

Electrolytes—Acid, Bases and Salts



C11CH3



Learning Objectives

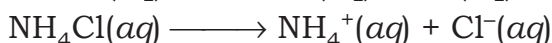
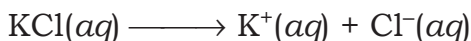
Upon completion of this topic, learners will:

- Discuss electrolytes and non-electrolytes
- Elaborate on Acids and Bases involving the Arrhenius and Bronsted-Lowry theories
- Solve sample problems involving the concept of pH and pOH
- Demonstrate calculations that analyze amounts of acid and base dissociated
- Determine the effects of salt on pH and pOH concentrations
- Discuss the concept of Lewis acids and bases
- Interpret the behavior of buffer solutions
- Describe the behavior of certain salts towards hydrolysis and
- Analyze the concentrations of acids and bases using titration

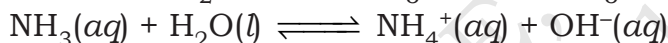
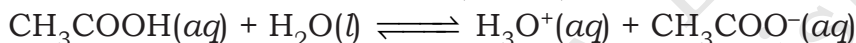
3.1. ELECTROLYTES AND NON-ELECTROLYTES

We know that aqueous solutions of certain substances such as sodium chloride, sulphuric acid, etc., conduct electricity whereas aqueous solutions of certain substances such as sugar, urea, etc., do not conduct electricity. Michael Faraday, in 1824, classified substances into electrolytes and non-electrolytes on the basis of conductivity behaviour of their aqueous solutions. *The substances which conduct electricity in their aqueous solutions* were termed **electrolytes** while those which do not conduct electricity were termed **non-electrolytes**. Svante Arrhenius (1880) explained that electrolytes, when dissolved in water split into charged particles, called ions. This process is called ionisation or dissociation. Certain electrolytes, such as NaCl, KCl, HCl

are almost completely ionized in solutions whereas electrolytes such as NH_4OH , CH_3COOH are weakly ionised. *The electrolytes which are almost completely ionized in solutions are called **strong electrolytes**.* On the other hand, *the electrolytes weakly ionized in their solutions are called **weak electrolytes**.* In case of solutions of weak electrolytes the ions produced by dissociation of electrolyte are in equilibrium with undissociated molecules of the electrolyte. The equations for the dissociation of strong electrolytes are written with only a single arrow directed to the right.



On the other hand, equations for the dissociation of weak electrolytes are written with double arrows (\rightleftharpoons).

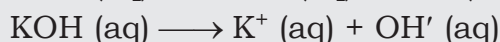
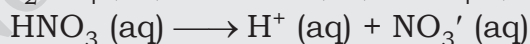
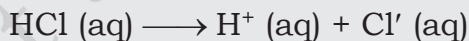


This type of equilibrium involving ions in aqueous solution is called **ionic equilibrium**.

Activities/Lab Work

List several acids and bases. Then write chemical equation to show how they behave as electrolytes.

As we know that electrolytes conduct electricity in their aqueous solution. These conduct electricity because aqueous solutions of electrolytes ionize into ions. More is the degree of ionization more strong the electrolyte is. Acids and bases ionize in their aqueous solutions hence these are electrolytes. Here are some acids and bases which behave as electrolytes.



Acids, Bases and Salts

Electrolytes may be acids, bases or salts. **Acids** are sour in taste. Vinegar contains acetic acid whereas citrus fruits such as orange, lemon, etc., contain citric acid. Tamarind contains tartaric acid. All these substances you know, are sour in taste. Acids turn litmus paper

red. **Bases** are bitter in taste. They turn litmus paper blue. Caustic soda (NaOH), washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) and aqueous ammonia are commonly used bases. **Salts** are made up of oppositely charged ions. In solid state these ions are held by strong electrostatic forces of attraction. When a salt is dissolved in water the attractive forces between the ions are highly weakened. This is due to the reason that electrostatic forces are inversely proportional to the dielectric constant of the medium and water has a very high dielectric constant of 80. This means that when some electrolyte such as sodium chloride is dissolved in water, the electrostatic interactions between the ions are reduced by a factor of 80 and this facilitates the free movement of ions in the solution. The ions, in solution, are further stabilized by their solvation with water molecules. Water molecules being polar molecules can have ion-dipole interactions with ions of the salt. Thus, ionic compounds get dissociated when dissolved in water.

Now let us consider the case of substances containing polar molecules, such as HCl , CH_3COOH , HCN , etc. These substances when dissolved in water ionize due to dipole-dipole interaction between molecules of water and the polar molecules of the substance.

It may be mentioned here that the term **dissociation** refers to the process of separation of ions in water in case of ionic solids whereas the term **ionization** is used in cases where a molecule splits into ions when dissolved in water.

EXPERIMENT 1

Aim: Experiment to demonstrate the conductivity of electrolytic solutions.

Requirements: Beaker, 6 volts battery, a bulb, a switch, two graphite rods or metal rods, connecting wire, any electrolyte (we take H_2SO_4 (aq) sol.)

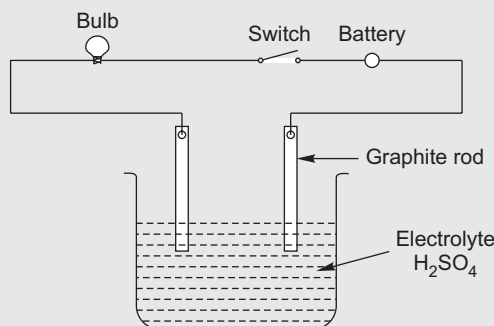


Fig. 3.1. Testing the conductivity of electrolyte

Procedure: Take aqueous solution of H_2SO_4 in a beaker. Place two graphite or metal rods in this solution. Connect graphite rods to the battery, a bulb, a switch with the help of connecting wires. Now switch the current on.

