCO_3^-

NH_3 : NH_4^+

CH_3COOH : $CH_3COOH_2^+$

(b) HS^- : S^{2-}

H_3O^+ : H_2O

$H_2PO_4^-$: HPO_4^{2-}

HF : F^-

CH_3COOH : CH_3COO^-

$[Al(H_2O)_6]^{3+}$: $[Al(H_2O)_5OH]^{2+}$

3. LEWIS CONCEPT OF ACIDS AND BASES

In 1938 G.N. Lewis put forward a more generalized acid-base concept.

According to this concept, an acid is a species (charged or uncharged) which, can accept a pair of electrons and a base is a species (charged and uncharged), which can donate a pair of electrons towards the formation of a covalent bond. Thus, a Lewis acid is an electrophilic, and a Lewis base is a nucleophile. For example, in the reaction: NH_3 is a donor of electron pair and BF_3 accepts a pair of electrons. So, according to he Lewis concept, : NH_3 is a Lewis base, and BF_3 is a Lewis acid.

Lewis acids

The following types of compounds or species are Lewis acids :

- All molecules possessing an atom with incomplete octet of electrons or Lewis acids.

  Examples : BF_3, $AlCl_3$

- All cations are Lewis acids,

  Examples : Ag^+, Cu^{2+}, Fe^{2+}, Fe^{3+} etc. are Lewis acids.

- All molecules in which the central atom can acquire more than eight valence electrons.

  Examples : $SiCl_4$, SiF_4, etc. are Lewis acids.

- Molecules with multiple bonds between atoms of different electronegativities e.g. CO_2, SO_2 etc. are Lewis acids.

Lewis bases

The following types of compounds or species are Lewis bases.

- All anions are Lewis bases e.g. OH^-, CN^-,CH_3COO^- etc.
- All molecules having ion–pair of electrons viz : HN_3, H_2O, CO; and amines etc. are Lewis bases. It may be noted that all Bronsted bases are also Lewis bases, but all Bronsted acids are not Lewis acids.

Lewis Acid–Base Reaction

Whenever a Lewis acid reacts with a Lewis base, a covalent bond is formed.

For example, CO_2 (Lewis acid) reacts with OH^-(Lewis base) to give HCO_3^- (bicarbonate ion), BF_3 (boron trifluoride) behaves as a Lewis acid and NH_3 (ammonia) as a Lewis base.

Calcium oxide (CaO) behaves as a Lewis base, and sulphur trioxide (SO_3) as a Lewis acid in the reaction between the two.

The Lewis concept of acids and bases suffers from the following limitations.

- It fails to account for the relative strength of acids and bases, as it is not based on ionization.
- An acid-base reaction being an electron-transfer reaction, should be quite fast. However, many Lewis acid-base reactions are slow.

IONIC EQUILIBRIUM

This type of equilibrium is observed in substances that undergo ionization easily, or in polar substances in which ionization can be induced. Ionic and polar substances are more easily soluble in polar solvents because of the ease of ionization taking place in the solvent medium. With the dissolution of ionic and polar substances in the solvent, these solutions become rich in mobile charge carriers (ions) and thus can conduct electricity. Substances, which are capable of conducting electricity are called as electrolytes while those substances which are non-conducting are called as non-electrolytes.

Ionization in electrolytes

Strong electrolytes are almost completely dissociated/ionized into the constituent ions in aqueous solution. Even at higher concentrations, very small amount of any strong electrolyte is present in the unionized form. Weak electrolytes are however, partially ionized and a dynamic equilibrium exist between the inonized and unionized forms.

In 1887, s. Arrhenius postulated the first theory of electrolytic ionization. The basic postulates of his theory are.

- When an electrolyte is dissolved in water, it ionizes to produce ions in the solution. These ions are free to move throughout the bulk of the solution.

- The total number of positive charges is equal to the total number of negative charges in any solution of any electrolyte. The ions tend to recombine to form the unionized electrolyte. Hence, a dynamic equilibrium exists between the ionized and unionized form of the electrolyte. For example, an electrolyte AB ionizes in the solution to form A^+ and B^-. The equilibrium established in the solution is :

$$AB \rightleftharpoons A^+ + B^-$$

The ionization constant (K) is then given by,

$$K = \frac{\left[A^+\right]\left[B^-\right]}{[AB]}$$

- The properties of an electrolyte in the solution are due to the ions it gives in the solution. For example, a solution of copper sulphate is blue due to the presence of $Cu^{2+}(aq)$ ions in it.

- The fraction of the total number of molecule present as free ions in the solution is known as the degree of ionization (α). This is defined as,

$$\alpha = \frac{\text{Number of molecules split into ions}}{\text{Total number of molecules dissolved}}$$

The degree of ionization at any concentration (C) of AB in moles per litre is denoted as (αC).

OSTWALD'S DILUTION LAW

This law deals with the law of mass action to the equilibrium between the ions and unionized molecules in aqueous solutions of weak binary electrolytes such as acetic acid, propionic acid, HCN, NH_4OH etc.

Consider a dilute solution of weak binary electrolyte AB containing C moles in 1 litre. At any given temperature, there will be equilibrium between the unionized molecules of AB and the ions A^+ and B^-. Let (α) be the degree of dissociation of AB at equilibrium.

$$\begin{array}{lcccc} \text{Initial Conc.} & AB & \rightleftharpoons & A^+ & + & B^- \\ & C & & O & & O \\ \text{Conc. at equilibrium} & C\,(1-\alpha) & & C\alpha & & C\alpha \end{array}$$

Then according to law of mass action,

$$K = \frac{\left[A^+\right]\left[B^-\right]}{[AB]} = \frac{(C\alpha)\,(C\alpha)}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

As 'α' is generally small, the term $1-\alpha \approx 1$.

Hence, $K = C\alpha^2$

or $\alpha = \sqrt{K/C} = \sqrt{K.V}$

where 'V' is the volume of the solution in litres containing one mole of the solute. From the above equation it follows that if the concentration decreases, the degree of ionization (α) must increase. Thus, at constant temperature, an electrolyte in solution gets ionized to a larger extent with increasing dilution. This is called Ostwald dilution law. This law is not applicable to solutions of strong electrolytes as they are completely dissociated and there is no equilibrium between the dissociated and undissociated molecules.

Ionization of an acid (weak)

An acid of the type HA can undergo ionization when dissolved in water as.

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

If 'n' moles of the acid are dissolved in 'V' units of volume (litres L) and (α) is the degree of ionization, then the equilibrium amounts of various species and the concentration in moles per litre in the solution are,

Number of moles of [HA] $= n\,(1-\alpha) = C\,(1-\alpha)$ mol L^{-1}

Number of moles of $[H_3O^+]$ $= n\alpha = C\alpha$ mol L^{-1}

Number of moles of $[A^-]$ = $n\alpha = C\alpha$ mol L^{-1}

Where 'C' is the molar concentration of the acid. The ionization constant for the above reaction is given by,

$$K_a = \frac{\left[H_3O^+\right]\left[A^-\right]}{[HA]} = \frac{(C\alpha)\,(C\alpha)}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

If 'α' is amall then $1-\alpha \approx 1$

Hence, $K_a = C\alpha^2$

or $\alpha = \sqrt{K_a / C} + \sqrt{K_a V}$

where 'V' is the volume of the solution in litres containing one mole of the acid HA. As the degree of ionization increases with-dilution the, the hydronium ion or hydrogen ion concentration is given by.

$$\boxed{[H_3O^+] = C\alpha = C\sqrt{\frac{Ka}{C}} = \sqrt{K_a C}}$$

Ionization of a base (weak)

The ionization of a weak base is characterized by the equilibrium,

$$MOH + H_2O\,(\text{excess}) \rightleftharpoons M^+(aq) + OH^-(aq)$$

If 'n' moles of the base are dissolved in 'V' units of volume (litres L) and α is the degree of ionization, then the equilibrium amounts of various species and the concentration in moles per litre in the solution are,

Number of moles of [MOH] = $n\,(1-\alpha) = C\,(1-\alpha)$ mol L^{-1}

Number of moles of $[OH^-]$ = $n\alpha = C\alpha$ mol L^{-1}

Number of moles of $[M^+]$ = $n\alpha = C\alpha$ mol L^{-1}

where 'C' is the molar concentration of the base. The ionization constant for the above reaction is given by,

$$K_b = \frac{\left[M^+\right]\left[OH^-\right]}{[MOH]} = \frac{(C\alpha)\,(C\alpha)}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

If 'α' is small then $1-\alpha \approx 1$

Hence, $K_b = C\alpha^2$

Or $\alpha = \sqrt{K_b / C} = \sqrt{K_b V}$

where 'V' is the volume of the solution in litres containing one mole of the base MOH. As the degree of ionization increase with dilution then, the hydroxide concentration is given by.

$$\boxed{[OH^-] = C\alpha = C\sqrt{\frac{K_b}{C}} = \sqrt{K_b C}}$$

Protic acids

Acids which contain ionizable hydrogen are called protic acids. These are classified as.

Types of protic acids

Monoprotic acids

These acids contains only one ionizable hydrogen in its molecule. It is denoted by HA.

Example : HCl, CH_3COOH, HNO_3 etc.

Diprotic acids

The diprotic acids contain two ionizable hydrogen in its molecule. They are denoted by H_2A.

Example : H_2SO_4, $(COOH)_2$, H_2CO_3 etc.

Triprotic acids

These acids contain three ionizable hydrogen in its molecule. It is denoted by H_3A.

Example : H_3PO_4 etc.

In all these acids, the primary ionization constant (K_1) is stronger than the secondary (K_2), which is much stronger than the tertiary (K_3) ionization constant. This is because a proton (H_3O^+) would be released more readily from an uncharged molecule than from a mono-negative ion, and more readily from a mono-negative ion than from a bi-negative ion. Also the hydronium concentration from the first ionization will suppress the subsequent ionizations due to common ion effect (this will be discussed a little later in the chapter)

Some general observations on the behaviour of protic acids in aqueous solution are :

- The protic acids which have very high value of the acid dissociation or ionization constant, ionize/dissociate almost completely in aqueous solution at ordinary dilutions. They are called strong acids.

  Example : HCl, H_2SO_4, and HNO_3.

- Acids, which dissociate in aqueous solution to a smaller extent at ordinary dilution, to give low concentration of H^+ ions in solution, are called weak acids.

  Example : CH_3COOH, $(COOH)_2$, H_3PO_4, HCN, HF, etc. The K_a or K_1 values of such acids are much smaller than one.
- On dilution, the ionization of an acids increase. So, concentration of H^+ ions also increase on dilution. Therefore, strength of the acid increases with dilution. It is for this reason that the acid strengths are compared at equal concentrations.
- For di-and tri- protic acids, first dissociation is stronger than the second, which in turn is much stronger than the third dissociation i.e., $K_1 \gg K_2 \gg K_3$. This is because the removal of a proton from a negatively charged species is more difficult than from a neutral molecule.

Example 2

Which of the following acids is the strongest and which one is the weakest. Explain.

Solution :

Nitrous acid (HNO_2)	$K_a = 5.1 \quad 10^{-4}$
Sulphurous acid (H_2SO_3)	$K_a = 1.7 \quad 10^{-2}$
Phosphoric acid (H_3PO_4)	$K_a = 7.1 \quad 10^{-3}$

For, $HA \rightleftharpoons A^- + H^+ \quad K_a = \dfrac{\left[A^-\right]\left[H^+\right]}{[HA]}$

Thus, larger the K_a value stronger is the acid. Therefore,

$$\underset{\text{strongest}}{H_2SO_3} > H_3PO_4 > \underset{\text{weakest}}{HNO_2}$$

Example 3

Calculate the degree of ionization and $[H_3O^+]$ of a 0.1 mol/L solution of acetic acid. Given $K_a(CH_3COOH)=1.8 \quad 10^{-5}$ mol/L.

Solution :

Let 'α' be the degree of ionization. The concentration of various species involved in the equilibrium are as follows.

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

At equilibrium : $C(1-\alpha) \qquad C\alpha \qquad C\alpha$

The equilibrium constant for the ionization of CH_3COOH can be written as follows :

$$K_a = \frac{\left[CH_3COO^-\right]\left[H_3O^+\right]}{[CH_3COOH]} = \frac{(C\alpha)\ (C\alpha)}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

CH_3COOH is very feebly ionized. So, ‘a’ may be ignored in comparison to 1. Then,

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8 \times 10^{-5}\ \text{mol/L}}{0.1\,\text{mol/L}}} = 1.34 \times 10^{-3}$$

Then, $[H_3O^+] = C\alpha = (0.1\ \text{mol/L}) \quad (1.34 \quad 10^{-2})$

$= 1.34 \quad 10^{-3}$ mol/L

Example 4

At 298 K a 0.1 M solution of acetic acid is 1.34% ionized. What is the ionization constant (K_a) for the acid ?

