Types of Electrolytes:

The compounds which give ions either in molten state or in solution are called electrolytes. In the solid state they are bad conductors, but become good conductors either in the molten state in solution.

There are two types of electrolytes:

(1) Strong electrolytes:

These electrolytes are almost completely ionized when dissolved in a polar medium like water. In solution they are excellent conductors, e.g., HNO₃, HCl, KOH, NaOH, etc. Their degree of ionization is high and approaches unity.

(2) Weak electrolytes:

These are not completely ionized when dissolved in a polar solvent and they behave as poor conductors of electricity, e.g., CH₃COOH, H₃PO₄, H₃BO₃, NH₄OH, etc., Equilibrium between ions and unionized molecules is established in solution, e.g.,

\[ \text{CH}_3\text{COOH} \leftrightarrow \text{CH}_3\text{COO}^- + \text{H}^+ \]

The above equilibrium is termed as ionic equilibrium. Degree of ionization of weak electrolytes is much less than unity.

Degree of ionization \( \alpha \) may be defined as a fraction of tital number of molecules of an electrolyte which dissociate into ions.

\[ \alpha = \text{%ionization}/100 \]

\[ = (\text{Number of molecules dissociated as ions})/(\text{Total number of molecules of electrolyte dissolved}) \]

The following classification of electrolytes is based on their behavior in a particular solvent, i.e., water.
electrolytes i.e. acids, bases (Solution of non-electrolytes such as and salts) urea, glucose, sugar, glycerine, etc.)

Strongly conducting (solns. of Weakly conducting

Strong electrolytes which ionize (solutions of weak ele-

Almost completely in water such ctrolytes which slightly

as HCl, H₂SO₄, HNO₃, NH₄Cl, ionize in water such as

NaCl, NaOH, KOH, etc.) CH₃COOH, NH₄OH, H₃PO₄, HCN, etc.)

However, an electrolyte may behave as a strong one in aqueous solution, but it may behave as a weak one in another solvent. For example, sodium chloride behaves as a strong electrolyte and acetic acid as a weak electrolyte when dissolved in water but their conducting abilities are comparable in liquid ammonia solvent.

Ostwald’s Dilution Law:

According to Arrhenius theory of electrolyte dissociation, the molecules of an electrolyte in solution are constantly splitting up into ions and the ions are constantly reuniting to form unionized molecules. Therefore, a dynamic equilibrium exists between ions and unionized molecules of the electrolyte in solution. It was pointed out by Ostwald that like chemical equilibrium, law of mass action can be applied to such systems also.

Consider a binary electrolyte AB which dissociates into A⁺ and B⁻ ions and the equilibrium state is represented by the equation:

\[ AB \leftrightarrow A^+ + B^- \]

Initially \( t = 0 \quad C \quad 0 \quad 0 \)

At equilibrium \( C(1-\alpha) \quad Ca \quad Ca \)

So, dissociation constant may be given as

\[ K = [A^+][B^-]/[AB] = (Ca \times Ca)/(1-\alpha) \]

\[ = Ca^2/(1-\alpha) \quad \ldots \ldots \text{ (i)} \]
For very weak electrolytes, 

\[ a \ll 1, \quad (1 - a) = 1 \]

\[ \therefore \quad K = C a^2 \]

\[ a = \sqrt{K/C} \quad \text{....... (ii)} \]

Concentration of any ion = \( C a = \sqrt{CK} \).

From equation (ii) it is clear that degree of ionization increases on dilution.

Thus, **degree of dissociation** of a weak electrolyte is proportional to the square root of dilution.

**Limitations of Ostwald's dilution law:**

The law holds good only for weak electrolytes and fails completely in the case of strong electrolytes. The value of '\( a \)' is determined by conductivity measurements by applying the formula \( \Lambda/\Lambda_\infty \). The value of '\( a \)' determined at various dilutions of an electrolyte when substituted in Eq. (i) gives a constant value of \( K \) only in the case of weak electrolytes like \( \text{CH}_3\text{COOH}, \text{NH}_4\text{OH}, \text{etc.} \) the cause of failure of **Ostwald's dilution law** in the case of strong electrolytes is due to the following factors:

(i) The law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. Strong electrolytes are almost completely ionized at all dilutions and \( \Lambda/\Lambda_\infty \) does not give accurate value of '\( a \)'.

(ii) When concentration of the ions is very high, the presence of charges on the ions appreciably effects the equilibrium. Hence, law of mass action its simple form cannot be strictly applied in the case of strong electrolytes.

**SOME SOLVED EXAMPLES**

**Example 1:** A 0.01 M solution of acetic is 5% ionized at 25° C. Calculate its dissociation constant.

**Solution:** According to **Ostwald's dilution law**

\[ K_a = \frac{a^2}{(1-a)V} \]

\[ a = 0.05, \quad V = 1/0.01 = 100 \text{ litres} \]

Hence,

\[ K_a = 0.05 \times 0.05/(1-0.05)100 = 2.63 \times 10^{-5} \]
Example 2: Calculate the H+ ion concentration of a 0.02 N weak monobasic acid. The value of **dissociation constant** is $4.0 \times 10^{-10}$.

**Solution:**

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

Applying **Ostwald's dilution law** of a weak acid,

\[ \alpha = \sqrt{k_a V} \]

$K_a = 4.0 \times 10^{-10}$, \hspace{1em} $V = 1/0.01 = 100$ litres

\[ \alpha = \sqrt{(4 \times 10^{-10} \times 10^2)} = 2 \times 10^{-4} \]

Concentration of hydrogen ions

\[ \frac{a}{\sqrt{V}} = \frac{(2 \times 10^{-4})}{100} = 2 \times 10^{-6} \text{ mol L}^{-1} \]

or Concentration of hydrogen ions

\[ \sqrt{CK} = \sqrt{(0.01 \times 4 \times 10^{-10})} = 2 \times 10^{-6} \text{ mol L}^{-1} \]

Example 3: The concentration of H+ ions in 0.10 M solution of a weak acid is $1.0 \times 10^{-5}$ mol L$^{-1}$. Calculate the **dissociation constant** of the acid.

**Solution:**

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

Initial concentration 0.1 0 0

Equilibrium concentration

(mol L$^{-1}$) 0.1-1.0×$10^{-5}$ 1.0×$10^{-5}$ 1.0×$10^{-5}$

[HA] can be taken as 0.1 M as $1.0 \times 10^{-5}$ is very small.

Applying law of mass action.

\[ K_o = \frac{[H^+][A^-]}{[HA]} = \frac{(1.0 \times 10^{-5} \times 1.0 \times 10^{-5})}{0.1} \]

\[ = 1 \times 10^{-9} \]

Example 4: What will be the **dissociation constant** of 0.1 N aqueous ammonia solution in terms of degree of dissociation 'α'? What will be the value if the concentration is 0.01 N?
Solution: \( \text{NH}_4\text{OH} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \)

At equilibrium \((1-\alpha) \quad \alpha \quad \alpha\)

Since the solution is 0.1 N,

\[ V = 1/0.1 = 10 \text{ litre} \]

\[ [\text{NH}_4\text{OH}] = (1-\alpha)/10, \quad [\text{NH}_4^-] = \alpha/10 \quad \text{and} \quad [\text{OH}^-] = \alpha/10 \]

Applying law of mass action,

For 0.01 N Solution, \( K_b \) remains the same at the same temperature but \textit{degree of dissociation} value becomes different.

Example 5: A 0.0128 N solution of acetic acid has \( A = 14 \) mho equiv\(^{-1}\) and \( A_\infty = 391 \) mho equiv\(^{-1}\) at 25\(^\circ\)C. Calculate the \textit{dissociation constant} of the acid.

Solution: Degree of dissociation,

\[ \alpha = \Lambda/\Lambda_\infty = 14/391 = 3.58*10^{-2} \]

Now applying \textit{Ostwald's dilution law},

\[ K_\alpha = \alpha^2/(1-\alpha)V \]

\[ \alpha = 3.58 \times 10^{-2} \quad \text{and} \quad V = 1/0.0128 \text{ litre} \]

\textbf{COMMON ION EFFECT:}

Let AB to the weak electrolyte. Considering its dissociation,

\( \text{AB} \leftrightarrow \text{A}^+ + \text{B}^- \)

and applying law of mass action we have

\[ K = [\text{A}^+][\text{B}^-]/[\text{AB}] \]

The equilibrium constant, \( K \), has a definite value at any given temperature. If now another electrolyte furnishing the \( \text{A}^+ \) and \( \text{B}^- \) ions be added to the above solution. It will increases the concentration of either \( \text{A}^+ \) ions or \( \text{B}^- \) ions (whichever has been added) and in order that \( K \) may remain constant, the concentration of AB must increases, i.e., the equilibrium will shift to the left hand side.
In other words, the degree of dissociation of an electrolyte (weak) is suppressed by the addition of another electrolyte (strong) containing a common ion. This is termed as common ion effect. Acetic acid is a weak electrolyte and its ionization is suppressed in presence of a strong acid (H\(^+\) ion as common ion) or a strong salt like sodium acetate (acetate ion as common ion). Similarly, the addition of NH\(_4\)Cl or NaOH to NH\(_4\)OH solution will suppress the dissociation of NH\(_4\)OH due to common ion either NH\(_3^-\) or OH\(^-\).

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

**Example 6:** The ionization constant of HCN is \(4 \times 10^{-10}\). Calculate the concentration of hydrogen ions in 0.2 M solution of HCN containing 1 mol L\(^{-1}\) of KCN?

**Solution:** The dissociation of HCN is represented as

\[
HCN \leftrightarrow H^+ + CN^- 
\]

Applying law of mass action,

\[
K_a = \frac{[H^+][CN^-]}{[HCN]} \text{ or } [H^+] = \frac{K_a[HCN]}{[CN^-]} 
\]

In presence of strong electrolyte, the total CN\(^-\) concentration comes from KCN which undergoes complete dissociation. It is further assumed that dissociation of HCN is very-very small and the concentration of HCN can be taken as the concentration of undissociated HCN.

Thus, [HCN] = 0.2 M and [CN\(^-\)] = 1M

Putting these values in the expression

\[
[H^+] = \frac{(K_a[HCN])}{([CN^-])} = \frac{(4 \times 10^{-10} \times 0.2)}{1} = 8 \times 10^{-11} \text{ mol L}^{-1}
\]

[Note: When KCN is not present, the [H\(^+\)] concentration is equal to \(\sqrt{CK}\) i.e., \(\sqrt{(0.2 \times 4 \times 10^{-10})} = 8.94 \times 10^{-8}\) mol L\(^{-1}\). This shows that concentration of H\(^+\) ions fails considerably when KCN is added to HCN solution.

**Example 7:** Determine the concentration of hydroxyl ions in 0.4 M NH\(_4\)OH solution having (i) no ammonium chloride, (ii) 5.35 g of NH\(_4\)Cl in a litre of the solution. Ionization constant of NH\(_4\)OH is \(1.8 \times 10^{-5}\).

**Solution:** (i) Let ‘α’ be the degree of dissociation of NH\(_4\)OH in absence of NH\(_4\)Cl.

\[
\alpha = \sqrt{K_b/c}
\]

So, [OH\(^-\)] = C \alpha = \sqrt{(K_b c)} = \sqrt{(1.8 \times 10^{-5} \times 0.4)}

\[
= 2.68 \times 10^{-3} \text{ mol L}^{-1}
\]
(ii) In presence of NH₄Cl

\[ [\text{NH}_4^-] = 5.35/53.5 = 0.1 \text{M and } [\text{NH}_4\text{OH}] = 0.4 \text{M} \]

So, \([\text{OH}^-] = (K_b \times [\text{NH}_4\text{OH}])/[\text{NH}_4^-] = (1.8 \times 10^{-3} \times 0.4)/0.1 \]

= 7.2 \times 10^{-5} \text{ mol L}^{-1}

**Example 8:** When 0.100 mole of ammonia, \(\text{NH}_3\), is dissolved in sufficient water to make 1.0 L solution, the solution is found to have a hydroxide ion concentration of \(1.34 \times 10^{-3}\) M. Calculate \(K_b\) for ammonia.

**Solution:**

\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ \\
\]

At equilibrium (0.100 - 1.34 \times 10^{-3}) M \hspace{1cm} 1.34 \times 10^{-3} M

= 0.09866 M + \text{OH}^-

1.34 \times 10^{-3} M

\[
K_b = \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_3]} = \frac{(1.34 \times 10^{-3} \times 1.34 \times 10^{-3})}{0.09866} \\
= 1.8199 \times 10^{-5}
\]

**Example 9:** \(K_a\) for HA is \(4.9 \times 10^{-8}\). After making the necessary approximation, calculate for its decimolar solution

(a) \% dissociation

(b) \(H^+\) ion concentration.

**Solution:** For a weak electrolyte.

\[
a = \sqrt{K/C} = \sqrt{(4.9 \times 10^{-8})/0.1) \\
= 7 \times 10^{-4}
\]

\% dissociation = 100 \times a = 100 \times 7 \times 10^{-4}

= 7 \times 10^{-2}

\[
\text{HA} \leftrightarrow \text{H}^+ + \text{A}^- \\
\text{C}(-1-a) \hspace{1cm} \text{Ca} \hspace{1cm} \text{Ca}
\]
Example 10: Nicotinic acid \((K_a = 1.4 \times 10^{-5})\) is represented by the formula \(\text{HNiC}\). Calculate its per cent dissociation in a solution which contains 0.10 mole of nicotine acid per 2 litre of solution.

Solution: Initial concentration of the nicotinic acid = \(0.10/2 = 0.05\text{molL}^{-1}\)

\[
\text{HNiC} \rightleftharpoons \text{H}^+ + \text{NiC}^-
\]

Equilibrium conc. \((0.05-x)\) \(x\) \(x\)

As \(x\) is very small, \((0.05 - x)\), can be taken as 0.05

\[
K_a = \frac{[\text{H}^+ ][\text{NiC}^-]}{[\text{HNiC}]} = \frac{(x \times x)}{0.05}
\]

or \(x^2 = (0.05) \times (1.4 \times 10^{-5})\)

or \(x = 0.83 \times 10^{-3}\text{ mol L}^{-1}\)

% dissociation = \(\frac{0.83 \times 10^{-3}}{0.05 \times 100} = 1.66\)

Alternative method: Let \(\alpha\) be the degree of dissociation

\[
\text{NHiC} \rightleftharpoons \text{H}^+ + \text{NiC}^-
\]

At equilibrium \(0.05 (1 - \alpha)\) \(0.05\alpha\) \(0.05\alpha\)

\[
K_a = \frac{(0.05\alpha \times 0.05\alpha)}{0.05(1-\alpha)}
\]

As \(\alpha\) is very small, \((1-\alpha) ightarrow 1\).

So, \(1.4 \times 10^{-5} = 0.05\ \alpha^2\)

or \(\alpha\sqrt{(1.4 \times 10^{-5})/0.05} = 1.67 \times 10^{-2}\)

Per cent dissociation = \(100 \times \alpha = 100 \times 1.67 \times 10^{-2}\)

= 1.67

Example 11: At 30\(^\circ\) C the degree of dissociation of 0.066 M HA is 0.0145. What would be the degree of dissociation of 0.02 M solution of the acid at the same temperature?

Solution: Let the ionization constant of the acid be \(K_a\).

Degree of dissociation at 0.66 M concentration = 0.0145.
Applying $\alpha = \sqrt{K_\alpha/C}$

$0.0145 = \sqrt{K_\alpha/0.066}$ ..... (i)

Let the degree of dissociation of the acid at 0.02 M concentration be $\alpha_1$.

$\alpha_1 = \sqrt{K_\alpha/0.02}$ ..... (ii)

Dividing Eq. (ii) by Eq. (i)

$\alpha_1/0.0145 = \sqrt{(0.066/0.02)}=1.8166$

or $\alpha_1 = 0.0145 \times 1.8166 = 0.0263$

**Example 12:** A solution contains 0.1 M H$_2$S and 0.3 M HCl. Calculate the concentration of S$^{2-}$ and HS$^-$ ions in solution. Given and for H$_2$S are $10^{-7}$ and $1.3 \times 10^{-13}$ respectively.

**Solution:** H$_2$S $\leftrightarrow$ H$^+$ + HS$^-$

$K_{a1} = [H^+][HS^-]/[H_2S]$ ....... (i)

Further HS$^-$ = H$^+$ + S$^{2-}$

$K_{a2} = [H^+][S^{2-}]/[H_2S]$ ....... (ii)

Multiplying both the equations

$K_{a1} \times K_{a2} = ([H^+]^2[S^{2-}])/[H_2S]$

Due to common ion, the ionization of H$_2$S is suppressed and the [H$^+$] in solution is due to the presence of 0.3 M HCl.