Solution :

Acetic acid ionized as follows :

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

Initial conc/mol L^{-1}	0.1	0	0
Equilibrium conc/mol L^{-1}	$0.1\ (1-\alpha)$	(0.1α)	(0.1α)

$$K_a = \frac{\left[CH_3COO^-\right]\left[H_3O^+\right]}{[CH_3COOCH]} = \frac{0.1\alpha \times 0.1\alpha}{0.1\,(1-\alpha)}$$

$$\alpha = \frac{1.34}{100} = 0.0134$$

So, $$K_a = \frac{0.1\alpha^2}{(1-\alpha)} = \frac{0.1 \times (0.0134)^2}{(1-0.0134)} = 1.82 \times 10^{-5}$$

Ionic Product of Water

The dissociation constant K of H_2O, dissociating very slightly into H^+ and OH^- ($H_2O \rightleftharpoons H^+ + OH^-$) is given by

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

The concentration of an undissociated molecule of H_2O (i.e., $[H_2O]$) is practically equal to the initial molar concentration of water as water dissociated feebly. $[H_2O]$ may thus be taken as constant, the value of which is equal to 100/18, i.e., 55.54 moles per litre supposing the density of water as 1 g per mL.

$$K \quad [H_2O] = [H^+]\,[OH^-]$$

or

$$K_w = [H^+]\,[OH^-]$$

K_w is known as ionic product of water which increases with the increase in temperature.

At 25 C, $\quad$ **$K_w = 1 \quad 10^{-14}$ (mole/L)^2.**

At the body temperature (37 C), $K_w = 2.5 \quad 10^{-14}$ (mole/L)^2

For pure water (neutral) $[H^+] = [OH^-]$

$$\therefore \quad [OH^+] = [OH^-] = \sqrt{K_w} = \sqrt{10^{-14}} = 10^{-7} \text{ mole/L}$$

For any acidic solution, $[H_3O^+] > [OH^-]$

$$\textbf{Or} \quad [H_3O^+] > 10^{-7}\ \text{M}$$

For any alkaline solution,

$$[H_3O^+] < [OH^-]$$

Or

$$[OH^-] > 10^{-7}\ \text{M}$$

Note : K_w is a constant irrespective of the presence of other ions in the solution.

Effect of temperature on K

The value of K_w varies with the change in temperature. The values of $[H_3O^+]$ and [OH] are always equal to each other at all temperatures but the values of K_w are different at different temperatures. The value of K_w increases with the rise in temperature. This is because increase in temperature will shift the equilibrium in the forward direction producing large concentrations of $[H_3O^+]$ and [OH] ions (Le Chateller's principle).

Hence, K_w increases with rise in temperature.

In acidic solution

When an acidic solution of HCl is added to a pure neutral solution of water, the concentration of $[H_3O^+]$ becomes larger than 1.0 10^{-7} mol L^{-1}. The dissociation equilibrium of water shifts in the reverse direction (Le Chatelier's principle). The excess $[OH]^-$ ions combine with hydronium ions to form undissociated water molecules so that he value of K_w remains constant in the solution. The concentration of [OH] ions will then be equal to

$$[OH^-] = \frac{K_w}{\left[H_3O^+\right]}$$

The concentration of $[H_3O^+]$ is more than the concentration of the $[OH^-]$ ions in acidic solution.

When a few drops of a base like NaOH is added to pure water, the concentration of $[OH^-]$ increases and that of hydrogen ions decreases. The concentration of $[H_3O^+]$ can be calculated as :

$$[H_3O^+] = \frac{K_w}{\left[OH^-\right]}$$

Thus in basic solution the concentration of [OH] will be greater than of $[H_3O^+]$

It can be concluded that the hydronium and hydroxyl ions are always present in solution whether they are acidic or basic. However their concentrations differ.

In acidic solution : $[H_3O^+] > [OH^-]$
In basic solution : $[H_3O^+] < [OH^-]$
In neutral solution : $[H_3O^+] = [OH^-]$

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pH SCALE :

pH of solution is the negative logarithm to the base 10 of the concentration of H^+ ions which it contains (Basically P acts as a mathematical operator : $p(A) = -\log_{10} [A]$)

$$\Rightarrow \quad \mathbf{pH = -\log_{10}[H^+]}$$

At 25 C, using this definition, a scale called pH scale is developed as follows :

For H_2O, $H^+ = 10^{-7}$ M
$pH\ (H_2O) = -\log\ (10^{-7}) = 7$

$\Rightarrow$ For a neutral solution; pH = 7

(1) If $[H^+] > 10^{-7}$ in a solution i.e., solution is acidic then $pH < 7$

(2) If $[H^+] < 10^{-7}$ (or $[OH^-] > 10^{-7}$) i.e. solution is basic then $pH > 7$.

		Acidic			H_2O			Basic	
At 25 C	3	4	5	6	7	8	9	10	11
(298 K)									

Acidity increases $\longleftarrow \underset{\text{(Neutral)}}{\text{pH}} \longrightarrow$ Basicity increases

1. pH Calculation of strong acid

A strong acid completely ionises in water.

For example, $HCl \rightarrow H^+ + Cl^-$

Let C be the concentration of HCl.

The concentration of H^+ obtained from HCl will also be C.

$$\therefore pH = -\log C$$

This process cannot be used to calculate the pH of 10^{-7} M HCl. Since, we know that any acidic solution will have pH less than 7, we must adopt some other method.

Method I

We already know the concentration of H^+ (or H_3O^+) ions from pure water is 10^{-7} M. So all we need to do is to add the H^+ ion concentration from water and H^+ (or H_3O^+) ion concentration from HCl to get the $[H^+]_{Total}$.

$\therefore \quad (H^+)_T = (H^+)_{HCl} + (H^+)_{water} = 10^{-7}\ M + 10^{-7}\ M = 2 \times 10^{-7} M$

$\therefore \quad pH = -\log\ (H^+) = -\log\ 2 \quad 10^{-7} = 6.6989$

Though the method looks correct but there is a mistake in it. In chemical equilibrium we have learnt about Le-Chatelier's Principle, which states that when concentration of a reactant or product is changed the reaction tends of go forward or reverse to finally reestablish equilibrium. We can see that in the present case, by adding 10^{-7} M HCl to water, we are increasing the $[H^+]$. This should make the reaction go in the reverse direction. Therefore the $[H^+]$ from water would become less than 10^{-7} M. **So the method will yield incorrect result.**

Method II

The statement given above that "the addition of an ion to an equilibrium, having the same ion makes the equilibrium move in a direction to consume that ion" is called the common ion effect. This implies that water would dissociate less in the presence of HCl. Let the amount of water dissociated be x´ in the presence of 10^{-7} M HCl.

$$\begin{array}{ccc} 2H_2O \rightleftharpoons & H_3O^+ & + \; OH^- \\ & (x' + 10^{-7}) & x' \end{array}$$

At equilibrium

$[H_3O^+]\ [OH^-] = 10^{-14}$

$(x' + 10^{-7})\ (x') = 10^{-14}$

Calculating for x´, we get $x' = 0.618 \quad 10^{-7}$ M.

Here we can clearly see the common ion effect in operation. Water which was dissociating to give 10^{-7} M H_3O^+ ions, has now experienced the common ion effect and has now yielded only $0.618 \quad 10^{-7}$ M H_3O^+ ions.

Therefore, $[H_3O^+]_T = (10^{-7} + 0.618 \quad 10^{-7})$ M

$\therefore \qquad pH = -\log\,(1.618 \quad 10^{-7}) = \mathbf{6.7910}$

Now, let us answer the question as to why we take the $[H^+]$ from water into account for calculating the pH of 10^{-7} MHCl while for calculating the pH of 10^{-6} M, 10^{-5} M, 10^{-4} M, 10^{-3} M, 10^{-2} M and 10^{-1} M HCl, we have not considered it. It can be seen that the H^+ ions from water, decreases due to the common ion from HCl. Greater the concentration of the common ion added, greater will be the effect. Therefore, for concentrations higher than 10^{-6} M (and inclusive of 10^{-6} M), the H^+ from water will be even less than $0.618 \quad 10^{-7}$ M and would be so small in comparison to the $[H^+]$ from HCl, that we can ignore it.

Thus, it is concluded that $[H_3O^+]$ from water needs to be considered only if the $[H_3O^+]$ from acid is $< 10^{-6}$ M and if $[H_3O^+]$ from acid is $\geq 10^{-6}$ M, the $[H_3O^+]$ from water can be ignored.

Example 6

While calculating the pH of 10^{-7} M HCl, we have taken into account the common ion effect of HCl on water. Why did we not take the common ion effect of water on HCl ?

Solution :

Let us assumed that the K_w of water be 10^{-10} at 25 C. Then in pure water, $x^2 = 10^{-10}$; $x = 10^{-5}$

Let us now calculate $[H_3O^+]$ from the water in the presence of 10^{-7} M HCl using the same value of K_w.

$$(x' + 10^{-7})\, x' = 10^{-10}$$

$$\therefore \quad x' = 0.995 \quad 10^{-5}\ \text{M}$$

The percentage decrease in the concentration of H_3O^+ of water is $\dfrac{10^{-5} - 0.995 \times 10^{-5}}{10^{-5}} \times 100 = 0.5\%$

Thus, it can be concluded that larger the value of equilibrium constant of the weak electrolyte, lesser is the common ion effect produced. So, the common ion effect is experienced more by the weak electrolyte (having smaller equilibrium constant) than the strong electrolyte (having larger equilibrium constant).

Example 7

Calculate the pH value of (i) 0.001 M HCl and (ii) 0.01 M NaOH

Solution :

(i) Since HCl is a strong acid, it completely ionizes and therefore, H_3O^+ ions concentration is equal to that of the acid itself i.e.,

$$[H_3O^+] = [HCl] = 0.001\ \text{M} = 1 \quad 10^{-3}\ \text{M}$$

now, $pH = -\log [H_3O^+]$

$$pH = -\log [1 \quad 10^{-3}]$$

$$= -(-3) \log 10 = 3$$

(ii) Since NaOH is a strong base, it completely ionizes and therefore, OH^- ions concentration is equal to that of the base itself i.e.,

$$[OH^-] = [NaOH] = 0.01\ \text{M} = 1 \quad 10^{-2}\ \text{M}$$

$$K_w = [H_3O^+]\,[OH^-]$$

$$[H_3O^+] = \frac{K_w}{\left[OH^-\right]} = \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = 1 \times 10^{-12}$$

$$pH = -\log [H_3O^+]$$

$$pH = -\log [1 \quad 10^{-12}]$$

$$= -(-12) \log 10 = 12$$

Example 8

Acid A, B, C and D have the following pKa values : A = 1.5, B = 3.5, C = 2.0, D = 5.0. Arrange these acids in the increasing order of acid strength.

Solution :

We know that,

$pK_a = -\log K_a$ or $K_a = 10^{-pKa}$

Therefore, for the given acids,

$K_a\ (A) = 10^{-1.5} \quad K_a\ (B) = 10^{-3.5}$

$K_a\ (C) = 10^{-2.0} \quad K_a\ (D) = 10^{-5.0}$

Since, $10^{-5.0} < 10^{-3.5} < 10^{-2.0} < 10^{-1.5}$

Hence, the strength of acids follows the order, $D < B < C < A$

Weakest Strongest

Example 9

The value of K_w is 9.55 10^{-14} at a certain temperature. Calculate the pH of water at this temperature.

Solution :

$K_w = 9.55 \quad 10^{-14}$

For water $[H_3O^+] = [OH^-]$

If $K_w = [H_3O^+]\,[OH^-] = 9.55 \quad 10^{-14}$ then,

$$[H_3O^+]\,[H_3O^+] = 9.55 \quad 10^{-14}$$

$$[H_3O^+]^2 = 9.55 \quad 10^{-14}$$

or $[H_3O^+] = \sqrt{9.55 \times 10^{-14}} = 3.09 \times 10^{-7}$ mol L^{-1}

$$pH = -\log [H_3O^+]$$

$$pH = -\log [3.09 \quad 10^{-7}]$$

$$= -(\log 3.09 + \log 10^{-7})$$

$$= -(0.49 - 7) = 6.51$$

2. pH Calculation of Weak Acid

Weak acid is that which dissociate partially in water and soon comes in equilibrium with its ions as

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

The equilibrium constant is called K_a (dissociation or ionization constant).

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

Let the degree of dissociation of weak acid be α.

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

Initial conc.	c	0	0
Conc. at equilib.	$c-c\alpha$	$c\alpha$	$c\alpha$

If $\alpha << 1$ than $1 - \alpha \approx 1$ (i.e. for α less than or equal to 0.1)

$$K_a \approx c\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{c}}$$

$$[H_3O^+] = c\alpha = c \times \sqrt{\frac{K_a}{c}} = \sqrt{K_a \times c}$$

Using the value of K_a and c, $[H_3O^+]$ can be calculated and then pH of the solution can be calculated.

Taking log of both the sides of above equation,

$$\log [H_3O^+] = ½\log K_a + ½\log c$$

Multiplying both sides by – 1,

$$-\log [H_3O^+] = -½\log K_a - ½\log c$$

$$\boxed{\mathbf{pH = ½pK_a - ½log\ c = ½(pK_a - log\ c)}}$$

Example 10

The self ionisation constant for pure formic acid, K = $[HCOOH_2^+]$ $[HCOO^-]$ has been estimated as 10^{-6} at room temperature. What percentage of formic acid molecules in pure formic acid are converted to formate ion ? The density of formic acid is 1.22 g/cm^3.

Solution:

Given density of formic acid = 1.22 g/cm^3

∴ Weight of formic acid in 1 litre solution = 1.22 10^3 g

Thus, $$[HCOOH] = \frac{1.22 \times 10^3}{46} = 26.5 \text{ M}$$

Since in case of auto ionisation $[HCOOH_2^+] = [HCOO^-]$

and $[HCOO^-]\,[HCOOH_2^+] = 10^{-6}$

$[HCOO^-] = 10^{-3}$

Now % dissociation of HCOOH = $\frac{[HCOO^-] \quad 100}{[HCOOH]} = \frac{10^{-3}}{26.5} \times 100$

$$\left[\alpha = \frac{C\alpha}{C(1-\alpha)}\right] \quad \mathbf{= 0.004\%}$$

Example 11

Liquid ammonia ionises to a slight extent. At –50 C, its self ionisation constant, K_{NH_3} = $[NH_4^+]\,[NH_2^-] = 10^{-30}$. How many amide ions, are present per cm^3 of pure liquid ammonia ? Assume N = 6.0 10^{23}.

Solution :

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^- \quad \text{(self ionization)}$$

and $K = [NH_4^+]\,[NH_2^-]$

∴ $[NH_4^+] = [NH_2^-]$

∴ $[NH_4^+] = [NH_2^-]$

∴ $[NH_2^-] = \sqrt{K} = \sqrt{10^{-30}} = 10^{-15}$ M

Number of amide ions in 10^3 cm^3 = 10^{-15} 6 10^{23}

Number of amide ions in one cm^3 = $\frac{10^{-15} \times 6 \times 10^{23}}{10^3}$

= 6 10^5 ions

Example 12

Calculate the concentration of fluoroacetic acid which is required to get $[H^+] = 1.50 \quad 10^{-3}$ M. K_a of acid = $2.6 \quad 10^{-3}$.

Solution : $$CH_2FCOOH \rightleftharpoons CH_2FCOO^- + H^+$$

Mole before dissociation	1	0	0
Mole after dissociation	$(1 - \alpha)$	α	α

Given, $[H^+] = C\alpha = 1.5 \quad 10^{-3}$ mol litre^{-1}

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

$$2.6 \times 10^{-3} = \frac{1.5 \times 10^{-3} \times \alpha}{(1-\alpha)}$$

$\therefore \quad \alpha = 0.634$

Now, $C\alpha = 1.50 \quad 10^{-3}$

$$\therefore \quad C = \frac{1.50 \times 10^{-3}}{0.634} = 2.37 \times 10^{-3} \text{ M}$$

Note : Since K_a is of the order of 10^{-3} M and thus it is not advisable to use $K_a = C\alpha^2$. Because $(1 - \alpha)$ is not equal to 1 since a is not small.

Example 13

Determine degree of dissociation of 0.05 M NH_3 at 25 C in a solution of pH = 11.

Solution : $$\because \; NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

1	0	0
$(1 - \alpha)$	α	α

Given, pH = 11

$\therefore \quad [H^+] = 10^{-11}$

$\therefore \quad [OH^-] = 10^{-3} = C\alpha$

Since, C = 0.05

$$\therefore \quad \alpha = \frac{10^{-3}}{C} = \frac{10^{-3}}{0.05} = 2 \times 10^{-2} \quad \text{or} \quad \mathbf{2\%}$$

Example 14

K_1 and K_2 for dissociation of H_2S are 4 $\quad 10^{-3}$ and 1 $\quad 10^{-5}$. Calculate sulphide ion concentration in 0.1 M H_2S solution. Also report $[H^+]$ and pH.

Solution :

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]} = 4 \times 10^{-3}$$

$\therefore$ $[H^+] = C\alpha$; $[H^-] = C\alpha$; $[H_2S] = C\,(1 - \alpha)$

or $$4 \times 10^{-3} = \frac{C\alpha \, . \, C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

or $$4 \times 10^{-3} = \frac{0.1}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$ (1 – α should not be neglected)

$\therefore$ $\alpha = 0.18$

$\therefore$ $[H^+] = C\alpha = 0.1 \quad 0.18 = 0.018$ M $\quad \therefore$ pH = 1.7447

$[HS^-] = C\alpha = 0.1 \quad 0.18 = 0.018$ M

$[H_2S] = C\,(1 - \alpha) = 0.1\,(1 - 0.18) = 0.082$ M

Now HS^- further dissociates to H^+ and S^{-2}; $C_1 = [HS^-] = 0.018$ M

$$\begin{array}{ccc} HS^- & \rightleftharpoons H^+ & + \; HS^- \\ 1 & 0 & 0 \\ (1-\alpha_1) & \alpha_1 & \alpha_1 \end{array}$$

$$\therefore \quad K_{a_2} = 1 \times 10^{-5} = \frac{[H^+][S^{-2}]}{[HS^-]}$$

$\because$ $[H^+]$ already in solution = 0.018 and thus, dissociation of HS^- further supresses due to common ion effect and $1 - \alpha \approx 1$.

$$\therefore \quad 1 \times 10^{-5} = \frac{0.018 \times C_1\alpha_1}{C_1(1-\alpha_1)} = 0.0018 \times \alpha_1$$

$$\therefore \quad \alpha_1 = \frac{1 \times 10^{-5}}{0.018} = 5.55 \quad 10^{-4}$$

$\therefore \qquad [S^{-2}] = C_1\alpha_1 = 0.018 \quad 5.55 \quad 10^{-4} = \mathbf{10^{-5}}$

$\qquad [HS^{-}] = C_1\,(1 - \alpha_1) = C_1 = \mathbf{0.018\ M}$

Example 15

Calculate the pH of 10^{-6} M CH_3COOH. $K_a(CH_3COOH) = 1.8 \quad 10^{-5}$.

Solution :

We can solve this problem by two methods. The methods are as follows :

Method 1 :

$[H_3O^+]$ due to a weak acid is given by

$$[H_3O^+] = \sqrt{K_a \times c} = \sqrt{1.8 \times 10^{-5} \times 10^{-6}} = 4.24 \times 10^{-6}$$

pH = **5.37**

Though it seems that we have solved the problem correctly, there is an error in this method. This error can be highlighted by comparing it with the pH of 10^{-6} M HCl. We can see that the pH of 10^{-6} M HCl would be 6. As we know that lesser pH implies higher concentration of H_3O^+ ions. So a weak acid having the same concentration as that of a strong acid cannot give higher concentration of H_3O^+ ions. The error in pH calculation has occurred because we have assumed that α is very much small compared to 1 without knowing the value of α. In fact, if we make this assumption, the α we get is,

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.8 \times 10^{-5}}{10^{-6}}} = 4.24$$

This value is no possible as α cannot be more than 1, ever. Therefore, the assumption made by us is not valid and pH of 10^{-6} M CH_3CO_2H is to be calculated without any assumption.

Method 2 :

$$K_a = \frac{c\alpha^2}{1-\alpha},\ 1.8 \times 10^{-5} = \frac{10^{-6} \times \alpha^2}{1-\alpha}$$

Solving for α, $\alpha = 0.95$

Note that the value of a is quite high, so it cannot be ignored with respect to 1.

$\therefore \quad [H_3O^+] = c\alpha = 0.95 \quad 10^{-6} = 9.5 \quad 10^{-7}$

The $[H_3O^+]$ from acetic acid < 10^{-6} M, so $[H_3O^+]$ from water should also be considered.

$\therefore \quad (x' + 9.5 \quad 10^{-7})\, x' = 10^{-14}$ (where x′ is the $[H_3O^+]$ coming from water in the presence of 10^{-6} M CH_3COOH).

$x' = 1.04 \quad 10^{-8}$

$[H_3O^+]_T = (9.5 \quad 10^{-7} + 1.04 \quad 10^{-8}) = 9.6 \quad 10^{-7}$

pH = **6.01.**

The above illustration shows a need to know when the assumption (that α is very small compared to 1) is valid and when not. Thus, to calculate the pH of a weak acid, we should proceed as

First calculate the value of α from the expression $\alpha = \sqrt{\frac{Ka}{c}}$.

If this value of α comes out to be less than or equal to 0.1, then the assumption is valid and $[H_3O^+]$ is calculated using the expression, $[H_3O^+] = \sqrt{K_a \times c}$ but if the α value obtained from the given expression > 1, then the assumption is not valid and one has to calculate α using the expression, $K_a = \frac{c\alpha^2}{1-\alpha}$ and then calculate $[H_3O^+]$ using the expression, $[H_3O^+] = c\alpha$.

It was suggested that for calculating the pH of weak acid, first calculate α from the expression, $\alpha = \sqrt{\frac{Ka}{C}}$ and then compare its, value with 0.1. This statement looks a little odd. How can we compare the value of α (which is obtained after making the assumption) with 0.1 and then claim that it is correct if $\alpha < 0.1$? Let us see how the given procedure works.

The actual expression for calculating the value of α is $K_a = \frac{c\alpha^2}{1-\alpha}$. If we make the assumption that α is very small compared to one and ignore it with respect to 1 in the denominator, we get $K_a = c\alpha^2$. By ignoring the α in the denominator, we increase the value of the denominator. This will consequently increase the value of the numerator (since the ratio is a constant). Thus, the value of a calculated after the assumption will be greater than the actual value of α. If this approximated value of a is less than or equal to 0.1 then it means that the actual value of α will be even less than 0.1. Therefore, the assumption is valid and if this approximated value of α is greater than 0.1, then the actual value of α may be greater than, equally to or less than 0.1. So in the later case, we are unable to predict and so we do not make any assumption and calculate actual value of α using the expression, $K_a = \frac{c\alpha^2}{1-\alpha}$.

Some Important Points :

- Relative strength of two weak acids is a measure of $[H_3O^+]$

$$\frac{[H_3O^+]_1}{[H_3O^+]_2} = \sqrt{\frac{K_1C_1}{K_2C_2}}$$

- pH of a weak monobasic acid

$$pH = -\log [H_3O^+] = -\log \sqrt{K_aC}$$

$$= \frac{1}{2}[pK_a - \log C]$$

Total $[H_3O^+]$ in a mixture of two weak acids.

$$[H_3O^+] = \sqrt{K_1C_1 + K_2C_2}$$

- **For weak bases :**

$$BOH \rightleftharpoons B^+ + OH^-$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{Cx^2}{(1-x)} = Cx^2$$

$$x = \sqrt{\frac{K_b}{C}}$$

$$[OH^-]_{\text{weak base}} = Cx = \sqrt{K_b C}$$

- Relative strength of two weak bases

$$\frac{[OH^-]_1}{[OH^-]_2} = \sqrt{\frac{K_1C_1}{K_2C_2}}$$

- pOH of weak monoacid base

$$pOH = -\log (OH^-) = \frac{1}{2}[pK_b - \log C]$$

$$pH = 14 - pOH$$

$$= 14 - \frac{1}{2}[pK_b - \log C]$$

Total $[OH^-]$ in a mixture of two weak bases.

$$\boxed{[OH^-] = \sqrt{K_1C_1 + K_2C_2}}$$

HYDROLYSIS OF SALTS

Dissolution of different salts in water does not always result in neutral solutions. For example, aqueous solution of copper sulphate is acidic whereas aqueous solution of sodium acetate is basic and aqueous solution of sodium chloride forms neutral solution. This is due to the dissociation of the salt in water to form ions. This process of the reaction of anion or cation of the salt with water to produce an acidic or an alkaline solution is called hydrolysis. Thus, hydrolysis is reverse of neutralization.