$[S^{2-}] = (K_{a1} \times K_{a2}[H_2S])/[H^+]^2 = (1.0 \times 10^{-7} \times 1.3 \times 10^{-13} \times 0.1)/(0.3)^2$

Putting the value of [S$^{2-}$] in Eq. (ii)

$1.3 \times 10^{-13} = (0.3 \times 1.44 \times 10^{-20})/([HS^-])$

or [HS$^-$] $= (0.3 \times 1.44 \times 10^{-20})/(1.3 \times 10^{-13}) = 3.3 \times 10^{-8}$ M

$K_\alpha = 3.58 \times 10^{-2} \times 3.58 \times 10^{-2} \times 0.0128 = 1.64 \times 10^{-5}$

**Acids and Bases:**

The earliest criteria for the characterization of acids and bases were the experimentally observed properties of aqueous solutions. An acid* was defined as a substance whose water solution tastes sour, turns blue litmus red, neutralizes bases and so on. A substance was a base if its aqueous solution tasted bitter, turns red litmus blue, neutralizes acids and so on.
Faraday termed acids, bases and salts as electrolytes and Liebig proposed that acids are compounds containing hydrogen that can be replaced by metals.

Different concepts have been put forth by different investigators to characterize acids and bases but the following are the three important modern concepts of acids and bases:

(1) **Arrhenius concept**

According to Arrhenius concept all substances which give $H^+$ ions when dissolved in water are called acids while those which ionize in water to furnish $OH^-$ ions are called bases.

$$\text{HA} \leftrightarrow H^+ + A^- \quad \text{(Acid)}$$

$$\text{BOH} \leftrightarrow B^+ + OH^- \quad \text{(Base)}$$

Thus, HCl is an acid because it gives $H^+$ ions in water. Similarly, NaOH is a base as it yields $OH^-$ ions in water.

$$\text{HCl} \leftrightarrow H^+ + Cl^-$$

$$\text{NaOH} \leftrightarrow Na^+ + OH^-$$

Some acids and bases ionize completely in solutions and are called strong acids and bases. Others are dissociated to a limited extent in solutions and are termed weak acids and bases. HCl, HNO$_3$, H$_2$SO$_4$, HClO$_4$, etc., are examples of strong acids and NaOH, KOH, (CH$_3$)$_4$NOH are strong bases. Every hydrogen compound cannot be regarded as an acid, e.g., CH$_4$ is not an acid. Similarly, CH$_3$OH, C$_2$H$_5$OH, etc., have OH groups but they are not bases.

Actually free $H^+$ ions do not exist in water. They combine with solvent molecules, i.e., have strong tendency to get hydrated.

$$\text{HX} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + X^-$$

(Hydronium ion)

The proton in aqueous solution is generally represented as $H^+$ (aq). It is now known that almost all the ion are hydrated to more or less extent and it is customary to put (aq) after each ion.

The oxides of many non-metals react with water to form acids and are called acidic oxides or acid anhydrides.

$$\text{CO}_2 + \text{H}_2\text{O} \quad \text{H}_2\text{CO}_3 \leftrightarrow 2\text{H}^+(\text{aq}) + (\text{aq})$$

$$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \quad 2\text{HNO}_3 \leftrightarrow 2\text{H}^+(\text{aq}) + (\text{aq})$$

Many oxides of metals dissolve in water to form hydroxides. Such oxides are termed basic oxides.
Na₂O + H₂O → 2NaOH ↔ 2Na⁺(aq) + 2OH⁻(aq)

The substance like NH₃ and N₂H₄ act as bases as they react with water to produce OH⁻ ions.

NH₃ + H₂O → NH₄OH ↔ NH₄⁺(aq) + OH⁻(aq)

The reaction between an acid and a base is termed neutralization. According to Arrhenius concept, the neutralization in aqueous solution involves the reaction between H⁺ and OH⁻ ions or hydronium and OH⁻. This can be represented as

H₃O⁺ + OH⁻ ↔ 2H₂O

**Limitations:**

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

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

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

(iv) It cannot explain the acidic character of certain salts such as AlCl₃ in aqueous solution.

(v) An artificial explanation is required to explain the basic nature of NH₃ and metallic oxides and acidic nature of non-metal oxides.

(2) **Bronsted-Lowry concept - The proton-donor-acceptor concept:**

In 1923, Bronsted and Lowry independently proposed a broader concept of acids and bases. According to Bronsted-Lowry concept an acid is a substance (molecule or ion) that can donate proton, i.e., a hydrogen ion, H⁺, to some other substance and a base is a substance that can accept a proton from an acid. More simply, an acid is a proton donor (protogenic) and a base is a proton acceptor (protophilic).

Consider the reaction,

HCl + H₂O ↔ H₃O + Cl⁻

In this reaction HCl acts as an acid because it donates a proton to the water molecule. Water, on the other hand, behaves as a base by accepting a proton from the acid.

The dissolution of ammonia in water may be represented as

NH₃ + H₂O ↔ NH₄⁺ + OH⁻
In this reaction, $H_2O$ acts as an acid and donated a proton to $NH_3$ molecule and $NH_3$ molecule behaves as a base as it accepts a proton.

When an acid loses a proton, the residual part of it has a tendency to regain a proton. Therefore, it behaves as a base.

\[ \text{Acid} \leftrightarrow H^+ + \text{Base} \]

The acid and base which differ by a proton are known to form a conjugate pair. Consider the following reaction.

\[ \text{CH}_3\text{COOH} + H_2O \leftrightarrow H_3O^+ + \text{CH}_3\text{COO}^- \]

It involves two conjugate pairs. The acid-base pairs are:

\[ \begin{array}{c|c|c}
\text{Acid} & -H^+ & \text{Base} + H^+ \\
\text{CH}_3\text{COOH} & \text{CH}_3\text{COO}^- & \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+
\end{array} \]

Such pairs of substances which can be formed one another by loss or gain of a proton are known as conjugate acid-base pairs.

If in the above reaction, the acid $\text{CH}_3\text{COOH}$ is labelled acid$_1$ and its conjugate base, $\text{CH}_3\text{COO}^-$ as base$_1$, $H_2O$ is labelled as base$_2$ and its conjugate acid $H_3O^+$ as acid$_2$, the reaction can be written as:

\[ \text{Acid}_1 + \text{Base}_2 \leftrightarrow \text{Base}_1 + \text{Acid}_2 \]

Thus, any acid-base reaction involves two conjugate pairs, i.e., when an acid reacts with a base, another acid and base are formed. Some more examples are given below:

\[ \begin{array}{l}
\text{Acid}_1 + \text{Base}_2 \equiv \text{Acid}_2 + \text{Base}_1 \\
H_2O + NH_3 \equiv NH_4^+ + OH^- \\
HCN + H_2O \equiv H_3O^+ + CN^- \\
HF + CH_3COOH \equiv CH_3COOH_2^- + F^- \\
CH_3COOH + NH_3 \equiv NH_4^+ + CH_3COO^- \\
NH_2 + NH_3 \equiv NH_4^+ + NH_2^- \\
H_2O + H_2O \equiv H_3O^+ + OH^- \\
HCO_2^- + H_2O \equiv H_3O^+ + CO_2^- \\
NH_4^+ + H_2O \equiv H_3O^+ + NH_3
\end{array} \]
Thus, every acid has its conjugate base and every base has its conjugate acid. It is further observed that strong acids have weak conjugate bases while weak acids have strong conjugate bases.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Conjugate base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>CH₃COO⁻</td>
</tr>
</tbody>
</table>

Strong acid  Weak base  Weak acid  Strong base

There are certain molecules which have dual character of an acid and a base. These are called amphiprotic or atmospheric.

Examples are NH₃, H₂O, CH₃COOH, etc.

The strength of an acid depends upon its tendency to lose its proton and the strength of the base depends upon its tendency to gain the proton.

**Acid-Base chart containing some common conjugate acid-base pairs**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Conjugate base</th>
</tr>
</thead>
<tbody>
<tr>
<td>KClO₄ (Perchloric acid)</td>
<td>(Perchlorate ion)</td>
</tr>
<tr>
<td>H₂SO₄ (Sulphuric acid)</td>
<td>(Hydrogen sulphate ion)</td>
</tr>
<tr>
<td>HCl (Hydrogen chloride)</td>
<td>Cl⁻ (Chloride ion)</td>
</tr>
<tr>
<td>HNO₃ (Nitric acid)</td>
<td>(Nitrate ion)</td>
</tr>
<tr>
<td>H₃O⁺ (Hydronium ion)</td>
<td>H₂O (Water)</td>
</tr>
<tr>
<td>(Hydrogen sulphate ion)</td>
<td>(Sulphide ion)</td>
</tr>
<tr>
<td>H₃PO₄ (Ortho phosphoric acid)</td>
<td>H₂ (Dihydrogen phosphate ion)</td>
</tr>
<tr>
<td>CH₃COOH (Acetic acid)</td>
<td>CH₃COO⁻ (Acetate ion)</td>
</tr>
<tr>
<td>H₂CO₃ (Carbonic acid)</td>
<td>(Hydrogen carbonate ion)</td>
</tr>
<tr>
<td>H₂S (Hydrogen sulphide)</td>
<td>(Hydrosulphide ion)</td>
</tr>
<tr>
<td>(Ammonium ion)</td>
<td>NH₃ (Ammonia)</td>
</tr>
<tr>
<td>HCN (Hydrogen cyanide)</td>
<td>CN⁻ (Cyanide ion)</td>
</tr>
</tbody>
</table>
In acid-base strength series, all acids above $H_3O^+$ in aqueous solution fall to the strength of $H_3O^+$. Similarly, the basic strength of bases below $OH^-$ fall to the strength of $OH^-$ in aqueous solution. This is known as levelling effect.

The strength of an acid also depends upon the solvent. The acids $HClO_4$, $H_2SO_4$, $HCl$ and $HN0_3$ which have nearly the same strength in water will be in the order of $HClO_4 > H_2SO_4 > HCl > HN0_3$ in acetic acid, since the proton accepting tendency of acetic acid is much weaker than water. So the real strength of acids can be judged by solvents. On the basis of proton interaction, solvents can be classified into four types:

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

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

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

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

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

$$HCl + HF \rightarrow H_2Cl^+ + F^-$$

Base       Acid       Acid       Base

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

A simple example of an acid-base is the reaction of a proton with hydroxyl ion.

$$H^+ + OH^- \rightarrow H_2O$$
Acid        Base

Some other examples are:

\[
\text{H}_3\text{N}: + \text{BF}_3 = \text{H}_3\text{N} \rightarrow \text{BF}_3
\]

Base   Acid

\[
\text{H}^+ +: \text{NH}_3 = [\text{H} \leftarrow \text{NH}_3]^+
\]

Acid   Base

\[
\text{BF}_3 + [\text{F}]^- = [\text{F} \rightarrow \text{BF}_3]^+
\]

Acid   Base

**Lewis concept** is more general than the Bronsted Lowry concept.

According to **Lewis concept**, the following species can act as **Lewis acids**.

(i) Molecules in which the central atom has incomplete octet: All compounds having central atom with less than 8 electrons are **Lewis acids**, e.g., BF$_3$, BC$_1$$_3$, AI$_1$$_3$, MgCl$_2$, BeCl$_2$, etc.

(ii) Simple cations: All cations are expected to act as **Lewis acids** since they are deficient in electrons. However, cations such as Na$^+$, K$^+$, Ca$^{2+}$, etc., have a very little tendency to accept electrons, while the cations like H$^+$, Ag$^+$, etc., have greater tendency to accept electrons and, therefore, act as **Lewis acids**.

(iii) Molecules in which the central atom has empty d-orbitals: The central atom of the halides such as SiX$_4$, GeX$_4$, TiCl$_4$, SnX$_4$, PX$_3$, PF$_5$, SF$_4$, SeF$_4$, TeCl$_4$, etc., have vacant d-orbitals. These can, therefore, accept an electron pair and act as **Lewis acids**.

(iv) Molecules having a multiple bond between atoms of dissimilar electronegativity: Typical examples of molecules falling in this class of **Lewis acids** are CO$_2$, SO$_2$ and SO$_3$. Under the influence of attacking Lewis base, one -electron pair will be shifted towards the more negative atom.

\[
\begin{align*}
\text{O= C=O} & + \text{OH}^- \rightarrow \text{O}^-\text{C}=\text{O} \quad \text{or} \quad \text{HCO}_3^-
\end{align*}
\]

**Lewis acid** **Lewis base**

The following species can act as **Lewis bases**.

(i) Neutral species having at least one lone pair of electrons: For example, ammonia, amines, alcohols, etc., act as **Lewis bases** because they contain a pair of electrons.
(ii) Negatively charged species or anions: For example, chloride, cyanide, hydroxide ions, etc., act as **Lewis bases**.

\[ \text{CN}^-, \text{Cl}^-, \text{OH}^- \]

It may be noted that all Bronsted bases are also **Lewis bases** but all Bronsted acids are not **Lewis acids**.

**Limitations:**

Since the strength of the **Lewis acids and bases** is found to depend on the type of reaction, it is not possible to arrange them in any order of their relative strength.

The choice of which definition of acids and bases one wishes to use in a particular instance depends largely on the sort of chemistry that is studied. But Arrhenius concept is perfectly satisfactory and simplest for dealing with reactions in aqueous solutions. It explains satisfactorily the strength of acids and bases in aqueous solutions, neutralisation, salt hydrolysis, etc.

**SOLUBILITY PRODUCT:**

If to a given amount of solvent at a particular temperature, a solute is added gradually in increasing amounts, a stage is reached when some of the solute remains undissolved, no matter how long we wait or how vigorously we stir. The solution is then said to be saturated. A **solution which remains in contact with undissolved solute is said to be saturated**. At saturated stage, the quantity of the solute dissolved is always constant for the given amount of a particular solvent at a definite temperature.

In case the solute is an electrolyte, its ionisation occurs in solution and degree of dissociation depends on the concentration of dissolved electrolyte at a particular temperature. Thus, in a saturated solution of an electrolyte two equilibria exist and can be represented as:

\[ \text{AB} \leftrightarrow \text{AB} \leftrightarrow \text{A}^+ + \text{B}^- \]

Solid unionized ions

(dissolved)

Applying the law of action to the **ionic equilibrium**, \[ \text{AB} \leftrightarrow \text{AB} \leftrightarrow \text{A}^+ + \text{B}^- \]
Since the solution is saturated, the concentration of unionised molecules of the electrolyte is constant at a particular temperature, i.e., \([AB] = K' = \text{constant}\).

Hence, \([A^+] [B^-] = K[AB] = KK = K_s (\text{constant})\)

\(K_s\) is termed as the **solubility product**. It is defined as the product of the concentration of ions in a saturated solution of an electrolyte at a given temperature.

Consider, in general, the electrolyte of the type \(A_xB_y\) which is dissociated as:

\[ A_xB_y \leftrightarrow xA^{y+} + yB^{x-} \]

Applying law of mass action,

\[ [Ay^+]x[Bx^-]y/[A_xB_y] = K \]

When the solution is saturated,

\[ [A_xB_y] = K' (\text{constant}) \]

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

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

Note: **Solubility product** is not the **ionic product** under all conditions but only when the solution is saturated.