The equilibrium constant of such a reaction is called hydrolysis constant.

Hydrolysis of anion (A^-)

$$\underset{\text{Salt}}{BA} + H_2O \longrightarrow \underset{\text{Acid}}{HA} + \underset{\text{Base}}{BOH}$$

or

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

$$\boxed{K_h = \frac{[HA]\,[OH^-]}{[A^-]}}$$

Hydrolysis of cation (B^+)

$$\boxed{K_h = \frac{[BOH]\,[H_3O^+]}{[B^+]}}$$

The fraction of the total salt that gets hydrolysed at equilibrium is called degree of hydrolysis. It is written as 'h'.

Relation of Hydrolysis Constant and K_a and K_b

(1) Salt of weak acid and strong base

Here, the anion (A^-) is a stronger base than OH^-, hence it undergoes hydrolysis to give free OH^- ions. Therefore the resulting solution will be basic in character having pH greater than 7. For example.

$$CH_3COONa + H_2O \rightleftharpoons \underset{\text{Weak acid}}{CH_3COOH} + Na^+ + OH^-$$

Other examples of this of salts are CH_3COONa, Na_2CO_3, Na_3PO_4, etc.

The aqueous solution of a salt of weak acid and strong base it alkaline. For the general reaction :

$$\underset{\text{Salt}}{BA} + H_2O \rightleftharpoons \underset{\text{Strong base}}{BOH} + \underset{\text{Weak acid}}{HA}$$

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

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

This is called **anion hydrolysis.**

Hydrolysis constant

The hydrolysis constant may be written as :

$$K_h = \frac{[HA][OH^-]}{[A^-]} \quad \text{...(i)}$$

For weak acid HA, HA $\rightleftharpoons$ $H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{...(ii)}$$

Also, $K_w = [H^+]\,[OH^-]$ ... (iii)

Multiplying equation (i) and (ii) and dividing by equation (iii), we get

$$\frac{K_h \, . \, K_a}{K_w} = \frac{[HA][OH^-]}{[A^-]} \times \frac{[H^+][A^-]}{[HA]} \times \frac{1}{[H^+]\,[OH^-]} = 1$$

$$\boxed{\mathbf{K_h = \frac{K_w}{K_a}}}$$

The hydrolysis constant 'K_h', of the salt is inversely proportional to the dissociation constant, 'K_a' of the weak acid. Therefore, the weaker the acid, the greater is the hydrolysis constant of the salt.

Degree of hydrolysis

If the original concentration of the salt in the solution is 'c' mol/litre and 'h' is the degree of hydrolysis at that concentration, then

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

Initial concentration	c	o	o
Concentration of equilibrium	c(1 – h)	ch	ch

The hydrolysis constant, $K_h = \dfrac{[HA][OH^-]}{[A^-]}$

$$= \frac{ch \,.\, ch}{c(1-h)} = \frac{ch^2}{(1-h)}$$

If ‘h’ is very small as compared to 1, we can assume $1 - h \approx 1$.

$$K_h = ch^2$$

or $$h = \sqrt{\frac{K_h}{c}}$$

Substituting the value of K_h, $h = \sqrt{\dfrac{K_w}{K_a . c}}$

pH of the hydrolysed salt solution $[OH^-] = CH$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{ch}$$

Substituting the value of h, $[H^+] = \dfrac{K_w}{c}\sqrt{\dfrac{K_a . c}{K_w}}$

or $$\boxed{[H^+] = \sqrt{\frac{K_w . Ka}{c}}}$$

Now, $pH = -\log [H^+]$

$$= -\log\left(\frac{K_w \,.\, K_a}{c}\right)^{\frac{1}{2}}$$

$$pH = \frac{1}{2}[\log K_w - \log K_a - \log c]$$

Now, $-\log K_w = pK_w$ $-\log K_a = pK_a$

$$\boxed{pH = \frac{1}{2}\, pK_w + \frac{1}{2}\, pK_a + \frac{1}{2}\log c}$$

(2) Salt of a Strong Acid and Weak Base

Let us take a salt, NH_4Cl. It is a salt made from the reaction of strong acid, HCl and weak base, NH_4OH.

$$NH_4Cl(s) \longrightarrow NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

Out of NH_4^+ and Cl–, only NH_4^+ ion hydrolyses and let its degree of hydrolysis be h and K_h be its hydrolysis constant. Let 'c' M be the concentration of the salt, so the concentration of NH_4^+ would also be 'c' M.

$$NH_4^+ \;+\; 2H_2O \rightleftharpoons NH_4OH \;+\; H_3O^+$$

Initial conc.	c	0	0
Conc. at equilib	c(1 – h)	ch	ch

$$K_{eq} = \frac{[NH_4OH]\,[H_3O^+]}{[H_2O]^2\,[NH_4^+]}$$

$$K_{eq}\;[H_2O]^2 = \frac{[NH_4OH]\,[H_3O^+]}{[NH_4^+]} = K_h \qquad \text{... (i)}$$

Multiplying numerator and denominator of equation (i) by OH^- gives

$$\frac{[NH_4OH]\,[H_3O^+][OH^-]}{[NH_4^+]\,[OH^-]} = K_h$$

$$\therefore \quad \boxed{K_h = \frac{K_w}{K_b}} \qquad \left(\text{since } [H_3O^+]\,[OH^-] = K_w \text{ and } \frac{[NH_4^+]\,[OH^-]}{[NH_4OH]} = K_b\right)$$

$$K_h = \frac{K_w}{K_b} = \frac{ch \times ch}{c(1-h)} = \frac{ch^2}{1-h}$$

Assuming h to be smaller than 0.1, it can be ignored with respect to 1. So, 1 – h ≈ 1.

$$K_h \approx ch^2$$

$$h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_b \times c}}$$

$$\therefore \quad [H_3O^+] = ch = c \times \sqrt{\frac{K_w}{K_b \times c}} = \sqrt{\frac{K_w \times c}{K_b}}$$

Taking log of both the sides

$$\log [H_3O^+] = ½\log K_w + ½\log c - ½\log K_b$$

Multiplying both sides by – 1,

$$-\log [H_3O^+] = -½\log K_w - ½\log c + ½\log K_b$$

$$\therefore \quad pH = ½pK_w - ½pK_b - ½\log c = ½(pK_w - pK_b - \log c)$$

$$(\text{since, } -\log K_w = pK_w \text{ and } \log K_b = -pK_b)$$

$$\therefore \quad \boxed{pH = 7 - ½pK_b - ½\log c.}$$

Since, two terms are to be subtracted from 7, so, the pH of such salt solutions would be less than 7 and will behave acidic in nature. 'c' in the above expression represents concentration of the ion undergoing hydrolysis and not the concentration of the salt.

(3) Salt of Weak Acid and a Weak Base

In this case both the cation and anion undergo hydrolysis to the same or different extents. The resulting solution may be neutral, acidic or basic depending upon the relative strengths of acids and bases. The hydrolysis may be written as :

$$CH_3COONH_4 + H_2O \rightleftharpoons \underset{\text{weak acid}}{CH_3COOH} + \underset{\text{weak base}}{NH_4OH}$$

Some common examples are CH_3COONH_4, $(NH_4)_2\ CO_3$, $AlPO_4$, etc.

The aqueous solution of a salt of strong acid and weak base is acidic. For the general reaction :

$$\underset{\text{Salt}}{BA} + H_2O \rightleftharpoons \underset{\text{Weak base}}{BOH} + \underset{\text{Weak acid}}{HA}$$

or

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA$$

This involves anionic and cationic hydrolysis.

Hydrolysis constant

The hydrolysis constant may be written as :

$$K_h = \frac{[BOH]\,[HA]}{[B^+]\,[A^-]} \qquad \text{... (vi)}$$

For weak acid,

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

For weak base BOH

$$BOH \rightleftharpoons B^+ + OH^-$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

Also, $K_w = [H^+]\ [OH^-]$

Multiplying equation (vi) by equation $[H^+]\ [OH^-]$, we get

$$K_h = \frac{[BOH][HA][H^+]}{[B^+][A^-][H^+][OH^-]}$$

$$K_h = \frac{[BOH][HA][H^+][OH^-]}{[B^+][A^-][H^+][OH^-]}$$

$$= \frac{[BOH]}{[B^+][OH^-]} . \frac{[HA]}{[H^+][A^-]} . [H^+][OH^-]$$

$$\boxed{K_h = \frac{K_w}{K_a \times K_b}}$$

Degree of hydrolysis

If the original concentration of the salt in the solution is 'c' mol/litre and 'h' is the degree of hydrolysis at that concentration, then

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA$$

Initial concentration	c	c	o	o
Concentration at equilibrium	$\pm c\ (1 - h)$	$c\ (1 - h)$	ch	ch

The hydrolysis constant, $K_h = \dfrac{\text{ch. ch.}}{c(1-h) \times c(1-h)} = \dfrac{h^2}{(1-h)^2}$

If 'h' is very small as compared to 1, we can assume $1 - h \approx 1$.

$$K_h = h^2$$

or $\quad h = \sqrt{K_h}$

Substituting the value of $h = \sqrt{\dfrac{K_w}{K_a \, . \, K_b}}$

Here the degree of hydrolysis is independent of the concentration of the solution. The weaker the acid and the base, the greater is the degree of hydrolysis of the salt.

pH of the hydrolysed salt solution

$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

$$[H^+] = K_a = \frac{[HA]}{[A^-]}$$

$$[H^+] = \frac{K_a \, . \, ch}{c\,(1-h)} = \frac{K_a \, . \, h}{(1-h)}$$

$$[H^+] = K_a \, . \, h$$

$$= K_a \sqrt{K_h}$$

Substituting the value of 'h', $[H^+] = K_a \sqrt{K_h}$

or $\quad [H^+] = K_a \sqrt{\dfrac{K_w}{K_a \, . \, K_b}}$

$$= \sqrt{\frac{K_w \, K_a}{K_b}}$$

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

$$= -\log \left(\frac{K_w \, . \, K_a}{K_b} \right)^{\frac{1}{2}}$$

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

$$\boxed{pH = \frac{1}{2}\,pK_w + \frac{1}{2}\,pK_a - \frac{1}{2}\,pK_b}$$

Knowing the molar concentration 'c' of the solution, K_a, K_b and K_w, the pH of the solution can be calculated. It is clear from the above equation that pH of the solution will depend upon the pK value of the acid and the base.

If $pK_a < pK_b$, pH of the solution will be less than $\frac{1}{2}pK_w$ and consequently the solution will be acidic.

If $pK_a > pK_b$, then pH of the solution will be more than $\frac{1}{2}pK_w$ and hence the solution will be alkaline.

If $pK_a = pK_a$, pH of the solution will be equal to $\frac{1}{2}pK_w$ and hence the solution will be neutral.

(4) Salt of A Strong Acid and a Strong Base

Let us consider a salt, NaCl made by the reaction of strong acid, HCl and strong base, NaOH.

$$NaCl(s) \longrightarrow NaCl(aq) \longrightarrow Na^{+}(aq) + Cl^{-}(aq)$$

Neither of the two ions of the salt undergoes hydrolysis. So, the solution contain only the equilibrium of ionization of water.

$$2H_2O(l) \rightleftharpoons H_3O^{+}(aq) + OH^{-}(aq)$$

Thus, the pH of such salts always remain constant and the solution behaves neutral at pH = 7 at 25 C.

Example 16

Calculate the hydrolysis constant of the salt containing NO_2^- ions. Given K_a for HNO_2 = $4.5 \quad 10^{-10}$.

Solution :

$$K_H = \frac{K_w}{K_a} = \frac{10^{-14}}{4.5 \times 10^{-10}} = \mathbf{2.2 \quad 10^{-5}}$$

Example 17

What is the pH of a 0.5 M aqueous NaCN solution ? pK_b of CN^- = 4.70.