**Different Expressions for Solubility Products**

(i) Electrolyte of the type \(AB\):

Its ionisation is represented as:

\[ AB \leftrightarrow A^+ + B^- \]

Thus, \( K_s = [A^+][B^-] \)

\( \text{AgCl} \leftrightarrow \text{Ag}^+ + \text{Cl}^-; \quad K_s = [\text{Ag}^+][\text{Cl}^-] \)

\( \text{BaSO}_4 \leftrightarrow \text{Ba}^{2+} + \text{SO}_4^{2-} ; \quad K_s = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \)

(ii) Electrolyte of the type \(AB_2\):

Its ionisation is represented as:
\[ AB_2 \leftrightarrow A^{2+} + 2B^- \]

Thus, \[ K_s = [A^{2+}][B^-]^2 \]

\[ PbCl_2 \leftrightarrow Pb^{2+} + 2Cl^-; \quad K_s = [Pb^{2+}][Cl^-]^2 \]

\[ CaF_2 \leftrightarrow Ca^{2+} + 2F^-; \quad K_s = [Ca^{2+}][F^-]^2 \]

(iii) Electrolyte of the type \( A_2B \):

Its ionisation is represented as:

\[ A_2B \leftrightarrow 2A^{2+} + B^{2-} \]

Thus, \[ K_s = [A^{2+}][B^{2-}] \]

\[ Ag_2CrO_4 \leftrightarrow 2Ag^+ + CrO_4^{2-}; \quad K_s = [Ag^+]^2[CrO_4^{2-}] \]

\[ H_2S \leftrightarrow 2H^+ + S^{2-}; \quad K_s = [H^+]^2[S^{2-}] \]

(iv) Electrolyte of the type \( A_2B_3 \):

Its ionisation is represented as:

\[ A_2B_3 \leftrightarrow 2A^{3+} + 3B^{2-} \]

Thus, \[ K_s = [A^{3+}][B^{2-}]^3 \]

\[ As_2S_3 \leftrightarrow 2As^{3+} + 3S^{2-}; \quad K_s = [As^{3+}][S^{2-}]^3 \]

\[ Sb_2S_3 \leftrightarrow 2Sb^{3+} + 3S^{2-}; \quad K_s = [Sb^{3+}][S^{2-}]^3 \]

(v) Electrolyte of the type \( AB_3 \):

Its ionisation is represented as:

\[ AB_3 \leftrightarrow A^{3+} + 3B^- \]

Thus, \[ K_s = [A^{3+}][B^-]^3 \]

\[ Fe(OH)_3 \leftrightarrow Fe^{3+} + 3OH^-; \quad K_s = [Fe^{3+}][OH^-]^3 \]

\[ AH_3 \leftrightarrow Al^{3+} + 3I^-; \quad K_s = [Al^{3+}][I^-]^3 \]
**Solubility product of a weak electrolyte:**

Let degree of ionization of weak electrolyte \( A_mB_n \) be \('a'\).

\[
A_mB_n \leftrightarrow mA^{n+} + nB^{m-}
\]

<table>
<thead>
<tr>
<th>t = 0</th>
<th>s</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>t_{eq}</td>
<td>s-s\alpha</td>
<td>m\alpha</td>
<td>n\alpha</td>
</tr>
</tbody>
</table>

\[
K_{sp} = [A^{n+}]^m[B^{m-}]^n
\]

\[
= [m\alpha]^m[n\alpha]^n
\]

\[
K_{sp} = m^n n^m (s\alpha)^{m+n}
\]

**Criteria of precipitation of an electrolyte:**

A very useful conclusion is derived from the solubility product concept. No precipitation of the electrolyte occurs if the ionic product is less than the solubility product, i.e., the solution has not reached the saturation stage.

**Case I:** When \( K_{ip} < K_{sp} \), then solution is unsaturated in which more solute can be dissolved.

**Case II:** When \( K_{ip} = K_{sp} \), then solution is saturated in which no more solute can be dissolved.

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

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

Thus, for the precipitation of an electrolyte, it is necessary that the ionic product must exceed its solubility product For example, if equal volumes of 0.02 M \( AgNO_3 \) solution and 0.02 M \( K_2CrO_4 \) solution are mixed, the precipitation of \( Ag_2CrO_4 \) occurs as the ionic product exceeds the solubility product of \( Ag_2CrO_4 \) which is \( 2 \times 10^{-12} \).

In the resulting solution,

\[
[Ag^+] = 0.02/2 = 0.01 = 1*10^{-2} \text{ M}
\]

and  \( [CrO^{2-}_4] = 0.02/2 = 0.01 = 1*10^{-2} \text{ M} \)
Ionic product of Ag\(_2\)CrO\(_4\) = \([Ag^+]^2[CrO_4^{2-}]\)

\[= (1 \times 10^{-2})^2 (1 \times 10^{-2})\]

\[= 1 \times 10^{-6}\]

1 \times 10^{-6} is higher than 2 \times 10^{-12} and thus precipitation of Ag\(_2\)CrO\(_4\) occurs.

**Applications of Solubility Product**

(i) **Purification of common salt**

Natural common salt consists of many insoluble and soluble impurities. Saturated solution of common salt is prepared and insoluble impurities are filtered off. Hydrogen chloride gas (HCl) is circulated through the saturated solution. HCl and NaCl dissociate into their respective ions as:

\[
NaCl \leftrightarrow Na^+ + Cl^- \\
HCl \leftrightarrow H^+ + Cl^- 
\]

The concentration of Cl\(^-\) ions increases considerably in solution due to ionization HCl. Hence, the ionic product \([Na^+][Cl^-]\) exceeds the solubility product of sodium chloride and, therefore, pure sodium chloride precipitates out from solution.

(ii) **Salting out of soap**

Soap is a sodium salt of higher acids. From the solution, soap is precipitated by the addition of concentrated solution of sodium chloride. Soap and sodium chloride are present in the form of ions.

\[
C_nH_{2n+1} COONa \leftrightarrow C_nH_{2n+1} COO^- + Na^+ \\
NaCl \leftrightarrow Na^+ + Cl^- 
\]

Thus, the concentration of Na\(^+\) ions increases considerably on addition of NaCl solution. Hence, the ionic product \([C_nH_{2n+1}COO^-][Na^+]\) exceeds the solubility product of soap and, therefore, soap precipitates out from the solution.

(iii) **Manufacture of sodium bicarbonate (baking soda):**

In Solvay’s soda process, CO\(_2\) gas is passed through ammonical brine to precipitate out NaHCO\(_3\).

\[
NH_4OH + CO_2 \rightarrow NH_4HCO_3 
\]
\[
\text{NH}_4\text{HCO}_3 + \text{NaCl} \rightarrow \text{NaHCO}_3 + \text{NH}_4\text{Cl}
\]

\(\text{NaHCO}_3\) is precipitated first because of its lower solubility product as compared to those of \(\text{NH}_4\text{Cl}, \text{NH}_3\text{HCO}_3\) and \(\text{NaCl}\).

Thus, baking soda (\(\text{NaHCO}_3\)) can be quantifiably estimated.

(iv) Application of solubility product in quantitative analysis

1. Estimation of barium as barium sulphate:

\(\text{H}_2\text{SO}_4\) as precipitating agent is added to the aqueous solution of \(\text{BaCl}_2\).

\[
\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{HCl}
\]

Precipitation of \(\text{BaSO}_4\) takes place when its ionic product exceeds solubility product. \(\text{H}_2\text{SO}_4\) is added in slight excess to ensure complete precipitation. Large excess of \(\text{H}_2\text{SO}_4\) is harmful for complex formation.

2. Estimation of silver as silver chloride:

\(\text{NaCl}\) solution is added to the silver nitrate solution, slight excess of \(\text{NaCl}\) is added to ensure complete precipitation.

\[
\text{AgNO}_3 + \text{NaCl} \rightarrow \text{AgCl} + \text{NaBO}_3
\]

Again, precipitation of \(\text{AgCl}\) takes place when ionic product of \(\text{AgCl}\) exceeds its solubility product.

3. In a similar manner. We estimate lead as lead chromate, calcium as calcium oxalate, etc.

(i) Precipitation of the sulphides of group II and IV

Hydrogen sulphide is a weak electrolyte and is used for the precipitation of various sulphides of group II and IV in quantitative analysis.

It ionizes to a small extent in water:

\[
\text{H}_2\text{S} \leftrightarrow 2\text{H}^+ + \text{S}^{2-}
\]

Applying law of mass action,

\[
K = ([\text{H}^+]^2 [\text{S}^{2-}])/[\text{H}_2 \text{S}]
\]

The concentrations of \(\text{S}^{2-}\) ions can be decreased by increasing concentration of \(\text{H}^+\) ions and it can be increased by decreasing concentration of \(\text{H}^+\) ions. In group II, lower concentration of sulphide ions is required as the solubility products of the sulphides of group II are low while higher concentration of sulphide ions is required in group IV as the solubility products
of the sulphides of group IV are high. The values of solubility products of various sulphides are given below.

<table>
<thead>
<tr>
<th>Metal sulphide</th>
<th>Solubility product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₂S₃</td>
<td>1.6×10⁻⁷²</td>
</tr>
<tr>
<td>HgS</td>
<td>4×10⁻⁵⁴</td>
</tr>
<tr>
<td>CuS</td>
<td>1×10⁻⁴⁴</td>
</tr>
<tr>
<td>PbS</td>
<td>5×10⁻²⁹</td>
</tr>
<tr>
<td>CdS</td>
<td>1.4×10⁻²⁸</td>
</tr>
<tr>
<td>CoS</td>
<td>3×10⁻²⁶</td>
</tr>
<tr>
<td>NiS</td>
<td>1.4×10⁻²⁴</td>
</tr>
<tr>
<td>ZnS</td>
<td>1.0×10⁻²²</td>
</tr>
<tr>
<td>MnS</td>
<td>1.4×10⁻¹⁵</td>
</tr>
</tbody>
</table>

The concentration of S²⁻ ions in group II is lowered by maintaining acidic medium. In the presence of HCl, the ionization of H₂S is suppressed due to common ion effect. The concentration is so adjusted that only ionic products of the sulphides of group II exceed their solubility products and, therefore, get precipitated. However, CdS has somewhat higher value. For its precipitation, dilution of the solution is done which increases ionization of H₂S and thereby increasing concentration of S²⁻ ions.

In group IV, higher concentration of S²⁻ ions is needed. This is done by changing the medium for acidic to alkaline. Ammonium hydroxide is added, the OH⁻ ions furnished by NH₄OH remove H⁺ ions from solution in the form of water molecules as,

\[
H^+ + OH^- \leftrightarrow H_2O
\]

More of the ionization of H₂S occurs and, thus, concentration of S²⁻ ions increases. It becomes so high that ionic products of the sulphides of group IV exceed their solubility products and they get precipitated.

(i) Precipitation of III group hydroxides

When NH₄OH is added in presence of NH₄Cl then precipitation of II group hydroxides takes place, i.e., Al(OH)₃, Fe(OH)₃ and Cr(OH)₃ are precipitated. Solubility product of III group hydroxides is less than those of higher group hydroxides.

\[
NH_4Cl \rightarrow NH_4^+ + Cl^- \\
NH_4OH \leftrightarrow NH_4^+ + OH^-
\]
NH₄⁺ ion furnished by NH₄Cl lowers the ionisatin of NH₄OH and hence the concentration of hydroxide ion OH⁻. At low concentration of hydroxide ion only III group hydroxides precipitate.

**Fractional Precipitation**

It is a technique of separating two or more ions from a solution by adding a reagent that precipitates first one ion and then the second.

Let us suppose 0.1 M Ba²⁺ and 0.1 M Sr²⁺ in aqueous solution. K₂CrO₄ is added as precipitating agent. K_{sp}BaCrO₄ is 1.2 × 10⁻¹⁰ and K_{sp}SrCrO₄ is 3.5 × 10⁻⁵.

\[ [\text{CrO}_4^{2-}] \text{concentration required to precipitate BaCrO}_4 = \frac{K_{sp}}{[\text{Ba}^{2+}]} = \frac{1.2 \times 10^{-10}}{0.1} = 1.2 \times 10^{-9} \]

BaCrO₄ will precipitate first because it requires low concentration of CrO²⁻ ions. On addition of chromate ions, BaCrO₄ starts precipitating when chromate ion concentration reaches 1.2 × 10⁻⁹ M. When CrO²⁻ ion concentration reaches upto 3.5 × 10⁻⁴ M, then SrCrO₄ also starts precipitating.

Remaining concentration of Ba²⁺ when SrCrO₄ starts precipitation.

\[ = \frac{(K_{sp} \text{BaCrO}_4)/[\text{CrO}_4^{2-}]}{= \frac{(1.2 \times 10^{-10})/(3.5 \times 10^{-4})}{= 3.4 \times 10^{-7} M} \]

% remaining concentration = \frac{(3.4 \times 10^{-7})/0.1 \times 100}{= 0.00034\%}

**Stability Constant**

Let us consider dissociation of the ion FeBr⁺.

\[ \text{FeBr}^+ \leftrightarrow \text{Fe}^{2+} + \text{Br}^- \]

Dissociation constant for above equilibria may be given as

\[ K_d = \frac{[\text{Fe}^{2+} ][\text{Br}^-]}{[\text{FeBr}^+] } \]

Reciprocal of dissociation constant is called stability constant.

\[ K_s = \frac{[\text{FeBr}^+ ]}{([\text{Fe}^{2+} ][\text{Br}^-])} \]

Let us consider the formation of complex K₂Cd(CN)₄. Complex ion is Cd(CN₄²⁻) where oxidation state of central metal Cd²⁺ is (2+). Complexing process proceeds in four steps as
Here \[ K_s = K_1 K_2 K_3 K_4. \]

Significance of stability constant:

Greater will be the value of stability constant more stable will be the complex.

Note:

(a) If on addition of a common ion in a salt solution (sparingly soluble), formation of complex ion takes place, then ionization increases, i.e., equilibrium shifts towards right hand direction to maintain the value of \( K_{sp} \) constant. It means, addition of common ion in the case of complex formation increases the solubility of the sparingly soluble salt which is against the concept of common ion effect.

(b) When we add an electrolyte to another electrolyte solution having no common ion, then ionization of the later increases.

(c) For a given electrolyte solubility product is always constant at a particular temperature.

Solubility of Metal Hydroxides in Acid Medium

\( H^+ \) ion furnished by the medium effects the solubility of metal hydroxide, say \( M(OH)^2 \), because of neutralization of \( OH^- \) ion by \( H^+ \) ion.

\[
M(OH)^2 \leftrightarrow M^{2+} + 2OH^-
\]

\( K_{sp} \) of \( M(OH)^2 = [M^{2+}][OH^-]^2 \)

\( [M^{2+}] = \frac{K_{sp}}{[OH^-]^2} \)
\[ [H^+] [OH^-] = K_w = 10^{-14} \]

\[ [OH^-]^2 = 10^{-28}/[H^+]^2 \]

From Eqs. (i) and (ii), we have

\[ [M^{2+}] = K_{sp}[H^+]^2/10^{-28} \]

**Periodic variations of acidic and basic properties:**

(a) Hydracids of the elements of the same periods:

Consider the hydracids of the elements of II period, Viz., CH\(_4\), NH\(_3\), H\(_2\)O and HF. These hydrides become increasingly acidic as we move from CH\(_4\) to HF. CH\(_4\) has negligible acidic properties while HF is a fairly stronger acid. The increase in acidic properties is due to the fact that the stability of their conjugate bases increases in the order

\[ CH^-_3 < NH^-_2 < OH^- < F^- \]

The increase in acidic properties is supported by the successive increase in the dissociation constant.

\[ CH_4 (=10^{-58}) < NH_3 (=10^{-35}) < H_2O (=10^{-14}) < HF (=10^{-4}) \]

(b) Hydracids of the elements of same group:

(i) Hydrides of V group elements (NH\(_3\), PH\(_3\), AsH\(_3\), SbH\(_3\), BiH\(_3\)) show basic character which decreases due to increase in size and decrease in electronegativity from N to Bi. There is a decrease in electron density in, sp\(^3\)-hybrid orbital and thus electron donor capacity decreases.

(ii) Hydracids of VI group elements (H\(_2\)O, H\(_2\)S, H\(_2\)Se, H\(_2\)Te) act as weak acids. The strength increases in the order H\(_2\)O < H\(_2\)S < H\(_2\)Se < H\(_2\)Te.

The increasing acidic properties reflects decreasing trend in the electron donor capacity of OH\(^-\), HS\(^-\), HSe\(^-\) or HTe\(^-\) ions.

(iii) Hydracids of VII group elements (HF, HCl, HBr, HI) show acidic properties which increase from HF to HI. This is explained by the fact that bond energies decrease. (\(H-F = 135\) kcal/mol, HCl = 103, HBr = 88 and HI = 71 kcal/mol).

(c) Oxyacids:

(i) The acidic properties of oxyacids of the same element which is in different oxidation states increases with increase in oxidation number.
But this rule fails in **oxyacids** of phosphorus.

\[ \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_4 \]

(ii) The **acidic properties** of the **oxyacids** of different elements which are in the same oxidation state decreases as the atomic number increases. This is due to increase in size and decrease in electronegativity.

\[ \text{HCIO}_4 > \text{HBrO}_4 > \text{HIO}_4 \]

\[ \text{H}_2\text{SO}_3 > \text{H}_2\text{SeO}_3 \]

**Limitations:**

There are a number of acid-base reactions in which no proton transfer takes place, e.g.,

\[ \text{SO}_2 + \text{SO}_2 \leftrightarrow \text{SO}^{2+} + \text{S} \]

\[ \text{Acid}_1 \text{ Base}_2 \leftrightarrow \text{Acid}_2 \text{ Base}_1 \]

Thus, the protonic definition cannot be used to explain the reactions occurring in non-protonic solvents such as COCl\(_2\), SO\(_2\), N\(_2\)O\(_4\), etc.

**Relative Strength of Acids and Bases:**

According to Arrhenius concept, an acid is a substance which furnishes H\(^+\) ions when dissolved in water. All the acid properties on an acid are due to H\(^+\) ions present in the solution.

The extent to which an acid property is given by an acid is a measure of its **acid strength**. The **acid strength** of a solution does not depend on its concentration but on the number of H\(^+\) ions present. The concentration of H\(^+\) ions depends on the ionisation of an acid in solution. On dilution, the ionisation increases and more of H\(^+\) ions come to solution with the result that the **acid strength** increases. Thus, **acid strength** increases on dilution while its concentration decreases.

At infinite dilution the dissociation of an acid is nearly complete and all acids are equally strong at infinite dilution.
The concentration of $H^+$ ions at all other dilutions of equimolar solutions of the acids may not be equal and depends on their degree of dissociation. Thus, to measure the relative acid strength of the two acids, the measurements of hydrogen ion concentration, i.e., degree of dissociation is made of equinormal solutions of the two acids. Various methods are used for this purpose. Some are described below.

(i) The conductivity method: The degree of dissociation of a weak acid is equal to conductivity ratio $\Lambda_1/\Lambda_\infty$. Thus, the degrees of dissociation $\alpha_1$ and $\alpha_2$ for two equinormal acids are given by:

For acid I, $\alpha_1 = \Lambda_1/\Lambda_\infty$

For acid II, $\alpha_2 = \Lambda_2/\Lambda_\infty$

At infinite dilution, all weak electrolytes have almost the same value of $\Lambda_\infty$; hence,

$\Lambda_\infty_1 = \Lambda_\infty_2$

$(\text{Strength of acid I})/(\text{Strength of acid II}) = \alpha_1/\alpha_2 = \Lambda_1/\Lambda_2 = ((1000\times\text{sp.cond.acid I})/C)/((1000\times\text{sp.cond.acid II})/C)$

$= (\text{Sp.cond.acid I})/(\text{Sp.cond.acid II})$

The relative strength of two acids is, thus, equal to the ratio of their equivalent conductance or specific conductance of equinormal solutions which can be determined experimentally.

(ii) Comparing dissociation constants: Let $K_1$ and $K_2$ be the dissociation constants of two acids and let and $\alpha_2$ be their degree of dissociation in equinormal solutions.

Applying Ostwald’s dilution law, $\alpha_1 = \sqrt{K_1/c}$ and $\alpha_2 = \sqrt{K_2/c}$

Thus, $(\text{Strength of acid I})/(\text{Strength of acid II}) = \alpha_1/\alpha_2 = \sqrt{(K_1/K_2)}$

Dissociation constants of some weak acids are given in the table:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>$HC_3H_3O_2$</td>
<td>$1.7\times10^{-5}$</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>$HC_7H_5O_2$</td>
<td>$6.3\times10^{-5}$</td>
</tr>
<tr>
<td>Boric acid</td>
<td>$H_3BO_3$</td>
<td>$5.9\times10^{-10}$</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>$H_2CO_3$</td>
<td>$4.3\times10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>$HCO^-_3$</td>
<td>$4.8\times10^{-11}$</td>
</tr>
<tr>
<td>Cyanic acid</td>
<td>$HOCN$</td>
<td>$3.5\times10^{-4}$</td>
</tr>
<tr>
<td>Substance</td>
<td>Formula</td>
<td>$K_a$</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCHO$_2$</td>
<td>$1.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hydrocyanic acid</td>
<td>HCN</td>
<td>$4.9 \times 10^{-10}$</td>
</tr>
<tr>
<td>Hydroflourine acid</td>
<td>HF</td>
<td>$6.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hydrogen Sulfate ion</td>
<td>HSO$_4^-$</td>
<td>$1.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>H$_2$S</td>
<td>$8.9 \times 10^{-8}$</td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>HClO</td>
<td>$3.5 \times 10^{-8}$</td>
</tr>
<tr>
<td>Nitrous acid</td>
<td>HNO$_2$</td>
<td>$4.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>H$_2$C$_2$O$_4$</td>
<td>$5.6 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>HC$_2$O$_4^-$</td>
<td>$5.1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H$_3$PO$_4$</td>
<td>$6.9 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>H$_2$PO$_4^-$</td>
<td>$6.2 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>H$_3$PO$_2^-$</td>
<td>$4.8 \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>H$_2$PHO$_3$</td>
<td>$1.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>Phosphorous acid</td>
<td>HPHO$_3^-$</td>
<td>$7.0 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>HC$_3$H$_5$O$_2$</td>
<td>$1.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>HC$_3$H$_3$O$_3$</td>
<td>$1.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>Pyruvic acid</td>
<td>H$_2$SO$_3$</td>
<td>$1.3 \times 10^{-2}$</td>
</tr>
<tr>
<td>Sulfurous acid</td>
<td>HSO$_3^-$</td>
<td>$6.3 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

(iii) Thomson thermal method: In this method, heat of neutralisation of two acids is first determined separately with NaOH. Let it be 'x' and 'y' calorie. The one gram equivalent of each of the two acids is mixed and one gram equivalent of NaOH is added. Let the heat evolved in this case be 'z' calorie. The two acids will neutralise a fraction of the base proportional to their relative strength. Suppose n gram equivalent of NaOH is neutralised by acid I and the rest (1 - n) by acid II.

Total Heat solved, $z = nx + (1-n)y$
$$= nx + y - ny$$

or \[ z-y = n(x-y) \]

or \[ n = (z-y)/(x-y) \]

So \( (\text{Strength of acid I})/(\text{Strength of acid II}) = n/((1-n) ) = (((z-y))/((x-y) ))/(1-((z-y))/((x-y) )) = ((z-y))/((x-z) ) \)

Relative strength of bases: A base is a substance which gives OH⁻ ions when dissolved in water. The base strength depends on OH⁻ ion concentration. The above methods can be used for measuring relative base strengths also. In the Thomson thermal method, the two bases and their mixtures will be neutralised by strong acid, say HCl.

The relative strengths of some of the acids are as follows:

(i) \( \text{HCIO}_4 > \text{HBr} > \text{HC}_1 > \text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{H}_3\text{O}^+ > \text{H}_2\text{SO}_3 > \text{H}_2\text{CO}_3 > \text{CH}_3\text{COOH} \)

(ii) \( \text{HCIO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HCIO} \)

(iii) \( \text{HI} > \text{HBr} > \text{HCl} > \text{HF} \)

(iv) \( \text{HClO}_3 > \text{HBrO}_3 > \text{HIO}_3 \)

(v) \( \text{CCI}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{CH}_2\text{C1COOH} > \text{CH3COOH} \)

(vi) \( \text{HCOOH} > \text{CH}_3\text{COOH} > \text{C}_2\text{H}_5\text{COOH} \)

The relative strengths of some of the bases are as follows:

(i) \( \text{KOH} > \text{NaOH} > \text{Ca(OH)_2} > \text{NH}_4\text{OH} \)

(ii) \( (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3 \)

(iii) \( (\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3 > (\text{C}_2\text{H}_5)_3\text{N} \)

(iv) \( \text{NaOH} > \text{NH}_3 > \text{H}_2\text{O} \)

(v) \( \text{NH}_3 > \text{NH}_2\text{NH}_2 > \text{NH}_2\text{OH} \)

(vi) \( \text{NH}_3 > \text{C5H5N} > \text{C}_6\text{H}_5\text{NH}_2 \)

**Ionic Product of Water:**

Pure water is a very weak electrolyte and ionises according to the equation

\[ \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \]

Applying law of mass action at equilibrium, the value of dissociation constant, \( K \) comes to
\begin{align*}
K &= \frac{[H^+] \cdot [OH^-]}{[H_2O]} \\
\text{or} \quad [H^+][OH^-] &= K[H_2O]
\end{align*}

Since dissociation takes place to a very small extent, the concentration of undissociated water molecules, \([H_2O]\), may be regarded as constant. Thus, the product \([H_2O]\) gives another constant which is designated as \(K_w\). So,

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

The constant, \(K_w\), is termed as ionic product of water.

The product of concentrations of \(H^+\) and \(OH^-\) ions in water at a particular temperature is known as ionic product of water. The value of \(K_w\) increases with the increase of temperature, i.e., the concentration of \(H^+\) and \(OH^-\) ions increases with increase in temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Value of (K_w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(0.11 \times 10^{-14})</td>
</tr>
<tr>
<td>10</td>
<td>(0.31 \times 10^{-14})</td>
</tr>
<tr>
<td>25</td>
<td>(1.00 \times 10^{-14})</td>
</tr>
<tr>
<td>100</td>
<td>(7.50 \times 10^{-14})</td>
</tr>
</tbody>
</table>

The value of \(K_w\) at 25°C is \(1 \times 10^{-14}\). Since pure water is neutral in nature, \(H^+\) ion concentration must be equal to \(OH^-\) ion concentration.

\[ [H^+] = [OH^-] = x \]

or \([H^+][OH^-]=x^2=1 \times 10^{-14}\]

or \(x = 1 \times 10^{-7} M\)

or \([H^+] = [OH^-] = 1 \times 10^{-7} \text{ mol litre}^{-1}\)

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

When an acid or a base is added to water, the ionic concentration product, \([H^+][OH^-]\), remains constant, i.e., equal to \(K_w\) but concentrations of \(H^+\) and \(OH^-\) ions do not remain equal. The addition of acid increases the hydrogen ion concentration while that of hydroxyl ion concentration decreases, i.e.,

\[ [H^+] > [OH^-]; \quad (\text{Acidic solution}) \]
Similarly, when a base is added, the OH\(^-\) ion concentration increases while H\(^+\) ion concentration decreases, i.e., \([\text{OH}^-] > [\text{H}^+]\); (Alkaline or basic solution)

In neutral solution, \([\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}\)

In acidic solution, \([\text{H}^+] > [\text{OH}^-]\)
or \([\text{H}^+] > 1 \times 10^{-7} \text{ M}\)
and \([\text{OH}^-] < 1 \times 10^{-7} \text{ M}\)

In alkaline solution, \([\text{OH}^-] > [\text{H}^+]\)
or \([\text{OH}^-] > 1 \times 10^{-7} \text{ M}\)
and \([\text{H}^+] < 1 \times 10^{-7} \text{ M}\)

Thus, if the hydrogen ion concentration is more than 1 \times 10^{-7} \text{ M}, the solution will be acidic in nature and if less than 1 \times 10^{-7} \text{ M}, the solution will be alkaline.

\[
\text{[H}^+] = 10^0 \quad 10^{-1} \quad 10^{-2} \quad 10^{-3} \quad 10^{-4} \quad 10^{-5} \quad 10^{-6} \quad \text{(Acidic)}
\]

\[
\text{[H}^+] = 10^{-7} \quad \text{(Neutral)}
\]

\[
\text{[H}^+] = 10^{-14} \quad 10^{-13} \quad 10^{-12} \quad 10^{-11} \quad 10^{-10} \quad 10^{-9} \quad 10^{-8} \quad \text{(Alkaline)}
\]

We shall have the following table if OH\(^-\) ion concentration is taken into account.

\[
\text{[OH}^-] = 10^{-14} \quad 10^{-13} \quad 10^{-12} \quad 10^{-11} \quad 10^{-10} \quad 10^{-9} \quad 10^{-8} \quad \text{(Acidic)}
\]

\[
\text{[OH}^-] = 10^{-7} \quad \text{(Neutral)}
\]

\[
\text{[OH}^-] = 10^0 \quad 10^{-1} \quad 10^{-2} \quad 10^{-3} \quad 10^{-4} \quad 10^{-5} \quad 10^{-6} \quad \text{(Alkaline)}
\]

It is, thus, concluded that every aqueous solution, whether acidic, neutral or alkaline contains both H\(^+\) and OH\(^-\) ions. The product of their concentrations is always constant, equal to 1 \times 10^{-14} at 25°C. If one increases, the other decrease accordingly so that the product remains 1\times10^{-14} at 25°C.

If \([\text{H}^+] = 10^{-2} \text{ M}\), then \([\text{OH}^-] = 10^{-12} \text{ M}\); the product, \([\text{H}^+][\text{OH}^-] = 10^{-2} \times 10^{-12} = 10^{-14}\); the solution is acidic.
If \([H^+] = 10^{-10}\) M, then \([OH^-] = 10^{-4}\) M; the product, \([H^+][OH^-] = 10^{-10} \times 10^{-4} = 10^{-14}\); the solution is alkaline.

**HYDROGENION CONCENTRATION-pH SCALE:**

It is clear from the above discussion that nature of the solution (acidic, alkaline or neutral) can be represented in terms of either hydrogen ion concentration or hydroxyl ion concentration but it is convenient to express acidity or alkalinity of a solution by referring to the concentration of hydrogen ions only. Since \(H^+\) ion concentration can vary within a wide range from 1 mol per litre to about \(1.0 \times 10^{-14}\) mol per litre, a logarithmic notation has been devised by Sorensen, in 1909, to simplify the expression of these quantities. The notation used is termed as the pH scale.

The hydrogen ion concentrations are expressed in terms of the numerical value of negative power to which 10 must be raised. This numerical value of negative power was termed as pH, i.e.,

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

or \(\log [H^+] = \log 10^{-pH} = -pH \log 10 = -pH\)

or \(pH = -\log [H^+]\)

or \(pH = \log 1/[H^+]\)

\(pH\) of a solution is, thus, defined as the **negative logarithm of the concentration (in mol per litre) of hydrogen ions which it contains** or **pH of the solution is the logarithm of the reciprocal of \(H^+\) ion concentration**.

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

\(pOH = -\log [OH^-]\)

Considering the relationship,

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

Taking log on both sides, we have

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

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

or \(pH + pOH = PK_w = 14\)

i.e., sum of \(pH\) and \(pOH\) is equal to 14 in any aqueous solution at 25°C. The above discussion can be summarised in the following manner:
<table>
<thead>
<tr>
<th>Nature of solution</th>
<th>[H⁺]</th>
<th>[OH⁻]</th>
<th>pH</th>
<th>pOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strongly acidic</td>
<td>10⁻¹⁴</td>
<td>10⁻⁰</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>Acidic</td>
<td>10⁻⁻²</td>
<td>10⁻¹²</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>Weakly acidic</td>
<td>10⁻⁵</td>
<td>10⁻⁹</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>Neutral</td>
<td>10⁻⁻⁷</td>
<td>10⁻⁷</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Weakly basic</td>
<td>10⁻⁻⁹</td>
<td>10⁻⁵</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>Basic</td>
<td>10⁻¹¹</td>
<td>10⁻³</td>
<td>11</td>
<td>3</td>
</tr>
<tr>
<td>Strongly basic</td>
<td>10⁻¹⁴</td>
<td>10⁻⁰</td>
<td>14</td>
<td>0</td>
</tr>
</tbody>
</table>

The following table shows the pH range for a few common substances:

<table>
<thead>
<tr>
<th>Substance</th>
<th>pH range</th>
<th>Substance</th>
<th>pH range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gastric contents</td>
<td>1.0-3.0</td>
<td>Milk (cow)</td>
<td>6.3-6.6</td>
</tr>
<tr>
<td>Soft drinks</td>
<td>2.0-4.0</td>
<td>Saliva (human)</td>
<td>6.5-7.5</td>
</tr>
<tr>
<td>Lemons</td>
<td>2.2-2.4</td>
<td>Blood plasma</td>
<td>7.3-7.5</td>
</tr>
<tr>
<td>Vinegar</td>
<td>2.4-3.4</td>
<td>Milk of magnesia</td>
<td>10.5</td>
</tr>
<tr>
<td>Apples</td>
<td>2.9-3.3</td>
<td>Sea water</td>
<td>8.5</td>
</tr>
<tr>
<td>Urine(human)</td>
<td>4.8-8.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Any method which can measure the concentration of H⁺ ions or OH⁻ ions in a solution can serve for finding pH value.
Limitations of pH Scale:

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

(ii) pH value of zero is obtained in 1 A' solution of strong acid. In case the concentration is 2 M, 3 M, 10 M, etc. The respective pH values will be negative.