Solution :

$$pK_a \text{ for HCN} = 14 - 4.70 = 9.30$$

$$\begin{array}{lcccccc} NaCN & + & H_2O & \rightleftharpoons & NaOH & + & HCN \\ 1 & & & & 0 & & 0 \\ 1-h & & & & h & & h \end{array}$$

$$\therefore \qquad [OH^-] = C.h. = C\sqrt{\frac{K_H}{C}} = \sqrt{K_H\,.\,C} = \sqrt{\frac{K_w\,.\,C}{K_a}}$$

$$\text{or} \qquad pOH = \frac{1}{2}[p\,K_w - \log C - pK_a]$$

$$= \frac{1}{2}[14 + 0.3010 - 9.30]$$

$$= 2.5$$

$$\therefore \qquad pH = 14 - 2.5 = \mathbf{11.5}$$

Example 18

Calculate the percentage hydrolysis in 0.003 M aqueous solution of NaOCN. Ka for HOCN = $3.33\quad 10^{-4}$.

Solution :

$$NaOCN + H_2O \rightleftharpoons NaOH + HCN$$

$$h = \sqrt{\left[\frac{K_H}{C}\right]} = \sqrt{\left[\frac{K_w}{K_aC}\right]} = \sqrt{\frac{10^{-14}}{3.33 \times 10^{-4} \times 0.003}}$$

$$h = 10^{-4}$$

$$\therefore \qquad \%\ \text{hydrolysis} = \frac{10^{-4}}{100} = \mathbf{10^{-2}}$$

Problem 19

Calculate degree of hydrolysis and pH of 0.2 M solution of NH_4Cl. Given K_b for NH_4OH is $1.8 \quad 10^{-5}$.

Solution :

	NH_4Cl	+ H_2O $\rightleftharpoons$	NH_4OH	+ HCl
Before hydrolysis	1		0	0
After hydrolysis	1 – h		h	h

where h is degree of hydrolysis

$$h = \sqrt{\left[\frac{K_H}{C\cdot}\right]} = \sqrt{\left[\frac{K_w}{K_b.C}\right]} = \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5} \times 0.2}} \;\mathbf{= 5.27 \quad 10^{-5}}$$

From HCl, a strong acid

$$\therefore \quad [H^+] = C.h = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{(K_H\,.C)} = \sqrt{\left(\frac{K_w}{K_b}.C\right)}$$

$$= \sqrt{\left(\frac{10^{-14} \times 0.2}{1.8 \times 10^{-5}}\right)} = 1.054 \times 10^{-5}$$

$$\therefore \quad pH = -\log[H^+] = -\log 1.054 \quad 10^{-5}$$

$$\mathbf{= 4.9771}$$

Example 20

Find out the amount of NH_4Cl dissolved in 500 mL to have pH = 4.5. K_b for NH_4OH is $1.8 \quad 10^{-5}$

Solution :

Let conc. of NH_4Cl be C mol litre^{-1}

	NH_4Cl	+ H_2O $\rightleftharpoons$	NH_4OH	+ HCl
Before hydrolysis	1		0	0
After hydrolysis	(1 – h)		h	h

$$\therefore \quad [H^+] = \sqrt{(K_H\,.C)} = \sqrt{\left(\frac{K_w}{K_b}.\,C\right)} = \sqrt{\left(\frac{10^{-14} \times C}{1.8 \times 10^{-5}}\right)}$$

$$10^{-4.5} = \sqrt{\left(\frac{10^{-14} \times C}{1.8 \times 10^{-5}}\right)}$$

$$C = 1.8 \text{ mol litre}^{-1}$$

$$\therefore \quad \text{Wt. of } NH_4Cl = 1.8 \quad 53.5 \text{ g/litre}^{-1}$$

$$= 1.8 \quad 53.5 \quad \frac{1}{2} \text{g/500 mL}$$

$$= \mathbf{48.15\ g}$$

Example 21

Calculate the degree of hydrolysis of a mixture of aniline & acetic acid each of them being 0.01 M. K_a of acetic acid = 1.8 10^{-5} & K_b (aniline) = 4.6 10^{-10}. Also calculate pH of the mixture.

Solution :

Now when we mix equal concentrations of aniline and acetic acid, they will neutralise each other to form acetanilide (salt). The alt is of weak base & weak acid, so hydrolysis takes place. The degree of hydrolysis of the salt of weak acid and weak base is given by :

$$h = \sqrt{K_h}$$

$$\Rightarrow \quad K_h = \frac{K_w}{K_a\ K_b} = \frac{1 \times 10^{-14}}{(1.8 \times 10^{-5})\,(4.6 \times 10^{-10})}$$

$$K_h = 1.21 \qquad \Rightarrow \qquad h = \sqrt{1.21} = 1.09$$

Which is impossible.

Hence, as done in earlier example 15, here also we cannot use the approximate formula. Therefore,

Use :

$$K_h = \frac{h^2}{(1-h)^2}$$

$$\Rightarrow \quad 1.21 = \frac{h^2}{(1-h)^2}$$

$$\Rightarrow \quad \frac{h}{1-h} = \sqrt{K_h} = 1.09 \qquad \Rightarrow \qquad h = 0.523$$

However the pH of solution can be calculated by using the standard result :

$$pH = 7 + \frac{1}{2}(pK_a - pK_b)$$

$$pH = 7 + \frac{1}{2}\left[-\log 1.8 \times 10^{-5} - \left(-\log 4.6 \times 10^{-10}\right)\right]$$

$$pH = 4.703$$

Note : Solution in this case is acidic. In such salts, pH depends upon which of two i.e. weak acid or weak base is stronger than the other, i.e. by comparing K_a & K_b ; one can theoretically get an ideal about the pH of solution.

COMMON ION EFFECT

The addition of an ionic salt having a common ion (anion or cation) to weak acids or weak bases, suppresses their degree of dissociation (following Lechatlier's principle).

Weak Acids :

Let HA be a weak acid (like CH_3COOH, HCN etc.) & $B^+ A^-$ be the ionic salt containing common anion (A^-) that is added to the acid.

$$HA_{aq} \rightleftharpoons H^+_{aq} + A^-_{aq}$$

$$BA_{aq} \rightleftharpoons B^+_{aq} + A^-_{aq}$$

Now, the solution has excess of A^- ions. This means increasing concentration of products, in an equilibrium state. (Following Lechatlier's principle) the reaction ($HA \rightleftharpoons H^+ + A^-$) must go in backward direction, in order to mullity the effect of added A^- ions. As a consequence, amount of H^+ in new equilibrium state will be less than before, or one can see that the degree of dissociation of acid (HA) is decreased.

Quantitative Aspect :

$HA \rightleftharpoons H^+ + A^-$; its degree of dissociation = α is given by :

$$\alpha = \sqrt{\frac{K_a}{c}}$$

Let M molar BA be added to it & α' be its new degree of dissociation

$$\begin{array}{ccccc} BA & \rightleftharpoons & B^+_{aq} & + & A^-_{aq} \\ & & M & & M \end{array}$$

(Assuming BA to be 100% ionised)

$$\begin{array}{cccc} HA & \rightleftharpoons & H^+ & + & A^- \\ c - c\alpha' & & c\alpha' & & c\alpha' \end{array}$$

Now in solution : $[HA] = c - c\alpha'$; $[H^+] = c\alpha'$

$[A^-] = [A^-]_{HA} + [A^-]_{BA} = c\alpha' + M$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(c\alpha')\,(c\alpha' + M)}{(c - ca')} = \frac{\alpha'(c\alpha' + M)}{1 - \alpha'}$$

$\Rightarrow$ $K_a = c\alpha'^2 + M\alpha'$ (as $1 - \alpha' \approx 1$)

$\Rightarrow$ $K_a = M\alpha'$

(neglecting $C\alpha'^2$ in comparison to $M\alpha'$ as $\alpha' << 1$ & $\alpha'^2 <<< 1$]

$$\Rightarrow \quad \alpha' = \frac{K_a}{E}$$

Note :

One similar lines you can find α' for a weak base, BOH and adding B^+ ions to it.

BUFFERS

Certain solutions, such as that of ammonium acetate, have a tendency to resist any change in its hydronium ion concentration or pH, whenever a small amount of a strong acid or a strong base is added to it. This property of a solution is known as buffer action.

Buffer Solution

A solution which resists any change of pH when a small amount of a strong acid or a strong base is added to it, is called a buffer solution or simply as a buffer.

Alternatively, a buffer solution may be defined as a solution whose pH value does not change appreciatbly upon the addition of small amounts of a strong acid, base and/or water from outside.

Thus, buffers have reserve acidity and reserve alkalinity.

Buffer solutions usually consist of a mixture of a weak acid and its salt with a strong base e.g., CH_3COOH and CH_3COONa, or that of a weak base and its salt with a strong acid e.g., NH_4OH and NH_4Cl. The solution of any salt of a weak acid and weak base e.g., ammonium acetate, also shows buffering property.

Types of Buffers

There are two types of buffers, acid buffer and basic buffer.

Acid buffer

A buffer solution containing a large amounts of a weak acid, and its salt with a strong base, is termed as an acid buffer. Such buffer solutions have pH on the acidic side i.e., pH is less than 7 at 298 K. The pH of an acid buffer is given by the equation.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

where K_a is the acid dissociation constant of the weak acid.

Basic buffer

A buffer solution containing relatively large amounts of a weak base and its salt with a strong acid, it termed as a basic buffer. Such buffers have pH on the alkaline side i.e., pH is higher than 7 at 298 K.

The pH of a basic buffer is given by the equation :

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

where K_b is the base dissociation constant of the weak base.

These equations are called **Henderson equation.**

Buffer-capacity and Buffer-range

The effectiveness of any buffer is described in terms of its buffer capacity. It is defined as, 'the number of equivalents of a strong acid (or a strong base) required to change the pH of one litre of a buffer solution by one unit, keeping the total amount of the acid and the salt in the buffer constant'.

The buffer capacity of a buffer in maximum when acid to salt or base to salt ratio is equal to 1 i.e. it contains equal number of moles of acid (or base) and the salt. All buffer solutions remain effective over a small pH range : this pH-range is characteristic of the buffer and is termed as the buffer-range.

For the two types of buffers, it is given by

Buffer range in pH units

Acid buffer :	$\text{pK}_a - 1$	to	$\text{pK}_a + 1$
Basic buffer :	$(\text{pK}_w - \text{pK}_b) - 1$	to	$(\text{pK}_b) - \text{pK}_b) + 1$

Consider acetic acid – sodium acetate buffer, an acid buffer. the acid dissociation constant (K_a) of acetic acid is 1.84 10^{-5}.

Therefore, pK_a for acetic acid is 4.74. Then, the buffer range of an acetic acid - sodium acetate buffer is,

$$\begin{aligned} pH &= (pK_a) - 1 \text{ to } (pK_a) + 1 \\ &= 4.74 - 1 \text{ to } 4.74 + 1 \\ &= 3.74 \text{ to } 5.74 \end{aligned}$$

Thus, the acetic acid - sodium acetate buffer will act as an effective buffer over the pH range 3.74 to 5.74.

The pH of a buffer solution depends only on the ratio of the concentrations of the salt and the acid, or salt and the base. It does not depend on the individual concentration. Since, the ratio remains the same even when the solution is diluted. However, at high dilutions, buffers do not remain effective as, they are not able to resist a change in the pH value due to the addition of a strong acid or a strong base.

Example 22

Calculate the pH of a buffer solution containing 0.2 mole of NH_4Cl and 0.1 mole of NH_4OH per litre. K_b for $NH_4OH = 1.85 \quad 10^{-5}$.

Solution :

According to Henderson's equation :

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

$$pK_b = -\log K_b = -\log 1.85 \quad 1^{-5} = 4.733$$

$$\begin{aligned} pOH &= 4.733 + \log \frac{0.2}{0.1} \\ &= 4.733 + 0.301 = 5.034 \end{aligned}$$

$$pH = 14 - pOH = 14 - 5.034 = 8.966$$

Example 23

A buffer solution contains 0.04 mole of Na_2HPO_4 and 0.02 mole of NaH_2PO_4 per litre. (a) Calculate pH if pK_a of NaH_2PO_4 is 6.84. (b) If 1 ml of 1 N HCl is added to a litre of the buffer, calculate the change in pH.

Solution :

In this mixture NaH_2PO_4 is the acid and Na_2HPO_4 is the salt.

$$pH = pKa + \log \frac{[\text{Salt}]}{[\text{Acid}]} = 6.84 + \log \frac{0.04}{0.02} = 6.84 + \log 2 = 6.84 + 0.30 = \mathbf{7.14}$$

(b) 1 ml of 1 N HCl contains 0.001 mole of H^+. It will convert 0.001 mole of Na_2HPO_4 to 0.001 mole of NaH_2PO_4.

$$pH = pK_a + \log \frac{0.04 - 0.001}{0.02 + 0.001} = 6.84 + \log \frac{0.039}{0.021} = 7.109$$

The change in pH is **0.031.**

Example 24

Calculate the pH of a solution made by adding 0.001 mole of NaOH to 100 ml of 0.5 M acetic acid and 0.5 M sodium acetate solution.