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

Note:

(i) Normality of strong acid = $[H_3O^+]$

Normality of strong base = $[OH^-]$

\[ \therefore \text{pH} = -\log[N] \quad \text{for strong acids} \]

\[ \text{pOH} = -\log[N] \quad \text{for strong acids} \]

(ii) Sometimes pH of acid comes more than 7 and that of base comes less than 7. It shows that the solution is very dilute; in such cases, $H^+$ or $OH^-$ contribution from water is also considered, e.g., in 10 M HCl,

\[ [H^+]_{\text{Total}} = [10^{-8}]_{\text{Acid}} + [10^{-7}]_{\text{Water}} \]

\[ = 11 \times 10^{-8} \text{M} = 1.1 \times 10^{-7} \text{M} \]

(iii) pH of mixture:

Let one litre of an acidic solution of pH 2 be mixed with two litre of other acidic solution of pH 3. The resultant pH of the mixture can be evaluated in the following way.

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 2</td>
<td>pH = 3</td>
</tr>
<tr>
<td>$[H^+] = 10^{-2}$ M</td>
<td>$[H^+] = 10^{-3}$ M</td>
</tr>
<tr>
<td>V = 1 litre</td>
<td>V = 2 litre</td>
</tr>
</tbody>
</table>

\[ M_1V_1 + M_2V_2 = M_R(V_1 + V_2) \]

\[ 10^{-2} \times 1 + 10^{-3} \times 2 = M_R (1 + 2) \]

\[ (12 + 10^{-3})/3 = M_R \]

\[ 4 \times 10^{-3} = M_R \text{(Here, } M_R = \text{Resultant molarity}) \]
\[
pH = -\log (4 \times 10^{-3})
\]

(iv) Total concentration of \([H^+]\) or \([H_3^+\text{O}^-]\) in a mixture of weak acid and a strong acid.

\[
= (C_2 + \sqrt{C_2^2 + 4K_aC_1})/2
\]

where \(C_1\) is the concentration of weak acid (in mol litre having dissociation constant \(K_a\))

\(C_2\) is the concentration of strong acid

(v) Total \([OH^-]\) concentration in a mixture of two weak bases.

\[
= \sqrt{K_1C_1 + K_2C_2}
\]

where \(K_1\) and \(K_2\) are dissociation constants of two weak bases having \(C_1\) and \(C_2\) as their mol litre\(^{-1}\) concentration respectively.

**pH OF Weak Acids and Bases:**

Weak acids and bases are not completely ionised; an equilibrium is found to have been established between ions and unionised molecule. Let us consider a weak acid of basicity 'n'.

\[
AH_n \leftrightarrow A^{n-} + nH^+
\]

\[
i = 0 \quad C \quad 0 \quad 0
\]

\[
t_{eq} \quad C(1-a) \quad Ca \quad nCa
\]

\([H^+] = nCa; \quad \therefore \quad \text{pH} = -\log_{10} [nCa] \quad \ldots \ldots (i)
\]

For monobasic and, \(n=1\)

\[
\text{pH} = -\log_{10} [Ca] \quad \ldots \ldots (ii)
\]

Dissociation constant of acid \(K_a\) may be calculated as

\[
K_a = \frac{[A^{n-}][H^+]^n/[AH_n]}{[Ca][nCa]^n/[C(1-a)]}
\]

\[
= a[nCa]^n/(1-a) \quad \text{For weak acids, } a \ll 1
\]

\[
\therefore \quad (1-a) = 1
\]

\[
= a[nCa]^n/(1-a)
\]
\[ nC_K = nCa \ [nCa]^n \]
\[ = [nCa]^{(n+1)} \]
\[ = [nCa] = [nC_K]^{1/(n+1)} \]
\[ = [H^+] = [nC_K]^{1/(n+1)} \]
\[ \therefore \text{pH} = -1/(n+1) \log_{10}(nC_K) \quad \ldots \text{ (iii)} \]

For monobasic acid, \( n = 1 \)
\[ \text{pH} = -\log\sqrt{C_K \alpha} \quad \ldots \text{ (iv)} \]

Since \( K_a = \alpha[nCa]^n \)
\[ k_a/\alpha = (nCa)^n \]
\[ [nCa] = [K_a/\alpha]^{1/n} = [H^+] \]
\[ \text{pH} = -1/n \log_{10}(K_a/\alpha) \quad \ldots \text{ (v)} \]

For \( n = 1 \) \[ \text{pH} = -\log_{10}(K_a/\alpha) \quad \ldots \text{ (vi)} \]

**Example 28:** The hydrogen ion concentration of a solution is 0.001 M. What will be the hydroxyl ion concentration of solution?

**Solution:** We know that \([H^+][OH^-] = 1.0 \times 10^{-14}\)

Given that, \([H^+] = 0.001 \text{ M} = 10^{-3} \text{ M}\)

So \([OH^-] = 1.0 \times 10^{-14}/[H^+] = (1*10^{-14})/10^{-3} = 10^{-11}\text{M}\)

**Example 29:** What is the pH of the following solutions?

(a) 10^{-3} \text{ M HCl} 

(b) 0.0001 \text{ M NaOH} 

(c) 0.0001 \text{ MH}_2\text{SO}_4 

**Solution:** HCl is a strong electrolyte and is completely ionised.

\[ \text{HCl} \leftrightarrow \text{H}^+ + \text{Cl}^- \]

So \([H^+] = 10^{-3} \text{ M}\)
\[ \text{pH} = -\log [H^+] = -\log (10^{-3}) = 3 \]

(b) \( \text{NaOH} \) is a strong electrolyte and is completely ionised.

\[
\text{NaOH} \quad \leftrightarrow \quad \text{Na}^+ + \text{OH}^- 
\]

So \( [\text{OH}^-] = 0.0001 \text{ M} = 10^{-4} \text{ M} \)

\[ \text{pOH} = -\log(10^{-4}) = 4 \]

As \( \text{pH} + \text{pOH} = 14 \)

So \( \text{pH} + 4 = 14 \) or \( \text{pH}=10 \)

Alternative method: \( [\text{OH}^-] = 10^{-4} \text{ M} \)

We know that \( [H^+][\text{OH}^-] = 1.0 \times 10^{-14} \)

So \( [H^+] = (1.0 \times 10^{-14})/10^{-14} \)

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

(c) \( \text{H}_2\text{SO}_4 \) is a strong electrolyte and is ionized completely.

\[
\text{H}_2\text{SO}_4 \leftrightarrow 2\text{H}^+ + \text{SO}^{2-}_4 
\]

One molecule of \( \text{H}_2\text{SO}_4 \) furnishes ions.

So \( [H^+] = 2 \times 10^{-4} \text{ M} \)

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

\[ = -\log (2\times10^{-4}) \]

\[ = 3.70 \]

**Example 30:** Calculate the pH of the following solutions assuming complete dissociation:

(a) 0.365 g L\(^{-1}\) HCl solution

(b) 0.001 M Ba(OH)\(_2\) solution.

**Solution:** (a) Mole, mass of HCl = 36.5

Concentration of HCl = 0.365/36.5 = 1.0 \times 10^{-2} \text{ mol L}^{-1}

HCl is a strong electrolyte and is completely ionised.

So \( [H^+] = 1 \times 10^{-2} \text{ mol L}^{-1} \)
\[
\text{pH} \quad -\log [H^+] = -\log (1 \times 10^{-2}) = 2
\]

(b) \(\text{Ba(OH)}_2\) is a strong electrolyte and is completely ionised

\[
\text{Ba(OH)}_2 \leftrightarrow \text{Ba}^{2+} + 2\text{OH}^-
\]

One molecule on dissociation furnishes 2 \(\text{OH}^-\) ions.

So \(\text{[OH}^-\text{]} = 2 \times 10^{-3} \text{ M}\)

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

\[
= -\log (2 \times 10^{-3}) = 2.7
\]

We know that \(\text{pH} + \text{pOH} = 14\)

So \(\text{pH} = (14-2.7) = 11.3\)

**Example 31:** Find the pH of a 0.002 N acetic acid solution, if it is 2.3% ionised at a given dilution.

**Solution:** Degree of dissociation, \(\alpha = \frac{2.3}{100} = 0.023\)

Concentration of acetic acid, \(C = 0.002 \text{ M}\)

The equilibrium is

\[
\text{CH}_3\text{COOH} \leftrightarrow \text{CH}_3\text{COO}^- + \text{H}^+
\]

\[
C(1-\alpha) \quad C\alpha \quad C\alpha
\]

So \([\text{H}^+] = C\alpha = 0.002 \times 0.023\)

\(= 4.6 \times 10^{-5} \text{ M}\)

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

\[
= -\log (4.6 \times 10^{-5}) = 4.3372
\]

**Example 32:** Calculate the pH value of a solution obtained by mixing 50 mh of 0.2 N HCl with 50 mL of 0.1 N NaOH.

**Solution:** Number of milli-equivalents of the acid
Number of milli-equivalents of the base
= 50 \times 0.1 = 5

Number of milli-equivalents of the acid left after the addition of base
= (10 - 5) = 5

Total volume of the solution
= 50 + 50 = 100 \text{ mL}

Thus, 5 milli-equivalents of the acid are present in 100 mL of solution.
or 50 milli-equivalents of the acid are present in one litre of solution.
or 0.05 equivalents of the acid are present in one litre of solution.

The acid is monobasic and completely ionised in solution.

0.05 \text{ N HCl} = 0.05 \text{ M HCl}

\[ [H^+] = 0.05 \text{ M} \]

\[ \text{pH} = -\log [H^+] = -\log 5 \times 10^{-2} = -[\log 5.0 + \log 10^{-2}] \]
\[ = -[0.70 - 2] = 1.3 \]

**Example 33:** What will be the pH of a solution obtained by mixing 800 mL of 0.05 \text{ N} sodium hydroxide and 200 mL of O.A \text{ N HCl}, assuming complete ionisation of the acid and the base?

**Solution:** Number of milli-equivalents of NaOH

= 800 \times 0.05 = 40

Number of milli-equivalents of HCl

= 200 \times 0.1 = 20

Number of milli-equivalents of NaOH left after the addition of HCl

= (40 - 20) = 20

Total volume = (200 + 800) \text{ mL} = 1000 \text{ mL} = 1 \text{ litre}

20 milli-equivalents or 0.02 equivalents of NaOH are present in one litre, i.e.,

0.02 \text{ N NaOH} = 0.02 \text{ M NaOH} \text{ (Mono-acidic)} and the base is completely ionised.
So $[\text{OH}^-] = 0.02 \text{ M}$

or $[\text{OH}^-] = 2 \times 10^{-2} \text{ M}$

$p\text{OH} = -\log(2 \times 10^{-2}) = 1.7$

We know that, $p\text{H} + p\text{OH} = 14$

So $p\text{H} = (14 - 1.7) = 12.3$

**Relationship between solubility and solubility product:**

Salts like AgI, BaSO$_4$, PbSO$_4$, PbI$_2$, etc., are ordinarily considered insoluble but they do possess some **solubility**. These are sparingly soluble electrolytes. A saturated solution of sparingly soluble electrolyte contains a very small amount of the dissolved electrolyte. It is assumed that whole of the dissolved electrolyte is present in the form of ions, i.e., it is completely dissociated.

The equilibrium for a saturated solution of any sparingly soluble salt may be expressed as:

$$A_xB_y \leftrightarrow xA^{y+} + yB^{x-}$$

Thus, **solubility product**, $K_s = [A^{y+}]^x[B^{x-}]^y$

Let 's' mole per litre be the **solubility** of the salt, then

$$A_xB_y \leftrightarrow xA^{y+} + yB^{x-}$$

$$xs \quad ys$$

So $K_s = [xs]^x[ys]^y = x^x.y^y(s)^{x+y}$

(i) **1:1 type salts:**

Examples: AgCl, AgI, BaSO$_4$, PbSO$_4$, etc.

Binary electrolyte: $AB \leftrightarrow A^+ + B^-$

$$s \quad s$$

Let **solubility** of AB be s mol litre$^{-1}$.

So $K_s = [A^+][B^-] = s \times s = s^2$
or \[ s = \sqrt{H_s} \]

(ii) **1:2 or 2:1 type salts:**
Examples: \( \text{Ag}_2\text{CO}_3, \text{Ag}_2\text{CrO}_4, \text{PbCl}_2, \text{CaF}_2, \text{etc.} \)

Ternary electrolyte:
\[ \text{AB}_2 \leftrightarrow \text{A}^{2+} + 2\text{B}^- \]
\[ s \quad 2s \]
Let **solubility** of \( \text{AB}_2 \) be \( s \) mol litre\(^{-1} \).
So \[ K_s = [\text{A}^{2+}][\text{B}^-]^2 = s \times (2s)^2 = 4s^3 \]
or \[ s = 3\sqrt[3]{K_s}/4 \]
\[ A_2\text{B} \leftrightarrow 2\text{A}^+ + \text{B}^{2-} \]
\[ s \quad s \]
Let \( s \) be the **solubility** of \( A_2\text{B} \).
\[ K_s = [\text{A}^+]^2[\text{B}^{2-}] \]
\[ = (2s)^2(s) = 4s^3 \]
or \[ s = 3\sqrt[3]{K_s}/4 \]

(iii) **1:3 type salts:**
Examples: \( \text{Al}_3, \text{Fe(OH)}_3, \text{Cr(OH)}_3, \text{Al(OH)}_3, \text{etc.} \)

Quaternary electrolyte: \( \text{AB}_3 \leftrightarrow \text{A}^{3+} + 3\text{B}^- \)
Let \( s \) mol litre\(^{-1} \) be the **solubility** of \( \text{AB}_3 \).
\[ K_s = [\text{A}^{3+}][\text{B}^-]^3 = s \times (3s)^3 = 27s^4 \]
or \[ s = 4\sqrt[4]{K_s}/27 \]

The presence of common ion affects the **solubility** of a salt. Let \( \text{AB} \) be a sparingly soluble salt in solution and \( \text{A}'\text{B} \) be added to it. Let \( s \) and \( s' \) be the **solubilities** of the salt \( \text{AB} \) before and after addition of the electrolyte \( \text{A}'\text{B} \). Let \( c \) be the concentration of \( \text{A}'\text{B} \).
Before addition of A'B, \( K_s = s^2 \) ... (i)

After addition of A'B, the concentration of A\(^+\) and B\(^-\) ions become \( s' \) and \((s' + c)\), respectively.

So \( K_s = s'(s' + c) \) .... (ii)

Equating Eqs. (i) and (ii),

\[ s^2 = s'(s' + c) \]

**Calculation of remaining concentration after precipitation:**

Sometimes an ion remains after precipitation if it is in excess. Remaining concentration can be determined, e.g.,

(i) \( [A^+]_{left} = K_{sp} \frac{[AB]}{[B^-]} \)

(ii) \( [Ca^{2+}]_{left} = K_{sp}[Ca(OH)_2]/[OH^-]^2 \)

(iii) \( [A^{n+}]_{m\ left} = K_{sp}[A_mB_n]/[B^{-n}]^n \)

Percentage precipitation of an ion

\[ = \frac{\text{Initial conc.} - \text{Left conc.}}{\text{Initial conc.}} \times 100 \]

**Simultaneous Solubility**

**Solubility** of two electrolytes having common ion; when they are dissolved in the same solution, is called simultaneous solubility, e.g.,

(i) **Solubility** of AgBr and AgSCN, when dissolved together.

(ii) **Solubility** of CaF\(_2\) and SrF\(_2\), when dissolved together.

(iii) **Solubility** of MgF\(_2\) and CaF\(_2\) when dissolved together.

Calculation of simultaneous **solubility** is divided into two cases.

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

\[ \text{AgBr} (K_{sp} = 5 \times 10^{-13}); \quad \text{AgSCN} \ (K_{sp} = 10^{-12}) \]

(See Example 23)
Here, charge balancing concept is applied.

Charge of Ag⁺ = Charge of Br⁻ + Charge of SCN⁻

\[ [\text{Ag}^+] = [\text{Br}^-] + [\text{SCN}^-] \]

\( (a + b) = a + b \)

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

CaF₂ \( (K_{sp} = 3.4 \times 10^{-11}) \); SrF₂ \( (K_{sp} = 2.9 \times 10^{-9}) \)

Most of fluoride ions come of stronger electrolyte.

**Example 16:** The solubility product of silver chloride is \( 1.5625 \times 10^{-10} \) at 25°C. Find its solubility in g L\(^{-1}\).

**Solution:** Let the solubility of AgCl be 5 mol litre\(^{-1}\).

\[ \text{AgCl} \rightarrow \text{Ag}^+ + \text{Cl}^- \]

Hence, \( s^2 = 1.5625 \times 10^{-10} \)

or \( s^2 = 1.25 \times 10^{-5} \) mol L\(^{-1}\)

Molecular mass of AgCl = \((108 + 35.5) = 143.5\)

So, Solubility in g litre\(^{-1}\) = mol. mass \times s

\[ = 143.5 \times 1.25 \times 10^{-5} \]

\[ = 1.79 \times 10^{-3} \text{ g L}^{-1} \]

**Example 17.** The solubility of PbSO₄ in water is 0.038 g L\(^{-1}\) at 25°C. Calculate its solubility product at the same temperature.

**Solution:** Solubility (s) of PbSO₄ in mol L\(^{-1}\),

\[ = 0.038/(\text{Mol. mass of PbSO}_4) = 0.038/303 = 1.254 \times 10^{-4} \]

The equilibrium is

\[ \text{PbSO}_4 \leftrightarrow \text{Pb}^{2+} + \text{SO}^{2-}_4 \]

\( s \quad s \)
Example 18. The concentration of Ag$^+$ ion in a saturated solution of Ag$_2$CrO$_4$ at 20°C is 1.5 × 10$^{-4}$ mol L$^{-1}$. Determine the solubility product of Ag$_2$CrO$_4$ at 20°C.

**Solution:** The equilibrium is

$$\text{Ag}_2\text{CrO}_4 \leftrightarrow 2\text{Ag}^+ + \text{CrO}_4^{2-}$$

On the basis of this equation, the concentration of CrO$_4^{2-}$ ions will be half of the concentration of Ag$^+$ ions.

Thus, $[\text{Ag}^+] = 1.5 \times 10^{-4} \text{ M}$ and $[\text{CrO}_4^{2-}]$

= $0.75 \times 10^{-4} \text{ M}$

$$K_s = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (1.5 \times 10^{-4})^2 (0.75 \times 10^{-4})$$

= $1.6875 \times 10^{-12}$

Example 19: The solubility product of BaSO$_4$ is $1.5 \times 10^{-9}$. Find out the solubility in

(i) pure water and
(ii) 0.1 M BaCl$_2$ solution.

**Solution:** The equilibrium is

(i) $\text{BaSO}_4 \leftrightarrow \text{Ba}^{2+} + \text{SO}_4^{2-}$

Let $s$ be the solubility in mol litre$^{-1}$; then

$$K_s = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = s^2$$

or $1.5 \times 10^{-9} = s^2$

So $s = 3.87 \times 10^{-5} \text{ mol L}^{-1}$

(ii) Let $s'$ be the solubility of BaSO$_4$ in 0.1 M BaCl$_2$ solution.

Total Ba$^{2+}$ ions concentration = $(s' + c) \text{ mol L}^{-1}$ and SO$_4^{2-}$ ions concentration = $s' \text{ mol L}^{-1}$

So $K_s = (s' + c)s' = (s' + 0.1)s'$
or \[ 1.5 \times 10^{-9} = (s' + 0.1)s' \]

or \[ (s')^2 + 0.1s' = 1.5 \times 10^{-9} \]

Neglecting \((s')^2\),

\[ 0.1s' = 1.5 \times 10^{-9} \]

or \[(s') = 1.5 \times 10^{-8} \text{ mol L}^{-1}\]

\textbf{Example 20:} The solubility of Mg(OH)\(_2\) in pure water is \(9.57 \times 10^{-3}\) g L\(^{-1}\). Calculate its solubility in g L\(^{-1}\) in 0.02 M Mg(NO\(_3\))\(_2\) solution.

\textbf{Solution: Solubility} of Mg(OH)\(_2\) in pure water

\[ \text{Solubility} = 9.57 \times 10^{-3} \text{ g L}^{-1} \]

\[ = \frac{(9.57 \times 10^{-3})}{(\text{mol mass})} = \text{mol L}^{-1} \]

\[ = \frac{(9.57 \times 10^{-3})}{58} = 1.65 \times 10^{-4} \text{ mol L}^{-1} \]

Further, Mg (OH)\(_2\) \(\leftrightarrow\) Mg\(^{2+}\) + 2OH\(^-\)

\[ K_s = [\text{Mg}^{2+}][\text{OH}^-]^2 = s \times (2s)^2 = 4s^3 \]

\[ = 4 \times (1.63 \times 10^{-4})^3 \]

\[ = 17.9685 \times 10^{-12} \]

Let \(s'\) be \textbf{solubility} of Mg(OH)\(_2\) in presence of Mg(NO\(_3\))\(_2\)

\[ [\text{Mg}^{2+}] = (s' + c) = (s' + 0.02) \]

\[ [\text{OH}^-] = 2s' \]

So \[ K_s = (s' + 0.02) (2s')^2 \]

\[ 17.9685 \times 10^{-12} = 4(s')^2(s' + 0.02) \]

\[ (17.9685 \times 10^{-12})/4 = (s')^3 + 0.02(s')^2 \]

\[ [\text{neclecting} \ (s')^3] \]

\[ 4.4921 \times 10^{-12} = 0.02 \ (s')^2 \]

or \((s')^2 = 4.4921/0.02 \times 10^{-12}\)
or \( s' = 14.9869 \times 10^{-6} \text{ mol L}^{-1} \)

**Solubility** of \( \text{Mg(OH)}_2 \) in \( \text{g litre}^{-1} \) = \( s' \times M \)

\[
= 14.9868 \times 10^{-6} \times 58 \\
= 8.69 \times 10^{-4} \text{ g L}^{-1}
\]

**ACID-BASE NEUTRALISATION-SALTS**

When aqueous solutions of hydrochloric acid and sodium hydroxide are mixed in the proper proportion, a reaction takes place to form sodium chloride and water.

\[
\text{HCl(aq)} + \text{NaOH(aq)} \leftrightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}
\]

Sodium chloride

Such a reaction is termed neutralisation because both acidic (\( \text{H}^+ \)) and basic (\( \text{OH}^- \)) properties are eliminated during the reaction. The hydrogen ion, which is responsible for the acidic properties, has reacted with the hydroxyl ion which is responsible for the basic properties, producing neutral water. The Na\(^+\) and Cl\(^-\) ions have undergone no chemical change and appear in the form of crystalline sodium chloride upon evaporation of the solution. Sodium chloride is an example of the class of compounds called salts.

\[
\text{HCl(aq)} + \text{Cl}^-(aq) + \text{Na}^+(aq) \leftrightarrow \text{H}_2\text{O(l)} + \text{Na}^+(aq) + \text{Cl}^-(aq)
\]

or

\[
\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O(l)}
\]

Thus, the neutralisation of a base with an acid involves the interaction between \( \text{OH}^- \) and \( \text{H}^+ \) ions.

or

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

The process of neutralization does not produce the resulting solution always neutral; no doubt it involves the interaction of \( \text{H}^+ \) and \( \text{OH}^- \) ions. The nature of the resulting solution depends on the particular acid and a particular base involved in the reaction. The following examples illustrate this point when equivalent amounts of acids and bases are reacted in aqueous solution.

(i) A strong acid plus a strong base gives a neutral solution because both are completely ionised and the reaction goes to completion.

\[
\text{H}^+ + \text{Cl}^- + \text{Na}^+ + \text{OH}^- \leftrightarrow \text{H}_2\text{O} + \text{Na}^+ + \text{Cl}^-
\]
(ii) A strong acid plus a weak base gives an acidic solution as the weak base is not completely ionised. The reaction does not go to completion and there is an excess of hydrogen ions in solution.

\[ H^+ + Cl^- + NH_4OH \leftrightarrow H_2O + NH_4^+ + Cl^- \]

(iii) A weak acid plus a strong base gives a basic solution as the weak acid is not completely ionised. The reaction does not go to completion and there is an excess of hydroxyl ions in solution.

\[ CH_3COOH + Na^+ + OH^- \leftrightarrow H_2O + CH_3COO^- + Na^+ \]

(iv) A weak acid plus a weak base gives an acidic or a basic or a neutral solution depending on the relative strength of acid and base. In case both have equal strength, the resulting solution is neutral in nature.

\[ CH_3COOH + NH_4OH \rightarrow H_2O + NH_4^+ + CH_3COO^- \]

**Salts:**

Salts are regarded as compounds made up of positive and negative ions. The positive part comes from a base while negative part from an acid. Salts are ionic compounds. Salts may taste salty, sour, bitter, astringent or sweet or tasteless. Solutions of salts may be acidic, basic or neutral. Fused salts and aqueous solutions of salts conduct electricity and undergo electrolysis. The properties of salts in aqueous solutions are the properties of ions. The salts are generally crystalline solids.

The salts are classified into the following classes:

(i) **Simple salts:**

The salt formed by the neutralization process, i.e., interaction between acid and base, is termed simple salt. These are of three types:

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

Examples are: NaCl, NaNO\(_3\), K\(_2\)SO\(_4\), Ca\(_3\)(PO\(_4\))\(_2\), Na\(_3\)BO\(_3\), Na\(_2\)HPO\(_3\) (one H atom is not replaceable as H\(_3\)PO\(_3\) is a dibasic acid), NaH\(_2\)PO\(_2\) (both H atoms are not replaceable as H\(_3\)PO\(_2\) is a monobasic acid), etc.
(b) Acid salts: Salts formed by incomplete neutralization of poly-basic acids are called acid salts. Such salts still contain one or more replaceable hydrogen atoms. These salts when neutralised by bases form normal salts.

Examples are: NaHCO₃, NaHSO₄, NaH₂PO₄, Na₂HPO₄, etc.,

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

Examples are: Zn(OH)Cl, Mg(OH)Cl, Fe(OH)₂Cl, Bi(OH)₂Cl, etc.

(ii) Double salts:

The addition compounds formed by the combination of two simple salts are termed double salts. Such salts are stable in solid state only.

Examples are: Ferrous ammonium sulphate, FeSO₄·(NH₄)₂SO₄·6H₂O, Potash alum, K₂SO₄·Al₂(SO₄)₃·24H₂O, and other alums.

Properties:

(a) When dissolved in water, it furnishes all the ions present in the simple salts from which it has been constituted.

(b) The solution of double salt shows the properties of the simple salts from which it has been constituted.

(iii) Complex salts:

These are formed by combination of simple salts or molecular compounds. These are stable in solid state as well as in solutions.

\[
\text{FeSO}_4 + 6\text{KCN} \rightarrow \text{K}_4\text{Fe(CN)}_6 + \text{K}_2\text{SO}_4
\]

Simple salt \hspace{1cm} Complex salt

\[
\text{CoSO}_4 + 6\text{NH}_3 \rightarrow \text{Co(NH}_3)_6\text{SO}_4
\]

Simple salt \hspace{1cm} Molecular compound \hspace{1cm} Complex salt
Properties:

(a) On dissolving in water it furnishes a complex ion.

\[ K_4F_2(CN)_6 \leftrightarrow 4K^+ + [Fe(CN)_6]^{4-} \]
\[ Cu(NH_3)_4SO_4 \leftrightarrow [Cu(NH_3)_4]^{2+} + SO_4^{2-} \]

Complex ion

(b) The properties of the solution are different from the properties of the substances from which it has been constituted.

(iv) Mixed salts:

The salt which furnishes more than one cation or more than one anion when dissolved in water is called a mixed salt.

Examples are:

Acidic, Basic and Amphoteric oxides

(i) Non-metal oxides are acidic, they dissolve in water to form acid. These oxides form salt with bases.

\[ \text{e.g., } SO_2, SO_3, P_4O_{10}, CO_2, NO_2, N_2O_5, SiO_2, B_2O_3 \]

\[ \text{Non-metal oxides} \]

Some Transition metal oxides are also acidic

\[ \text{e.g., } CrO_3, MoO_3, WO_3, Mn_2O_7 \]

\[ CO_2 + H_2O \rightarrow H_2CO_3 \] Carbonic acid

\[ 2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \] (nitrous and nitric acid)
\[
P_2O_5 + 3H_3O \rightarrow 2H_3PO_4
\]
(Phosphoric acid)

\[
NaOH + SO_3 \rightarrow NaHSO_4
\]
Salt

\[
2KOH + CO_2 \rightarrow K_2CO_3 + H_2O
\]
Salt

(ii) Usually, oxides of highly electropositive metals are basic. These oxides dissolve in water to form base and they form salt with acids.

\[\text{e.g., } Na_2O, K_2O, MgO, CaO, Sc_2O_3, TiO_2, ZrO_2\]

\[
Na_2O + H_2O \rightarrow 2NaOH
\]
(Sodium hydroxide, a base)

\[
CaO + 2HC1 \rightarrow CaCl_2 + H_2O
\]
Salt

\[
Mg + H_2SO_4 \rightarrow MgSO_4 + H_2O
\]
Salt

(iii) Oxides of metalloids and less electropositive metals are amphoteric. These oxides form salt with both acids and bases.

\[\text{e.g., } BeO, Al_2O_3, GeO, SnO, Sb_2O_3, PbO\]

\[
ZnO, Cr_2O_3
\]

\[
Al_2O_3 + 6HC1 \rightarrow 2AlCl_3 + 3H_2O
\]

\[
Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O
\]

**Salt Hydrolysis:**

Pure water is a weak electrolyte and neutral in nature, i.e., \(H^+\) ion concentration is exactly equal to \(OH^-\) ion concentration

\[
[H^+] = [OH^-]
\]
When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic. When \([H^+] > [OH^-]\), the water becomes acidic and when \([H^+] < [OH^-]\), the water acquires basic nature. This is exactly the change which occurs during the phenomenon known as salt hydrolysis. It is defined as a reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity.

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations are more reactive in comparison to anions and these react with water to produce \(H^+\) ions. Thus, the solution acquires acidic nature.

\[
M^+ + H_2O \leftrightarrow MOH + H^+
\]

Weak base

In other salts, anions may be more reactive in comparison to cations and these react with water to produce \(OH^-\) ions. Thus, the solution becomes basic.

\[
A^- + H_2O \leftrightarrow HA + OH^-
\]

Weak acid

The process of salt hydrolysis is actually the reverse of neutralization.

Salt + Water $\leftrightarrow$ Acid + Base

If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both the acid and the base are either strong or weak, the solution is generally neutral in nature.

As the nature of the cation or the anion of the salt determines whether its solution will be acidic or basic, it is proper to divide the salts into four categories.

(i) Salt of a strong acid and a weak base.

**Examples:** FeCl\(_3\), CuCl\(_2\), AlCl\(_3\), NH\(_4\)Cl, CuSO\(_4\), etc.

(ii) Salt of a strong base and a weak acid.

**Examples:** CH\(_3\)COONa, NaCN, NaHCO\(_3\), Na\(_2\)CO\(_3\), etc.

(iii) Salt of a weak acid and a weak base.

**Examples:** CH\(_3\)COONH\(_4\), (NH\(_4\))\(_2\)CO\(_3\), NH\(_4\)HCO\(_3\), etc.

(iv) Salt of a strong acid and a strong base.

**Examples:** NaCl, K\(_2\)SO\(_4\), NaNO\(_3\), NaBr, etc.
Salt of a strong acid and a weak base:

The solution of such a salt is acidic in nature. The cation of the salt which has come from weak base is reactive. It reacts with water to form a weak base and H⁺ ions.

\[ B^+ + H_2O \leftrightarrow BOH + H^+ \]

**Weak base**

Consider, for example, NH₄Cl. It ionises in water completely into NH₄ and CF ions. ions react with water to form a weak base (NH₄OH) and H⁺ ions.

\[ NH^+ + H_2O \leftrightarrow NH_4OH + H^+ \]

Thus, hydrogen ion concentration increases and the solution becomes acidic.

Applying law of mass action,

\[ K_h = \frac{[H^+][NH_4 OH]}{[NH^+_4]} = \frac{(Cx \cdot C x)}{C (1-x)} = \frac{(x^2 \cdot C)}{(1-x)} \quad \ldots \quad (i) \]

where C is the concentration of salt and x the degree of hydrolysis.