Solution :

Moles of acetic acid in 100 ml of solution = $\frac{0.5}{1000} \times 100 = 0.05$

Moles of sodium acetate in 100 ml of solution = $\frac{0.5}{1000} \times 100 = 0.05$

When NaOH is added, acetic acid is converted into sodium acetate.

Moles of acetic acid after addition of 0.001 mole of NaOH = (0.05 – 0.001) = 0.049

Moles of sodium acetate after addition of 0.001 mole of NaOH = (0.05 + 0.001)

= 0.051

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} = -\log (1.8 \times 10^{-5}) + \log \frac{0.051 \times 10}{0.049 \times 10}$$

= 4.7447 + 0.0174 = **4.7621.**

Example 25

20 ml of 0.2 M NaOH is added to 50 ml of 0.2 M acetic acid to give 70 ml of the solution. What is the pH of the solution ? Calculate the additional volume of 0.2 M NaOH required to make pH of the solution 4.74. The ionisation constant of acetic acid is 1.8 10^{-5}.

Solution :

From the chemical reaction,

$$\underset{20\,ml}{CH_3COOH} + \underset{20\,ml}{NaOH} \longrightarrow \underset{20\,ml}{CH_3COONa} + H_2O$$

It is evident that 70 ml of the product will contain

(i) 30 ml of 0.2 M unused CH_3COOH

(ii) 20 ml of CH_3COONa.

$\therefore$ No. of moles of CH_3COOH in 70 ml of solution = $\dfrac{0.2}{1000} \times 30 = 0.006$ mole

Similarly, No. of moles of CH_3COONa in 70 ml of solution = $\dfrac{0.2}{1000} \times 20 = 0.004$ moles

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

Substituting the values of the various terms

$$pH = -\log 1.8 \times 10^{-5} + \log \frac{0.004}{0.006}$$

$$= 4.7447 - 0.1761 = \mathbf{4.5686}$$

Calculation of the additional volume of 0.2 M NaOH required to make pH of solution 4.74.

$$pH = -\log K_a + \log \frac{[Salt]}{[Acid]} \quad \text{or} \quad 4.74 = -\log 1.8 \times 10^{-5} + \log\left[\frac{Salt}{Acid}\right]$$

or $$4.74 = 4.7447 + \log\left[\frac{Salt}{Acid}\right]$$

$\therefore$ $$\log\left[\frac{Salt}{Acid}\right] = 0.0047 \quad \text{or} \quad \left[\frac{Salt}{Acid}\right] = \frac{1}{1.011}$$

Let x ml be the volume of additional 0.2 M NaOH added to make the pH of the solution 4.74. This will further neutralise x ml of 0.2 M CH_3COOH and produce x ml of 0.2 M sodium acetate. The resulting solution (70 + x) will now contain

(i) (30 – x) ml of 0.2 M acetic acid.

(ii) (20 + x) ml of 0.2 M sod. acetate.

Number of moles of acetic acid in (70 + x) ml solution $= \dfrac{0.2}{1000} \times (30 - x) = 2 \times 10^{-4}\ (30 - x)$

Number of moles of CH_3COONa in (70 + x) ml solution $= \dfrac{0.2}{1000} \times (20 + x) = 2 \times 10^{-4}\ (20 + x)$

Therefore, $\frac{[\text{Salt}]}{[\text{Acid}]} = \frac{2 \times 10^{-4}\ (20 + x)}{2 \times 10^{-4}\ (30 - x)} = \frac{20 + x}{30 - x}$

$$\frac{1}{1.011} = \frac{20 + x}{30 - x}$$

or $\quad 20.22 + 1.011\ x = 30 - x$

$2.011\ x = 9.78 \qquad$ or $\qquad x = 4.86$

Therefore, the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74 is **4.86 ml.**

Example 26

500 mL of 0.2 M queous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25 C.

(i) **Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.**

(ii) **If 6 g of NaOH is added to the above solution, determine the final pH. [Assume there is no change in volume on mixing; K_a of acetic acid is 1.75 $\quad 10^{-5}$ mol L^{-1}].**

Solution :

Concentration of CH_3COOH in 500 ml = 0.2 M

Concentration of HCl in 500 ml = 0.2 M

After mixing, $[CH_3COOH] = 0.1$ M; $[HCl] = 0.1$ M

HCl being a strong electrolyte is completely ionised, hence concentration of H^+ furnished by HCl = 0.1 M

CH_3COOH, being weak electrolyte, dissociates as below.

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

	CH_3COOH	CH_3COO^-	H^+
At start	c	0	0
At equilibrium	$c\ (1 - \alpha)$	$c\alpha$	$c\alpha + 0.1$

$$\therefore \quad K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c\alpha\ (c\alpha + 0.1)}{c(1 - \alpha)} = \frac{c\alpha^2 + 0.1\,\alpha}{(1 - \alpha)}$$

Since α is very very small, $c\alpha^2$ can be neglected and $1 - \alpha$ can be taken as unity

$$\therefore \quad K_a = 0.1\ \alpha$$

or $\alpha = \dfrac{K_a}{0.1}$

$$= \frac{1.75 \times 10^{-5}}{0.1} = 1.75 \times 10^{-4}$$

Calculation of pH of the solution

$[H^+]_{total} = 0.1 + c\alpha$

since ca is very very small, it can be neglected

$\therefore$ $[H^+]_{total} = 0.1$

$\therefore$ pH = 1

(ii) No. of moles of NaOH added = $\dfrac{6}{40}$ = 0.15

No. of moles of NaOH left after reacting with 0.l mole of HCl = 0.15 – 0.1 = 0.05 M

This 0.05 moles of NaOH will react with CH_3COOH in the following way.

	CH_3COOH	+	NaOH	$\longrightarrow$	CH_3COONa	+	H_2O
At start	0.1 mol		0.05 mol		0		0
At finish	0.05 mol		0 mol		0.05 mol		0.05 mol

Thus solution of CH_3COOH and CH_3COONa acts as an acid buffer. Hence in such cases

$$pH = pK_a + \log\frac{[Salt]}{[Acid]} = -\log(1.75 \times 10^{-5}) + \log 1$$

$$= 4.75$$

Example 27

Two buffers, (X) and (Y) of pH 4.0 and 6.0 respectively are prepared from acid HA and the salt NaH. Both the buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of the two buffers ? (K_{HA} **= 1.0 10^{-5})**

Solution :

Determination of concentration of salt, i.e. [Salt] in buffer X.

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

$$4.0 = 5.0 + \log\frac{[Salt]}{0.5}$$

$$\log \frac{[\text{Salt}]}{0.5} = -1$$

$$\frac{[\text{Salt}]}{0.5} = \frac{1}{10}$$

$$\therefore \qquad [\text{Salt} = \frac{0.5}{10} = \mathbf{0.05\ M}$$

Determination of [Salt] in buffer Y

$$6.0 = 5.0 + \log \frac{[\text{Salt}]}{0.5}$$

$$\log \frac{[\text{Salt}]}{0.5} = 1.0$$

$$[\text{Salt}] = 10 \quad 0.5 = 5.0 \text{ M}$$

$$\therefore \qquad [\text{Salt}]_{\text{mix}} = \frac{0.05 + 5.0}{2}$$

$$= 2.525 \text{ M}$$

Substituting the values in the relation

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

$$= 5.0 + \frac{2.525}{0.5}$$

$$= 5.0 + \log 5.05$$

$$= 5.0 + 0.70 = 5.7$$

Indicators

Indicators are substances, which indicate the completion (equivalence point or end point) of a chemical reaction by change in colour. For example, in volumetric analysis, during the titration of sodium hydroxide and hydrochloric acid (taken in the burette), phenolphthalein turns pink to colourless when the whole of sodium hydroxide has been neutralized by hydrochloric acid. All indicators show change in colour over some pH range, which varies considerably from one indicator to another.

Acid-Base Indicators

The amount of an acid (or a base), which is exactly equivalent chemically to the amount of some standard base (or an acid), is determined by an acid-base titration. The point of equivalence is called end point. The solution of a strong acid and strong base will be neutral at the end point and have a pH of 7 as they are strong electrolytes. However, if either the acid or the base is a weak electrolyte, the solution at the equivalence point will be either slightly alkaline (pH>7) or slightly acidic (pH<7). Hence, for an acid-base titration, the correct end point will be characterized by a definite value of H^+ ion concentration (i.e. pH), which depends upon the nature of the acid and the base and the concentration in the solution.

A large number of acid-base indicators are available which possess different colours according to H^+ ion concentration of the solution. These indicators do not change from predominantly 'acid' colour to predominantly 'base' suddently and abruptly, but within a small interval of pH (generally about 2 pH units). This is called colour-charge interval of the indicator. The position of the colour-charge interval in the pH scale varies widely with different indicators. Therefore, for acid base titrations, an indicator is chosen which shoes a distinct colour change at a pH close to that of equivalent point.

Acid-base indicator behaviour

The mechanism of acid-base indicator was developed by Ostwald, which offered an explanation for the colour change with change in pH. All acid-base indicators are weak organic acids or bases, which posses different colours in unionized and ionized states. If the indicator acid is represented as HIn and has its ionized form in, then equilibrium in aqueous solution may be represented as :

$$\underset{\text{Unionized colour}}{\mathrm{HIn}} \rightleftharpoons \underset{\text{Ionized colour}}{\mathrm{H^+ + In^-}}$$

For a basic indicator,

$$\underset{\text{Unionised colour}}{\mathrm{InOH}} \rightleftharpoons \underset{\text{Ionised colour}}{\mathrm{OH^- + In^+}}$$

The unionized molecule has one colour while the ionized ions has another colour.

The equilibrium constant for a weak acid indicator may be written as :

$$K_{Ind} = \frac{[H^+][In^-]}{[HIn]}$$

where, K_{Ind} is known as indicator constant.

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

Writing the above equation in logarithmic form

$$\log [H^+] = \log \frac{[HIn]}{[In^-]} \times KInd$$

or $$-\log [H^+] = -\log KInd + \log \frac{[In^+]}{[HIn]} \quad (\because pX = -\log X)$$

Thus the colour of the indicator, which is determined by the ratio

$\frac{[In^-]}{[HIn]}$ is governed by the pH of the solution,

Similarly, for a weak organic base indicator, In OH,

$$[OH^-] = \frac{[InOH]}{[In^+]} \times KInd$$

or $$[H^+] = \frac{Kw}{K_{Ind}} \cdot \frac{[In^+]}{[InOH]}$$

Taking logarithms

$$\log [H^+] = \log \frac{Kw}{K_{Ind}} + \log \frac{[In^+]}{[InOH]}$$

or $$-\log [H^+] = -\log Kw + \log K_{In} + \log \frac{[InOH]}{[In^+]}$$

$$\therefore \quad pH = pKw - pK_{In} + \log \frac{[InOH]}{[In^+]}$$

or $$pH = 14 - pK_{In} + \log \frac{[InOH]}{[In^+]} \text{ at } 25°C$$

As the pH of the solution changes the colour of the indictor changes. This change is so minute that it goes unnoticed by thehuman eye. therefore to see the colour change the concentration of one of the forms should predominate. The solution will have the acid colour (i.e. of HIn form) when the ratio [HIn] to [In] is approximately 10 and the alkaline colour (i.e. of In^-) when ratio [In–] to [HIn] is approximately 10.

The acid colour will be visible when

$$\frac{[\mathrm{HIn}]}{[\mathrm{In}^-]} \geq 10$$

Only basic colour will be visible when

$$\frac{[\mathrm{In}^-]}{[\mathrm{HIn}]} \geq 10$$

Hence the colour interval or indicator pH range is

Indicator pH range = $-1 + pK_{Ind}$ to $1 + pK_{Ind}$

Indicator pH range = $pK_{Ind} \pm 1$

This means that the colour change interval of an indictor lies over approximately 2 pH units. Within this range, the change from one colour to the other another will be visible to human eye.

Acid Base Titration Curves

In acid base titrations, a base is added to an acid successively (or vice versa) and the pH of the solution is noted after every addition. the plot of pH against the amount of base (or acid) added is called a titration curve. The shape of the curve depends upon the ionization constants of the acid and base used in the titration.