Other equilibria which exist in solution are

\[ NH_4OH \leftrightarrow NH^+_4 + OH^- \quad K_b = \frac{[NH^+_4][OH^-]}{[NH_4OH]} \quad \ldots \quad (ii) \]

\[ H_2O \leftrightarrow H^+ + OH^- \quad K_b = [H^+][H^-] \quad \ldots \quad (iii) \]

From eqs. (ii) and (iii)

\[ K_w/K_b = [H^+][NH_4 OH]/[NH^+_4] \quad = K_h \quad \ldots \quad (iv) \]

\[ [H^+] = [H^+][NH_4^+]/[NH_4OH] = K_w/K_b \times [NH_4^+]/[NH_4 OH] \]

\[ \log [H^+] = \log K_w - \log K_b + \log[\text{salt}]/[\text{base}] \]

\[ -pH = -pK_w + pK_b + \log[\text{salt}]/[\text{base}] \]

\[ pK_w - pH = pK_b + \log[\text{salt}]/[\text{base}] \]

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

**Relation between Hydrolysis constant and Degree of hydrolysis**
The extent to which hydrolysis proceeds is expressed as the degree of hydrolysis and is defined as the fraction of one mole of the salt that is hydrolysed when the equilibrium has been attained. It is generally expressed as $h$ or $x$.

$$h = \frac{\text{Amount of salt hydrolysed}}{\text{Total salt taken}}$$

Considering again eq. (i),

$$K_h = \frac{x^2C}{1-x} \quad \text{or} \quad K_h = \frac{h^2C}{1-h}$$

When $h$ is very small, $(1-h) \rightarrow 1$,

$$H_2 = K_h \times 1/c$$

or

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w K_b C}{K_h}}$$

$$\log[H^+] = \frac{1}{2} \log K_w + \frac{1}{2} \log C - \frac{1}{2} \log K_b$$

$$\text{pH} = \frac{1}{2} pK_w - \frac{1}{2} \log C - \frac{1}{2} pK_b = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log C$$

**Salt of a Weak Acid and a Strong Base:**

The solution of such a salt is basic in nature. The anion of the salt is reactive. It reacts with water to form a weak acid and $\text{OH}^-$ ions.

$$A^- + \text{H}_2\text{O} \leftrightarrow \text{HA} + \text{OH}^-$$

**Weak acid**

Consider, for example, the salt $\text{CH}_3\text{COONa}$. It ionises in water completely to give $\text{CH}_3\text{COO}^-$ and $\text{Na}^+$ ions. $\text{CH}_3\text{COO}^-$ ions react with water to form a weak acid, $\text{CH}_3\text{COOH}$ and $\text{OH}^-$ ions.

$$\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{COOH} + \text{OH}^-$$

$$C(1-x) \quad Cx \quad Cx$$

Thus, $\text{OH}^-$ ion concentration increases, the solution becomes alkaline.

Applying law of mass action,

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{(Cx \times Cx)/C(1-x)}{(Cx^2)/(1-x)} = (Cx^2)/(1-x)$$
Other equations present in the solution are:

\[ \text{CH}_3\text{COOH} \leftrightarrow \text{CH}_3\text{COO}^- + \text{H}^+, \quad K_a = [\text{CH}_3\text{COO}^-][\text{H}^+]/[\text{CH}_3\text{COOH}] \quad \ldots \quad (\text{ii}) \]

\[ \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-, \quad K_w = [\text{H}^+][\text{OH}^-] \quad \ldots \quad (\text{iii}) \]

From eqs. (ii) and (iii),

\[ \log [\text{OH}^-] = \log K_w - \log K_a + \log[\text{salt}]/[\text{acid}] \]

\[ -p\text{OH} = -pK_w + pK_a + \log[\text{salt}]/[\text{acid}] \]

\[ pK_w - p\text{OH} = pK_a + \log[\text{salt}]/[\text{acid}] \]

\[ \text{pH} = pK_a + \log[\text{salt}]/[\text{acid}] \]

Considering eq. (i) again,

\[ K_h = cx^2/(1-x) \quad \text{or} \quad K_h = Ch^2/(1-h) \]

When \( h \) is very small, \((1-h) \rightarrow 1\)

or \( h^2 = K_h/C \)

or \( h = \sqrt{K_h/C} \)

\[ [\text{OH}^-] = h \times C = \sqrt{(CK_h)} = \sqrt{(C*K_w/K_a)} \]

\[ [\text{H}^+] = K_w/[\text{OH}^-] \]

\[ = K_w/\sqrt{(C*K_w/K_a)} = \sqrt{(K_a*K_w)/K_c} \]

\[-\log [\text{H}^+] = -1/2\log K_w - 1/2\log K_a + 1/2\log C \]

\[ \text{pH} = 1/2pK_w + 1/2pK_a + 1/2\log C \]

\[ = 7 + 1/2pK_a + 1/2\log C. \]

\textbf{Salt of a weak acid and a weak base:}

Maximum \textit{hydrolysis} occurs in the case of such a salt as both the cation and anion are reactive and react with water to produce \( \text{H}^+ \) and \( \text{OH}^- \) ions. The solution is generally neutral but it can be either slightly acidic or slightly alkaline if both the reactions take place with slightly different rates. Consider, for example, the salt \( \text{CH}_3\text{COONH}_4 \). It gives \( \text{CH}_3\text{COO}^- \) and \( \text{NH}_4^+ \) ions in solution. Both react with water.
Other equilibria which exist in solution are:

\[ \text{CH}_3\text{COOH} \leftrightarrow \text{CH}_3\text{COO}^- + \text{H}^+ \quad \text{Ka} = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \text{..... (i)} \]

\[ \text{NH}_4\text{OH} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad \text{Kb} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \text{..... (ii)} \]

\[ \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \quad \text{Kw} = [\text{H}^+][\text{OH}^-] \quad \text{..... (iii)} \]

From Eqs. (i), (ii) and (iii),

\[ K_h = \frac{[\text{NH}_4\text{OH}] [\text{NH}_4^+]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \quad \text{.... (iv)} \]

Let C be the concentration and h be the degree of hydrolysis

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

When h is small, (1-h) \(\to\) 1.

\[ K_h = h^2 \]

\[ h = \sqrt{K_h} = \sqrt{K_w/K_a \cdot K_b} \]

\[ [\text{H}^+] \times K_a \times h = K_a \times \sqrt{K_w/K_a \cdot K_b} = \sqrt{K_w \cdot K_a / K_b} \]

\[ -\log [\text{H}^+] = -\frac{1}{2}\log K_a - \frac{1}{2}\log K_w + \frac{1}{2}\log K_b \]

\[ \text{pH} = \frac{1}{2}pK_a + \frac{1}{2}pK_w - \frac{1}{2}pK_b \]
\[ \text{pH} = 7 + \frac{1}{2}\text{pK}_a - \frac{1}{2}\text{pK}_b \]

When \(\text{pK}_a = \text{pK}_b\), pH = 7, i.e., solution will be neutral in nature.

When \(\text{pK}_a > \text{pK}_b\). The solution will be alkaline as the acid will be slightly weaker than base and pH value will be more than 7. In case \(\text{pK}_a < \text{pK}_b\), the solution will be acidic as the acid is relatively stronger than base and pH will be less than 7.

**Salt of a strong acid and a strong base**

Such a salt, say NaCl, does not undergo **hydrolysis** as both the ions are not reactive. The solution is thus, neutral in nature.

**Hydrolysis of Amphiprotic Anion:**

Let us consider hydrolysis of **amphiprotic anion** only, i.e., when counter cation is not hydrolysed, example of some salts of this category are NaHCO\(_3\), NaHS, Na\(_2\)HPO\(_4\), NaH\(_2\)PO\(_4\).

\[ \text{(i) } \text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+ \quad K_{a1} = \frac{[\text{H}_2\text{PO}_4^-][\text{H}^+]}{[\text{H}_2\text{PO}_4^-]} \]

\[ \text{(ii) } \text{H}_2\text{PO}_4^- \rightleftharpoons \text{HPO}_2^- + \text{H}^+ \quad K_{a2} = \frac{[\text{HPO}_2^-][\text{H}^+]}{[\text{H}_2\text{PO}_4^-]} \]

\[ \text{(iii) } \text{HPO}_2^- \rightleftharpoons \text{PO}_3^- + \text{H}^+ \quad K_{a3} = \frac{[\text{PO}_3^-][\text{H}^+]}{[\text{HPO}_2^-]} \]

Here, \(\text{H}_2\text{PO}_4^-\) and \(\text{HPO}_2^-\) are **amphiprotic anions**. pH after their **hydrolysis** can be calculated as,

\[ \text{pH of } \text{H}_2\text{PO}_4^- \text{ in aqueous medium} = \frac{\text{pK}_a + \text{pK}_b}{2} \]

\[ \text{pH of } \text{H}_2\text{PO}_2^- \text{ in aqueous medium} = \frac{\text{pK}_a + \text{pK}_b}{2} \]

Here, \(\text{H}_2\text{PO}_2^-\) is conjugate base of \(\text{H}_2\text{PO}_4^-\) and \(\text{H}_3\text{PO}_4\) is conjugate acid of \(\text{H}_2\text{PO}_4^-\).

Similarly, \(\text{PO}_3^-\) is conjugate base of \(\text{HPO}_2^-\) and \(\text{HPO}_4^-\) is conjugate acid of \(\text{PO}_3^-\).

(iv) Let us consider **amphiprotic** bicarbonate anion.
HCO$_3^-$ + H$_2$O $\rightleftharpoons$ CO$_3^{2-}$ + H$_3^+$O  \hspace{1cm} \text{(Ionisation)}

\begin{align*}
\text{Acid} & \quad \text{Conjugate base} \\
HCO$_3^-$ + H$_2$O & $\rightleftharpoons$ H$_2$CO$_3$ + OH$^-$ \hspace{1cm} \text{(Hydrolysis)}
\end{align*}

\begin{align*}
\text{Base} & \quad \text{Conjugate acid} \\
H_2CO_3 & \rightleftharpoons H^+ + HCO$_3^-$ \quad K_{a1} = \frac{[H^+][HCO$_3^-$]}{[H_2CO_3]} \\
HCO$_3^-$ & \rightleftharpoons H^+ + CO$_3^{2-}$ \quad K_{a2} = \frac{[H^+][CO$_3^{2-}$]}{[HCO$_3^-$]}
\end{align*}

pH HCO$_3^-$ ion after hydrolysis in aqueous medium

= \frac{(pK_{a1} + pK_{a2})}{2}

(v) Let us consider the hydrolysis of amphiprotic anion along with cation, e.g., NH$_4$HCO$_3$, NH$_4$HS.

In above examples both cations and anions are derived from weak base and weak acids respectively hence, both will undergo hydrolysis in aqueous medium.

When these salts are dissolved in water, [H$_3$O$^+$] concentration can be determined as,

\[ [H_3O^+] = \sqrt{k_{a1}[K_w/k_b + k_{a2}]} \]

\[ \text{pH} = -\log = \sqrt{k_{a1}[K_w/k_b + k_{a2}]} \]

**Hydrolysis at a Glance**

<table>
<thead>
<tr>
<th>Salt</th>
<th>Nature</th>
<th>Degree</th>
<th>Hydrolysis Constant</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. NaCl (Strong acid + Strong Base)</td>
<td>Neutral</td>
<td>No Hydrolysis</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2. CH$_3$COONa (Weak acid + Strong base)</td>
<td>Base</td>
<td>$h = \sqrt{Kw/Cka}$</td>
<td>$K_h = Kw/k_a$</td>
<td>pH=1/2[pKW + pKA + logC]</td>
</tr>
</tbody>
</table>
3. $\text{NH}_4\text{Cl}$
   (Strong acid + Weak base)

4. $\text{CH}_3\text{COONH}_4$ (Weak acid + Weak base)

|          | Acidic | $h = \sqrt{\text{kw}/\text{C}_{\text{kb}}}$ | $K_h = \text{kw}/\text{C}_{\text{kb}}$ | pH = $\frac{1}{2}[^{\text{pkw}}_\text{-}^{\text{p}_{\text{kb}}} - \text{logC}]$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$*$</td>
<td>$h = \sqrt{\text{kw}/(\text{ka} + \text{kb})}$</td>
<td>$K_h = \text{kw}/(\text{ka} + \text{kb})$</td>
<td>pH = $\frac{1}{2}[^{\text{pkw}}<em>\text{+}^{\text{p}</em>{\text{ka}} - \text{p}_{\text{kb}}}]$</td>
</tr>
</tbody>
</table>

In the case of salt of weak acid and weak base, nature of medium after **hydrolysis** is decided in the following manner:

(i) If $K_a = K_b$, the medium will be neutral.

(ii) If $K_a > K_b$, the medium will be acidic.

(iii) If $K_a < K_b$, the medium will be basic.

The degree of **hydrolysis** of salts of weak acids and weak bases is unaffected by dilution because there is no concentration term in the expression of degree of **hydrolysis**.

**Note**: Degree of **hydrolysis** always increases with increase in temperature because at elevated temperature increase in $K_w$ is greater as compared to $K_a$ and $K_b$.

**BUFFER SOLUTIONS:**

For several purposes, we need solutions which should have constant pH. Many reactions, particularly the biochemical reactions, are to be carried out at a constant pH. But it is observed that solutions and even pure water (pH = 7) cannot retain the constant pH for long. If the solution comes in contact with air, it will absorb CO₂ and becomes more acidic. If the solution is stored in a glass bottle, alkaline impurities dissolve from glass and the solution becomes alkaline.

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

(i) It has a definite pH, i.e., it has reserve acidity or alkalinity.
(ii) Its pH does not change on standing for long.
(iii) Its pH does not change on dilution.
(iv) Its pH is slightly changed by the addition of small quantity of an acid or a base.

Buffer solutions can be obtained:

(i) by mixing a weak acid with its salt with a strong base,

eg;
(a) \( \text{CH}_3\text{COOH} + \text{CH}_3\text{COONa} \)
(b) Boric acid + Borax
(c) Phthalic acid + Potassium acid phthalate

(ii) by mixing a weak base with its salt with a strong acid,

eg;
(a) \( \text{PNH}_4\text{OH} + \text{NH}_4\text{Cl} \)
(b) Glycine + Glycine hydrochloride

(iii) by a solution of ampholyte. The ampholytes or amphoteric electrolytes are the substances which show properties of both an acid and a base. Proteins and amino acids are the examples of such electrolytes.

(iv) by a mixture of an acid salt and a normal salt of a polybasic acid, e.g., \( \text{Na}_2\text{HPO}_4 + \text{Na}_3\text{PO}_4 \), or a salt of weak acid and a weak base, such as \( \text{CH}_3\text{COONH}_4 \).

The first and second type are also called acidic and basic buffers respectively.
Explanation of buffer action

(i) Acidic buffer:

Consider the case of the solution of acetic acid containing sodium acetate. Acetic acid is feebly ionised while sodium acetate is almost completely ionised. The mixture thus contains CH₃COOH molecules, CH₃COO⁻ ions, Na⁺ ions, H⁺ ions and OH⁻ ions. Thus, we have the following equilibria in solution:

\[
\text{CH}_3\text{COOH} \leftrightarrow \text{H}^+ + \text{CH}_3\text{COO}^- \quad \text{(Feebly ionised)}
\]

\[
\text{CH}_3\text{COONa} \leftrightarrow \text{Na}^+ + \text{CH}_3\text{COC}^- \quad \text{(Completely ionised)}
\]

\[
\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \quad \text{(Very feebly ionised)}
\]

When a drop of strong acid, say HCl, is added, the H⁺ ions furnished by HCl combine with CH₃COO⁻ ions to form feebly ionised CH₃COOH whose ionisation is further suppressed due to common ion effect. Thus, there will be a very slight effect in the overall H⁺ ion concentration or pH value.

When a drop of NaOH is added, it will react with free acid to form undissociated water molecules.

\[
\text{CH}_3\text{COOH} + \text{OH}^- \leftrightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}
\]

Thus, OH⁻ ions furnished by a base are removed and pH of the solution is practically unaltered.

Buffer capacity:

The property of buffer solution to resist alteration in its pH value is known as buffer capacity. It has been found that if the ratio [Salt]/[Acid] or [Salt]/[Base] is unity, the pH of a particular buffer does not change at all. Buffer capacity is defined quantitatively as number of moles of acid or base added in one litre of solution as to change the pH by unity,

\[ i.e. \]

Buffer capacity

\[
(\phi) = \frac{\text{(No.of moles of acid or base added to 1 litre)}}{\text{(Change in pH)}}
\]

or \[ \phi = \delta b/\delta (\text{pH}) \]

where \( \delta b \) → number of moles of acid or base added to 1 litre solution and \( \delta (\text{pH}) \) → change in pH.
Buffer capacity is maximum:

(i) When [Salt] = [Acid], i.e., pH = \( pK_a \) for acid buffer

(ii) When [Salt] = [Base], i.e., pOH = \( pK_b \) for base buffer under above conditions, the buffer is called efficient.

**Utility of buffer solutions in analytical chemistry**

Buffers are used:

(i) To determine the pH with the help of indicators.

(ii) For the removal of phosphate ion in the qualitative inorganic analysis after second group using \( \text{CH}_3\text{COOH} + \text{CH}_3\text{COONa} \) buffer.

(iii) For the precipitation of lead chromate quantitatively in gravimetric analysis, the buffer, \( \text{CH}_3\text{COOH} + \text{CH}_3\text{COONa} \), is used.