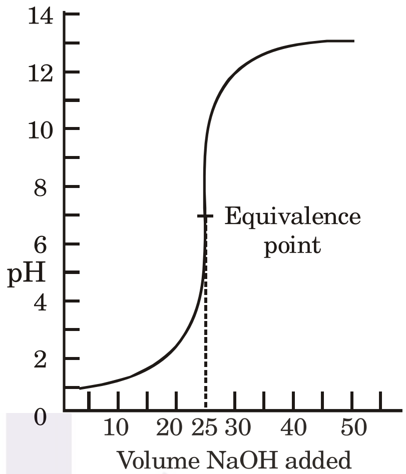
(1) Titration of strong acid and strong base

When we add a solution of NaOH to the solution of HCl, the pH progressively increases.

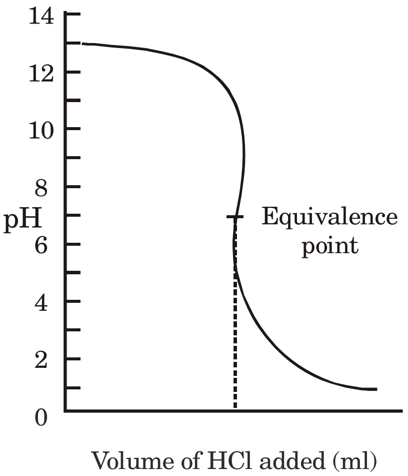
$$\mathrm{HCl(aq)} + \mathrm{NaOH(aq)} \longrightarrow \mathrm{NaCl(aq)} + \mathrm{H_2O(l)}$$

This is because OH^- ions from the base will react with H^+ ions of the acid to form water. This decreases the concentration of H^+ ions and therefore pH increases. The pH of the solution increases only slightly in the beginning until just before the stoichiometric point, there is a sudden jump in pH. The pH continues to increase after the stoichiometric point but then levels off because of the presence of excess strong base in the solution. At the equivalence point the pH is 7, but has increased sharply from 3.5 to 11 just before this point. Any indicator, which has effective range between pH 3.5 to 11 may be used to detect the equivalence point. For example, phenolphthalein and methyl orange are good indicators in this range.

When we tirtate the base (NaOH) with the continuous addition of acid (HCl), the curve obtained is exactly reversed. The pH decreases slowly in the beginning and near the equivalence point there is sudden fall through pH = 7 as the concentration of H^+ ions increases sharply.



Tiration curve of strong acid (HCl) with a strong base (NaOH)



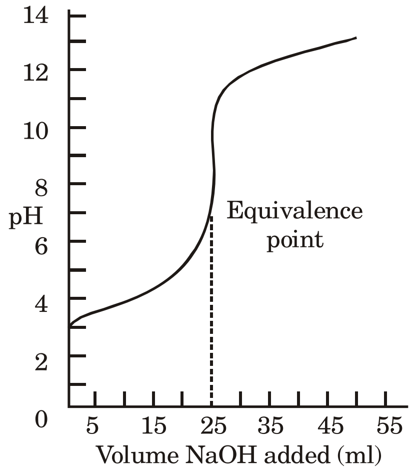
Tiration curve of strong base (NaOH) with strong acid (HCl)

(2) Titration of weak acid and a strong base

This type of titration is carried out between acetic acid and sodium hydroxide.

$$CH_3COOH_{(aq)} + NaOH(aq) \longrightarrow CH_3COONa_{(aq)} + H_2O\ (l)$$

The free H^+ ion from the weak acid is neutralized by OH^- ions from the base and there is a small increase in pH. Around the equivalence point large increase in pH is observed. However, the slope of the curve is not as sleep as in the case of strong base and strong acid titration curve. Sodium acetate formed after neutralization reacts with OH^- ions of water (hydrolysis) and so at the equivalence point the pH is not 7. The H^+ ion concentration decreases and the pH is about 8.7 at the equivalence point. By the addition of small amount of NaOH, pH change is observed from about 8.0 to 10.0 near the equivalence point. It is therefore necessary to use an indicator with pH range on alkaline side. Phenolphthalein is commonly used. Methyl orange cannot be used because it would give inaccurate indication of equivalence point.



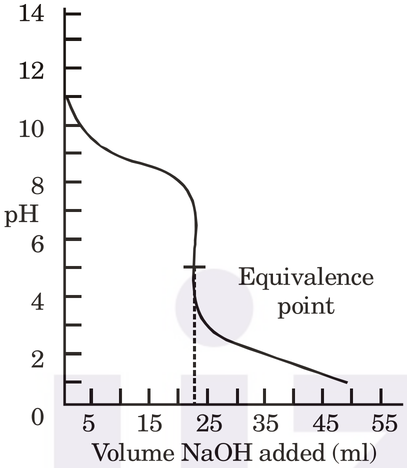
The pH titration curve of weak acid (CH_3COOH) and strong base (NaOH)

(3) Titration of weak base and a strong acid

This type of titration is carried out between a weak base such as ammonium hydroxide and strong acid such as hydrochloric acid.

$$NH_4OH_{(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)} + H_2O(l)$$

The equivalence point is below 7 because the salt (NH_4Cl) formed at the neutralization reacts with water to give H^+ ions. The equivalence point lies at about pH 5.3. It is, therefore necessary to use an indicator with pH range slightly on the acidic side. Methyl orange can be used. Phenolphthalein is not suitable because its colour change occurs away from the equivalence point.



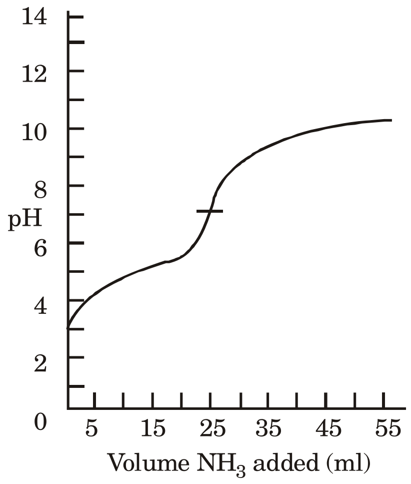
The pH titration curve of weak base (NH_4OH) and strong acid (HCl)

(4) Titration of weak acid and weak base

This type of titration is carried out between a weak acid such as acetic acid (CH_3COOH) and weak base such as ammonium hydroxide (NH_4OH).

$$NH_4OH_{(aq)} + CH_3COOH_{(aq)} \longrightarrow CH_3COONH_{4(aq)} + H_2O(l)$$

There is no sharp change in the pH during the titration. Hence, no sharp equivalence point can be obtained with common indicators. However, a mixed indicator, which shows a sharp colour change over limited pH range may be used.



Titration curve of weak base (NH_4OH) and weak acid (CH_3COOH)

SOLUBILITY, MOLAR SOLUBILITY AND SOLUBILITY PRODUCT

There are two ways to express a substance's solubility (a) solubility and (b) molar solubility.

(a) The number of grams os solute in one litre of a saturated solution (g/litre) is termed as solubility.

(b) The number of moles of solute in one litre of a saturated solution (moles / litre) is defined as molar solubility.

Both these definitions refer to the concentration of saturated solutions at some given temperature (usually 25).

Let us consider solubility of any general salt, A_xB_y. Let the solubility of this salt be 's' mol per litre.

$$A_x\,B_y(s) \rightleftharpoons xA^{y+}(aq) + yB^{x-}(aq)$$

$$\qquad\qquad xs \qquad\qquad ys$$

For saturated solution (at equilibrium),

$$K_{eq} = \frac{[A^{y+}]^x \times [B^{x-}]^y}{[A_xB_y]}$$

$$K_{eq}\ [A_xB_y] = [A^{y-}]^x\,[B^{x-}]^y$$

$$K_{sp} = [A^{y+}]^x\,[B^{x-}]^y \qquad \text{(since } A_xB_y \text{ is a pure solid)}$$

where Ksp is called **solubility product.** The term on right hand side is called solubility product if the solution is saturated and ionic product if the solution is not saturated (i.e., not at equilibrium).

$$K_{sp} = (xs)^x \times (yx)^y$$

$$K_{sp} = x^x \times y^y \times s^{(x+y)}$$

It should be noted that if the ionic product is more than K_{SP}, the equilibrium will shift in backward direction and some amount of salt is thrown out of solution (precipitation) and finally an equilibrium is developed in such a way that the ionic product becomes equal to solubility product. If ionic product is less than K_{SP}, the solution is **unsaturated** and more of the salt can be dissolved. If ionic product is equal to $K_{SP,}$ the solution is **saturated** and if ionic product is more than K_{SP}, the solution is called **super saturated.**

From the solubility product principle, we may infer that,

- When the ionic product of a salt in solution is equal to its solubility product, the solution is saturated and the undissociated salt remains in equilibrium with its ions in the solution.
- The solubility of a salt in water depends upon other substances (ions) present is water (at that time) and the solubility product is a constant value (at a given temperature) and is independent of presence of any other ion present. Like other equilibrium constants such as : K_p, K_c, K_a & K_b, it is also constant at a certain temperature & can change only when temperature changes.
- The salts like AgCl are regarded as sparingly soluble salts. Some of them are : Ag_2SO_4, Ag_2CO_3, $PbCl_2$, $PbCrO_4$, PbS, ZnS, $Al(OH)_3$, $Ca_3(PO_4)_2$, $BaSO_4$, $CaSO_4$, MnS etc.

K_{sp} for Ag_2SO_4 : $\quad Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{2-}$

$$K_{sp} = [2Ag^+]^2 \; [SO_4^{2-}]$$

K_{sp} for $Ca_3(PO_4)_2$ $\quad Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$

$$K_{sp} = [Ca^{2+}]^3 \; [PO_4^{3-}]^2$$

In solubilities of sparingly soluble salts, we will deal with mainly two types of problems : one to find out soloubility in water if K_{sp} of a salt is given & vice-versa. Secondly, to find out solubility of a salt in presence of other (common) ions in water.

Comparison of solubility product and ionic product

Solubility product	Ionic product
It is the product of the concentration of ions of the electrolyte each raised to the power of their coefficients in the balanced chemical equation in a saturated solution	It is the product of the concentration of ions of the electrolyte each raised to the power of their coefficients in the balanced chemical equation in a solution at any concentration.
It is applicable to only saturated solutions	It is applicable to all types of solutions of any concentration
It has a constant value for an electrolyte at a constant temperature	Its value is not constant and varies with change in concentration

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Example 28

Ksp of calcium iodate $Ca(IO_3)_3$ = 6.3 10^{-7} at 18 C, find the solubility of salt (in gm/L) in water at 18 C.

Solution :

Note : K_{sp} is expressed in concentration units.

In questions, solubility is generally asked (or given) to be expressed in gm/lt.

Now the following equilibrium is established.

$$Ca(IO_3)_2 \rightleftharpoons Ca^{2+} + 2IO_3^-$$

Let x mole/lt be solubility of $Ca(IO_3)_2$

$\Rightarrow$ $[Ca^{2+}] = xM$ & $[IO_3^-] = 2xM$

$$K_{sp} = [Ca^{2+}][IO_3^-]^2$$

$\Rightarrow$ $6.3 \quad 10^{-7} = (x)\ (2x)^2$

$\Rightarrow$ $4x^3 = 6.3 \quad 10^{-7}$

$\Rightarrow$ $x = 5.4 \quad 10^{-3}$ M

Now answer is to be expressed in gm/lt.

$\Rightarrow$ solubility $= x \quad M_0$

$= (5.4 \quad 10^{-3}) \quad 390 = 2.106$ g/lt

Example 29

The solubility of $BaSO_4$ in water is $2.3 \quad 10^{-4}$ gm/100 mL. Calculate the % age loss in weight when 0.2 gm of $BaSO_4$ is washed with (a) 1 lt of water (b) 1 lt of 0.01 N H_2SO_4.

Solution :

(a) Solubility is in general expressed in gm/lt,

so solubility of $BaSO_4$ = $2.3 \quad 10^{-3}$ g/lt.

Loss in weight of $BaSO_4$ = amount of $BaSO_4$ soluble.

$$\Rightarrow \quad \%\text{ loss} = \frac{2.3 \times 10^{-3}}{0.2} \times 100 = 1.15\%$$

(b) Now 0.01 N H_2SO_4 $\equiv 0.01\text{ N } SO_4^{2-}$ ions

$\equiv 0.005\text{ N } SO_4^{2-}$ ions

Now presence of SO_4^{2-} prior to washing $BaSO_4$ will suppress the solubility of $BaSO_4$ (due to common ion effect). The suppression will be governed by K_{sp} value of $BaSO_4$. So first calculate K_{sp} of $BaSO_4$.

Solubility of $BaSO_4$ in fresh water = $2 \quad 10^{-3}$ g/lt

$$\equiv \frac{2.3 \times 10^{-3}}{233.4} = \text{Mol/lt} = 9.85 \times 10^{-6}\text{M}$$

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

$$= (9.85 \quad 10^{-6})^2 = 9.71 \quad 10^{-11}$$

Now let x be solubility in mol/lt

$[Ba^{2+}]$ in solution = x mol/lt

& $[SO_4^{2-}]$ in solution = (x + 0.005) mol/lt

Ionic product = $[Ba^{2+}]\ [SO_4^{2-}]$ = (x) (x + 0.005)

K_{sp} = Ionic Product at equilibrium (saturation)

$\Rightarrow$ $9.11 \quad 10^{-11}$ = (x) (x + 0.005)

$\Rightarrow$ $x^2 + 0.005\,x - 9.71 \quad 10^{-11} = 0$

New neglecting x^2 (as x << 1)

$\Rightarrow \qquad x = \dfrac{9.71 \times 10^{-11}}{0.005} = 1.94 \quad 10^{-8}$ mol /lt

$= 1.94 \quad 10^{-8} \quad 233.4$ g/lt

$= 4.53 \quad 10^{-8}$ g/lt

$\Rightarrow$ $4.53 \quad 10^{-6}$ gm of $BaSO_4$ are washed away.

$$\Rightarrow \qquad \% \text{ loss} = \frac{4.53 \quad 10^{-6}}{0.2} = 2.26 \quad 10^{-3}\ \%$$

Precipitation of Salts :

For a salt (sparingly soluble) when dissolved in water : $AB \rightleftharpoons A^{+} + B^{-}$

at equilibrium (saturation) $K_{sp} = [A^{+}] + [B^{-}]$

When we mix ions or if there be two or more ions in water, we define reaction coefficient (Q), called as ionic-product (IP) in this case, giving the products of ions in water (ions of soluble salts & other common ions).

IP is product of ionic concentration due to ions already present in water or from a salt. It may be & may not be equal to K_{sp}.

1. If Ionic Product (IP) > K_{sp}; precipitation takes place till I.P. equals K_{sp}.
2. If Ionic Product < K_{sp} ; a precipitate will not be formed and the solution will be unsaturated.
3. If Ionic Product = K_{sp} ; a precipitate will not form and the solution is saturated in that salt.

   (Or we can say that solution is at a critical stage, when precipitation just begins, but actually has not occurred yet in real sense).

Example 30

A solution contains a mixture of Ag^{+}(0.1M) and Hg_2^{2+} (0.10 M) which are separated by selected precipitation. Calculate maximum concentration of Iodide ion at which one of them gets precipitated almost completely. What % age of that metal ion is precipitated ?

Solution :

First determine, which ion starts precipitating.

$[I^{-}]$ required to precipitate $AgI = \dfrac{K_{sp} \text{ of } AgI}{[Ag^{+}]}$

$$= \frac{8.5 \times 10^{-17}}{0.1} = 8.5 \times 10^{-16}\,\text{M}$$

$$[\text{I}^-] \text{ for } \text{Hg}_2\text{I}_2 = \sqrt{\frac{\text{K}_{\text{sp}} \text{ of } \text{Hg}_2\text{I}_2}{[\text{Hg}_2^{2+}]}}$$

$$= \sqrt{\frac{2.5 \times 10^{-26}}{0.1}} = 5 \times 10^{-13}$$

This means that AgI will be precipitated first as $[\text{I}^-]$ required for AgI is less.

But when $[\text{I}^-]$ reaches 5 10^{-13} M then precipitation of Hg_2I_2 also starts.

So $[\text{Ag}^+]$ left at that stage is given as :

$$[\text{Ag}^+] = \frac{\text{K}_{\text{sp}} \text{ of AgI}}{[\text{I}^-]_{\text{Hg}_2\text{I}_2}} = \frac{8.5 \times 10^{-17}}{5.0 \times 10^{-13}} = 1.7 \times 10^{-4}\ \text{M}$$

% of Ag^+ left unprecipitated

$$= \frac{1.7 \times 10^{-4}}{0.1} \times 100 = 0.17\%$$

$\Rightarrow$ % age of Ag^+ = 99.83 %

This means when Hg_2I_2 starts precipitating, Ag^+ is almost precipitated.

Example 31

Freshly precipitated Al & Mg Hydroxides are stirred vigorously in a buffer solution containing 0.25 mol/lt of NH_4Cl & 0.05 mol/lt of NH_4OH. Calculate $[\text{Al}^{3+}]$ & $[\text{Mg}^{2+}]$ in solution. K_b (NH_4OH) = 1.8 10^{-5}; K_{sp} (Mg(OH)_2) = 8.9 10^{-12}; K_{sp} (Al(OH)_3) = 6 10^{-32}.

Solution :

Note that Al $(\text{OH})_3$ & Mg $(\text{OH})_2$ are mixed with buffer which is basic. i.e. $[\text{OH}^-]$ are already present in the solution so it will decrease the solubility of Al $(\text{OH})_3$ & Mg(OH)_2 in the solution.

At equilibrium, $[\text{OH}^-]$ will determine the concentration of metal ions in solution.

First calculate $[\text{OH}^-]$ in the solution using basic buffer equation.

$$\text{pOH} = \text{pK}_\text{b} + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$= -\log(1.8 \quad 10^{-5}) + \log\left(\frac{0.25}{0.05}\right)$$

pOH $= 5.4431 = -\log[OH^-]$

$\Rightarrow$ $[OH^-] = 3.59 \quad 10^{-6}$ M

Now this controls the following equilibria.

1. $Mg(OH)^2$; $K_{sp} = [Mg^{2+}][OH^-]$

$$\Rightarrow \quad [Mg^{2+}] = \frac{8.9\times10^{-12}}{\left(3.59\times10^{-6}\right)} = 0.69 \text{ M}$$

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

$$\Rightarrow \quad [Al^{3+}] = \frac{6\times10^{-32}}{\left(3.59\times10^{-6}\right)} = 1.29\times10^{-15} \text{ M}$$

Example 32

The solubility product of CaF_2 is 3.9 10^{-11} at 25 C. What is the solubility (in grams) of this salt in a litre of 0.1 N NaF solution ?

Solution :

Let the solubility of CaF_2 in the presence of 0.1 N NaF be x.

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$$

$[Ca^{2+}] = x$

$[F^-] = 2x + 0.1$

$K_{sp} = [Ca^{2+}][F^-]^2 = x(2x + 0.1]^2 = 4x^3 + 0.4x^2 + 0.01x$

Since x is small, x^2 and x^3 terms would be very-very small and can be neglected.

$\therefore$ $0.01x = 3.9 \quad 10^{-11}$

$$x = \frac{3.9\times10^{-11}}{0.01} = 3.9\times10^{-9}$$

The smalleness of x justifies the earlier supposition that x^3 and x^2 is negligible.

Molecular weight of CaF_2 = (40 + 38) = 78

Mass of CaF_2 per litre = 3.9 10^{-9} 78 = **3.042 10^{-7} g litre^{-1}.**

Example 33

The solubility product (K_{sp}) of $Ca(OH)_2$ at 25 C is $4.42 \quad 10^{-5}$. A 500 ml of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much Ca(OH). How much $Ca(OH)_2$ in miligrams is precipitated ? [IIT 1992]

Solution :

Let the solubility of Ca $(OH)_2$ in pure water = S moles / litre

$$Ca(OH)_2 \rightleftharpoons \underset{s}{Ca^{2+}} + \underset{2s}{2OH^-}$$

Then $K_{sp} = [Ca^{2+}]\,[OH^-]^2$

$$4.42 \quad 10^{-5} = S \quad (2S)^2$$

$$4.42 \quad 10^{-5} = 4S^3$$

$$S = 2.224 \quad 10^{-2} = 0.0223 \text{ moles litre}^{-1}$$

$\therefore$ No. of moles of Ca^{2+} ions in 500 ml of solution = 0.01115

Now when 500 ml of saturated solution is mixed with 500 ml of 0.4 M NaOH, the resultant volume is 1000 ml. The molarity of OH^- ions in the resultant solution would therefore be 0.2 M.

$$\therefore \quad [Ca^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{4.42 \times 10^{-5}}{(0.2)^2} = 0.001105\text{ M}$$

Thus, No. of moles of Ca^{2+} or $Ca(OH)_2$ precipitated = 0.01115 – 0.001105 = 0.010045

Mass of $Ca(OH)_2$ precipitated = 0.010045   74 = **0.7433 g = 743.3 mg**

Example 34

Given : $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$, $K_c = 6.2 \quad 10^{-8}$ and K_{sp} of AgCl = $1.8 \quad 10^{-10}$ at 298 K. Calculate the concentration of the complex in 1.0 M aqueous ammonia.

Solution :

For AgCl $\quad AgCl \rightleftharpoons Ag^+ + Cl^-$

$\therefore \quad K_{sp} = [Ag^+]\,[C^-] \quad$ ... (i)

Again it is given that

$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3;\ K_c = 6.2 \times 10^{-8}$$

$$\text{or} \quad Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+;\ K_f = \frac{1}{6.2 \times 10^{-8}} = \frac{10^8}{6.2}$$

$$\therefore \quad K_f = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^+}$$

$$\text{or} \quad [Ag^+] = \frac{[Ag(NH_3)_2]^+}{K_f[NH_3]^2}$$

Since the formation constant of the complex is very high, most of the $[Ag^+]$ which dissolves must be converted into complex and each Ag^+ dissolved also requires dissolution of Cl^-.

$\therefore$ $[Cl^-] = [Ag(NH_3)2]^+$ and let it be c M

Equation (i) becomes

$$K_{sp} = \frac{[Ag(NH_3)_2]^+}{K_f[NH_3]^2}$$

$$K_{sp} = \frac{c}{K_f\,[1]^2} \times c$$

$$c^2 = K_{sp} \quad K_f\ [1]^2$$

$$= 1.8 \times 10^{-10} \times \frac{10^8}{6.2} \times (1)^2$$

$$c^2 = \frac{1.8 \times 10^{-2}}{6.2} = 0.2903 \quad 10^{-2}$$

$$c = 0.538 \quad 10^{-1} = \mathbf{0.0538\ M}$$

Example 35

Predict whether a precipitate will be formed or not when equal volumes of 2 10^{-6} M $BaCl_2$ solution and 2 10^{-5} M Na_2SO_4 solution are mixed ? The solubility product of barium sulphate is 1 10^{-10}.

Solution :

Calculation of concentrations of Ba^{2+} and SO_4^{2+} ions before mixing.

$$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$$

$\therefore$ $[Ba^{2+}] = 2 \quad 10^{-6}$ M

Similarly, $Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$

$$\therefore \quad \left[SO_4^{2-}\right] = 2 \times 10^{-5}\ M$$

Concentration of individual ions in the total solution which is doubled after mixing.

$$[Ba^{2+}] = \frac{2 \times 10^{-6}}{2} = 10^{-6}\ M \qquad \text{or} \qquad \left[SO_4^{2-}\right] = \frac{2 \times 10^{-5}}{2} = 10^{-5}\ M$$

Alternatively,

Let the volume before mixing = x litre

$\therefore$ The volume after mixing equal volumes of the two salts = x + x = 2x litres

Further let the molarity of the resulting solution $= M_2$

Now applying molarity formula to Ba^{2+} ions.

$$\underset{\text{(Before mixing)}}{M_1V_1} = \underset{\text{(After mixing)}}{M_2I_2}$$

$$2 \quad 10^{-6} \quad x = M_2 \quad 2x$$

$$M_2 = \frac{2 \times 10^{-6} \times x}{2x} = \frac{2 \times 10^{-6}}{2} = 10^{-6}$$

Similarly, for SO_4^{2-} ions

$$\underset{\text{(Before mixing)}}{M_1V_1} = \underset{\text{(After mixing)}}{M_2I_2}$$

$$2 \quad 10^{-5} \quad x = M_2 \quad 2x$$

$$M_2 = \frac{2 \times 10^{-5} \times x}{2x} = \frac{2 \times 10^{-5}}{2} = 10^{-5}$$

Calculation of ionic product of Ba^{2+} and SO_4^{2-} ions

$\therefore$ Ionic product of $BaSO_4 = 10^{-6} \quad 10^{-5} = 10^{-11}$

Since here Ionic product < Solubility product

$$10^{-11} < 10^{-10}$$

No precipitate will be formed.