(iv) For precipitation of hydroxides of third group of qualitative analysis, a buffer, \( \text{NH}_4\text{Cl} + \text{NH}_4\text{OH} \), is used.

(v) A buffer solution of \( \text{NH}_4\text{Cl} \), \( \text{NH}_4\text{OH} \), and \( (\text{NH}_4)_2\text{CO}_3 \) is used for precipitation of carbonates of fifth group in qualitative inorganic analysis.

(vi) The pH of intracellular fluid, blood is naturally maintained. This maintenance of pH is essential to sustain life because, enzyme catalysis is pH sensitive process. The normal pH of blood plasma is 7.4. Following two buffers in the blood help to maintain pH (7.4).

(a) Buffer of carbonic acid (\( \text{H}_2\text{CO}_3 \) and \( \text{NaHCO}_3 \))

(b) Buffer of phosphoric acid (\( \text{H}_2\text{PO}_4^- \), \( \text{HPO}_2^- \))

Buffers are used in industrial processes such as manufacture of paper, dyes, inks, paints, drugs, etc. Buffers are also employed in agriculture, dairy products and preservation of various types of foods and fruits.

**Example 40:** The pH of a buffer is 4.745. When 0.01 mole of NaOH is added to 1 litre of it, the pH changes to 4.832. Calculate its buffer capacity.

**Solution:** From definition,

\[
\text{Buffer capacity (} \varphi \text{) = } \frac{\delta b}{\delta \text{[ph]}}
\]

\[
\delta (\text{pH}) = (4.832 - 4.745) = 0.087; \quad \delta b = 0.01
\]

Substituting given values,
Example 41: Suppose it is required to make a buffer solution of pH = 4, using acetic acid and sodium acetate. How much of sodium acetate is to be added to 1 litre of N/10 acetic acid?

Solution: Applying Henderson's equation,

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

\[ 4 = \log [\text{Salt}] - \log (0.1) - \log 1.8 \times 10^{-5} \]

So \( \log [\text{Salt}] = (4 - 1 - 5 + 0.2552) = 2.2552 \)

The molecular mass of \( \text{CH}_3\text{COONa} = 82 \)

Amount of salt = \( 0.018 \times 82 = 1.476 \text{ g} \)

Example 42: What is the pH of the solution when 0.2 mole of hydrochloric acid is added to one litre of a solution containing 1 M acetic acid and acetate ion? Assume that the total volume is one litre. \( K_a \) for \( \text{CH}_3\text{COOH} = 1.8 \times 10^{-5} \).

Solution: On adding HCl, the free hydrogen ions will combine with \( \text{CH}_3\text{COO}^- \) ions to form \( \text{CH}_3\text{COOH} \). Thus, the concentration of acetic acid increases while that of \( \text{CH}_3\text{COO}^- \) ions decreases.

\[ [\text{CH}_3\text{COOH}] = (0.2 + 1) = 1.2 \text{ mol litre}^{-1} \]

\[ [\text{Salt}] = (1 - 0.2) = 0.8 \text{ mol litre}^{-1} \]

Applying Henderson's equation,

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

\[ = \log 0.8/1.2 \log 1.8 \times 10^{-5} \]

\[ = \log 2 - \log 3 - \log 1.8 \times 10^{-5} = 4.5687 \]

Example 43: 20 mL of 0.2 M sodium hydroxide 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 the pH of solution 4.74. The ionisation constant of acetic acid is \( 1.8 \times 10^{-5} \).

Solution: No. of moles of NaOH in

\[ 20 \text{ mL} = 0.2/1000 = 0.004 \text{ 02} \]
No. of moles of acetic acid in 50 mL = $0.2/1000 \times 50 = 0.01$

When NaOH is added, CH$_3$COONa is formed

\[
\text{CH}_3\text{COOH} + \text{NaOH} \rightleftharpoons \text{CH}_3\text{COONa} + \text{H}_2\text{O}
\]

1 mole 1 mole mole 1 mole

No. of moles of CH$_3$COONa in 70 mL solution = 0.004

No. of moles of CH$_3$COOH in 70 mL solution

$= (0.01 - 0.004) = 0.006$

Applying Henderson's equation,

\[
\text{pH} = \log\frac{\text{Salt}}{\text{Acid}} \log K_a
\]

\[
= \log\frac{0.004}{0.006} \log 1.8 \times 10^{-5} = 4.56787
\]

On further addition of NaOH, the pH becomes 4.74.

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

\[
= \log\frac{\text{Salt}}{\text{Acid}} - \log 1.8 \times 10^{-5}
\]

or \[
\log\frac{\text{Salt}}{\text{Acid}} = \text{pH} + \log1.8\times10^{-5} = (4.74 - 4.7448) = -0.0048
\]

So \[
\log\frac{\text{Salt}}{\text{Acid}} = 1.9952
\]

\[
\frac{\text{Salt}}{\text{Acid}} = -0.9891
\]

Let 'x' moles of NaOH be added.

[\text{Salt}] = (0.004 + x) mole

[\text{Acid}] = (0.006 - x) mole

[\text{Salt}]/[\text{Acid}] = (0.004+x)/(0.006-x) = 0.9891

or 0.004 + x = 0.9891 \times 0.006 - 0.9891x

x = 0.000972 mole

Volume of 0.2 M NaOH solution having 0.000972 mole

$= 1000/0.2 \times 0.000972 = 4.86$ mL
Example 44: Calculate pH of the buffer solution containing 0.15 mole of NH₄OH and 0.25 moles of NH₄Cl. $K_b$ for NH₄OH is $1.98 \times 10^{-5}$.

Solution: Applying the equation,

$$pOH = \log\left(\frac{\text{Salt}}{\text{Base}}\right) - \log K_b$$

$$= \log\left(\frac{0.25}{0.15}\right) - \log 1.8 \times 10^{-5}$$

$$= k\log 5 - \log 3 - \log 1.8 \times 10^{-5}$$

$$= 0.6989 - 0.4771 + 4.7448 = 4.966$$

$$pH = (14 - 4.966) = 9.034$$

Example 45: What volume of 0.10 M sodium formate solution should be added to 50 mL of 0.05 M formic acid to produce a buffer solution of pH 4.0? $pK_a$ for formic acid is 3.80.

Solution: Let x mL of 0.10 M sodium formate be added.

Number of moles in x mL of 0.10 M sodium formate = $0.10/1000 \times x$

Number of moles in 50 mL of 0.05 M formic acid = $0.05/1000 \times 50$

$$\frac{\text{Sod.formate}}{\text{formicacid}} = \frac{(1.10 \times x)/1000}{(0.05 \times 50)/1000}$$

$$\frac{x}{2.5} = 0.04x$$

Applying the equation

$$pH = \log\left(\frac{\text{NaCN}}{\text{HCN}}\right) - \log K_a$$

$$8.5 = \log\left(\frac{0.01-a}{a}\right) - \log4.1 \times 10^{-10}$$

So, $\log(0.01-a)/a = 8.5 + 0.6127 - 10.0 = 1.1127$

$$\frac{0.01-a}{a} = 0.1296$$

or $a = 0.01/1.1296 = 0.0089 \text{ mole}$

Henderson's Equation (pH of a buffer):

(i) Acidic buffer:

It consists of a mixture of weak acid and its salt (strong electrolyte). The ionisation of the weak acid, HA, can be shown by the equation

$$HA \leftrightarrow H^+ + A^-$$
Applying law of mass action,

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

It can be assumed that concentration of $A^-$ ions from complete ionisation of the salt $BA$ is too large to be compared with concentration of $A^-$ ions from the acid HA.

$$BA \leftrightarrow B^+ + A^-$$

Thus, $[HA] = \text{Initial concentration of the acid as it is feebly ionised in presence of common ion}$

and $[A^-] = \text{Initial concentration of the salt as it is completely ionised}$

So $[H^+] = K_a \cdot [\text{Acid}]/[\text{Salt}]$ \quad ...... (iii)

Taking logarithm and reversing sign,

$$-\log [H^+] = -\log K_a - \log[\text{Acid}]/[\text{Salt}]$$

or $$\text{pH} = \log[\text{Salt}]/[\text{Acid}] - \log K_a$$

or $$\text{pH} = pK_a + \log[\text{Salt}]/[\text{Acid}]$$ \quad ...... (iv)

This is known as Henderson's equation.

When $[\text{Salt}]/[\text{Acid}] = 10$, then

$$\text{pH} = 1 + pK_a$$

and when $[\text{Salt}]/[\text{Acid}]$, then

$$\text{pH} = pK_a - 1$$

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

(ii) Basic offer:

It consists of a weak base and its salt with strong acid. Ionization of a weak base, BOH, can be represented by the equation.

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

Applying law of mass action,
\[ K_b = \frac{[B^+][OH^-]}{[BOH]} \] \hspace{1cm} ...... (i)

or \[ [OH^-] = K_b \frac{[BOH]}{[B^+]} \] \hspace{1cm} ...... (ii)

As the salt is completely ionized, it can be assumed that whole of \( B^+ \) ion concentration comes from the salt and contribution of weak base to \( B^+ \) ions can be ignored.

\[ BA \leftrightarrow B^+ + A^- \] \hspace{1cm} (Completely ionised)

So \[ [OH^-] = K_b \frac{[Base]}{[Salt]} \] \hspace{1cm} .... (iii)

or \[ pOH = \log \frac{[Salt]}{[Base]} \log K_b \]

or \[ pOH = pK_b + \log \frac{[Salt]}{[Base]} \] \hspace{1cm} ...... (iv)

Knowing \( pOH \), \( pH \) can be calculated by the application of the formula.

\[ pH + pOH = 14 \]

**THEORY OF INDICATORS:**

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

<table>
<thead>
<tr>
<th>Indicator</th>
<th>( pH ) range</th>
<th>Colour change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>3.2-4.5</td>
<td>Pink to yellow</td>
</tr>
<tr>
<td>Methyl red</td>
<td>4.4-6.5</td>
<td>Red to yellow</td>
</tr>
<tr>
<td>Litmus</td>
<td>5.5-7.5</td>
<td>Red to blue</td>
</tr>
<tr>
<td>Phenol red</td>
<td>6.8-8.4</td>
<td>Yellow to red</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>8.3-10.5</td>
<td>Colourless to pink</td>
</tr>
</tbody>
</table>

Theory of acid-base indicators: Two theories have been proposed to explain the change of colour of acid-base **indicators** with change in \( pH \).

**1. Ostwald's theory:** According to this theory:

(a) The colour change is due to ionisation of the acid-base indicator. The unionised form has different colour than the ionised form.
(b) The ionisation of the indicator is largely affected in acids and bases as it is either a weak acid or a weak base. In case, the indicator is a weak acid, its ionisation is very much low in acids due to common H\(^+\) ions while it is fairly ionised in alkalies. Similarly if the indicator is a weak base, its ionisation is large in acids and low in alkalies due to common OH\(^-\) ions.

Considering two important indicators **phenolphthalein** (a weak acid) and **methyl orange** (a weak base), Ostwald theory can be illustrated as follows:

**Phenolphthalein**: It can be represented as HPh. It ionises in solution to a small extent as:

\[
\text{HPh} \leftrightarrow \text{H}^+ + \text{Ph}^-
\]

Colourless \hspace{1cm} Pink

Applying law of mass action,

\[
K = \frac{[\text{H}^+][\text{Ph}^-]}{[\text{HPh}]} \]

The undissociated molecules of **phenolphthalein** are colourless while Ph\(^-\) ions are pink in colour. In presence of an acid the ionisation of HPh is practically negligible as the equilibrium shifts to left hand side due to high concentration of H\(^+\) ions. Thus, the solution would remain colourless. On addition of alkali, hydrogen ions are removed by OH\(^-\) ions in the form of water molecules and the equilibrium shifts to right hand side. Thus, the concentration of Ph\(^-\) ions increases in solution and they impart pink colour to the solution.

Let us derive Handerson equation for an indicator

\[
\text{HIn} + \text{H}_2\text{O} \leftrightarrow \text{H}^+\text{O} + \text{In}^-
\]

'Acid form' \hspace{1cm} 'Base form'

Conjugate acid-base pair

\[
K_{\text{In}} = \frac{[\text{In}][\text{H}^+\text{O}]}{[\text{HIn}]}; \quad K_{\text{In}} = \text{Ionization constant for indicator}
\]

\[
[H^+\text{O}] = K_{\text{In}} \times \frac{[\text{In}]}{[\text{In}^-]}
\]

\[
\text{pH} = -\log_{10} [H^+\text{O}] = -\log_{10}[K_{\text{In}}] - \log_{10}[\text{HIn}]/[\text{In}^-]
\]

\[
\text{pH} = pK_{\text{In}} + \log_{10}[\text{In}^-]/[\text{In}^-] \quad \text{(Handerson equation for indicator)}
\]

At equivalence point
\[ [\text{In}^-] = [\text{HIn}] \text{ and } \text{pH} = \text{pK}_{\text{In}} \]

**Methyl orange**: It is a very weak base and can be represented as MeOH. It is ionized in solution to give Me\(^+\) and OH\(^-\) ions.

\[
\text{MeOH} \leftrightarrow \text{Me}^+ + \text{OH}^- \\
\text{Yellow} \quad \text{Red}
\]

Applying law of mass action,

\[
K = [\text{Me}^+][\text{OH}^-]/[\text{MeOH}]
\]

In presence of an acid, OH\(^-\) ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient Me\(^+\) ions are produced which impart red colour to the solution. On addition of alkali, the concentration of OH\(^-\) ions increases in the solution and the equilibrium shifts to left hand side, i.e., the ionisation of MeOH is practically negligible. Thus, the solution acquires the colour of unionised methyl orange molecules, i.e., yellow.

This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid. The OH\(^-\) ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why methyl orange is not a suitable indicator for the titration of weak acid with strong base.

1. **Quinonoid theory:**

According to this theory:

(a) The **acid-base indicators** exist in two tautomeric forms having different structures. Two forms are in equilibrium. One form is termed benzenoid form and the other quinonoid form.

![Quinonoid and benzenoid forms](image)

(b) The two forms have different colors. The color change in due to the interconversion of one tautomeric form into other.

(c) One form mainly exists in acidic medium and the other in alkaline medium.
Thus, during titration the medium changes from acidic to alkaline or vice-versa. The change in pH converts one tautomeric form into other and thus, the colour change occurs.

**Phenolphthalein** has benzoic form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.

![Phenolphthalein structure](image)

**Methyl orange** has quinonoid form in acidic solution and benzenoid form in alkaline solution. The color of benzenoid form is yellow while that of quinonoid form is red.

![Methyl orange structure](image)

**Selection of suitable indicator or choice of indicator**

The neutralisation reactions are of the following four types:

(i) A strong acid versus a strong base. (Fig. 10.1)

(ii) A weak acid versus a strong base. (Fig. 10.2)

(iii) A strong acid versus a weak base. (Fig. 10.3)

(iv) A weak acid versus a weak base. (Fig. 10.4)

In order to choose a suitable indicator, it is necessary to understand the pH changes in the above four types of titrations. The change in pH in the vicinity of the equivalence point is most important for this purpose. The curve obtained by plotting pH as ordinate against the
volume of alkali added as abscissa is known as neutralisation or **titration curve**. The **titration curves** of the above four types of neutralisation reactions are shown in Fig. 10.1, 10.2, 10.3 and 10.4.

In each case 25 mL of the acid (N/10) has been **titrated** against a standard solution of a base (N/10). Each **titration curve** becomes almost vertical for some distance (except curve 10.4) and then bends away again. This region of abrupt change in pH indicates the equivalence point. For a particular **titration**, the **indicator** should be so selected that it changes its colour within vertical distance of the curve.

(i) **Strong acid vs. strong base:**

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

(ii) **Weak acid vs. weak base:**

pH curve of weak acid (say CH₃COOH of oxalic acid) and strong base (say NaOH) is vertical over the approximate pH range 7 to 11. So phenolphthalein is the suitable indicator for such a titration.

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

(iii) Weak acid vs. weak base:

pH curve of weak acid and weak base indicates that there is no vertical part and hence, no suitable indicator can be used for such a titration.

**Titration of soluble carbonate with strong acid.**

pH curve of sodium carbonate with HCl shows two inflection points (Fig. 10.5). First inflection point (pH 8.5) indicates conversion of carbonate into bicarbonate.

\[
Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl
\]

As the inflection point lies in the pH range 8 to 10, phenolphthalein can be used to indicate the above conversion. The second inflection point (pH 4.3) indicates the following reaction:

\[
NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O
\]

As the point lies between 3 to 5, methyl orange can be used.