Precautions:

1. Wire connections should be tight.
2. There should be no earthing problem in the circuit.
3. Electrodes (graphite rods) should not touch with each other.

Observations: It is observed that the bulb starts glowing showing that solution of H_2SO_4 conducts electricity.

Result: Glowing of bulb shows that current is passing through the electrolyte hence electrolytes conduct electricity.

3.2. ARRHENIUS AND BRONSTED-LOWRY CONCEPT OF ACIDS AND BASES

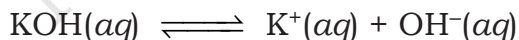
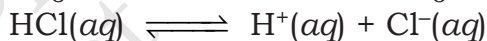
Arrhenius Concept of Acids and Bases

According to Arrhenius concept,

An acid is a substance which can furnish hydrogen ions in its aqueous solution.

A base is a substance which can furnish hydroxyl ions in its aqueous solution.

For example, substances such as HNO_3 , HCl , CH_3COOH are acids whereas substances such as NaOH , KOH , NH_4OH are bases, according to this concept



Acids such as HCl and HNO_3 , which are almost completely ionized in aqueous solutions are termed as **strong acids** whereas acids such as CH_3COOH which are weakly ionized are called **weak acids**.

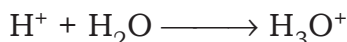
Similarly, bases which are almost completely ionized in aqueous solution are called **strong bases**, for example, NaOH and KOH . The bases such as NH_4OH are only slightly ionized and are called **weak bases**.

According to Arrhenius theory, neutralisation of acids and bases is basically a reaction between H^+ and OH^- ions in solutions.



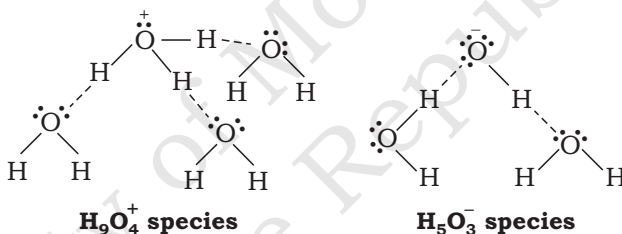
Nature of Hydrogen Ion and Hydroxyl Ion in Aqueous Solution

Hydrogen atom contains one proton and one electron. H^+ ion is formed by loss of this electron. Therefore, H^+ ion is simply a proton. Charge density of this unshielded proton is very high. Therefore, it is not likely to exist independently as H^+ ion. In an aqueous solution H^+ ion is considered to be present in hydrated form in combination with a water molecule as H_3O^+ .



H_3O^+ ion is called **hydronium ion**. It has **trigonal pyramidal** shape.

In aqueous solution hydronium ion is further hydrated to give species such as H_5O_2^+ , H_7O_3^+ and H_9O_4^+ . Similarly, hydroxyl ion is hydrated to give species such as H_3O_2^- , H_5O_3^- , etc.



Arrhenius concept of acids and bases has the following **limitations**:

1. Arrhenius concept is applicable only to aqueous solutions. Thus, this concept has a limited application.
2. It does not account for the acidity of substances such as sulphur dioxide, sulphur trioxide, etc., which do not contain any hydrogen ions.
3. It does not account for the basicity of substances such as ammonia, calcium oxide which do not possess hydroxyl group.

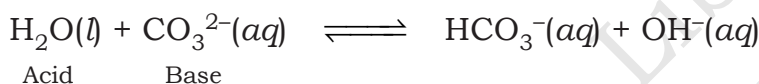
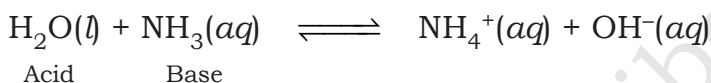
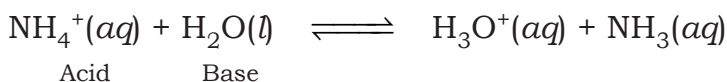
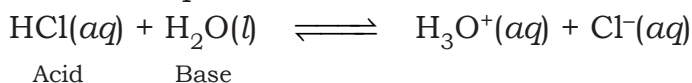
Bronsted-Lowry Concept of Acids and Bases

In 1923, a Danish Chemist J.H. Bronsted and an English Chemist T.M. Lowry independently proposed new definitions for acids and bases. They proposed that :

An acid is a substance that can donate a hydrogen ion or a proton.

A base is a substance that can accept a hydrogen ion or a proton.

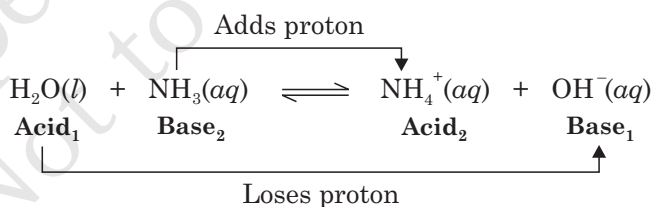
These definitions are more general because according to these definitions even ions can behave as acids or bases. Moreover, these definitions are not restricted to reactions taking place in aqueous solution only. In order to understand this concept of acids and bases let us take some specific examples.



From the above equations, it is obvious that acid base reactions according to Bronsted-Lowry concept involve transfer of a hydrogen ion or a proton from the acid to a base. A substance can act as an acid only if another substance capable of accepting a hydrogen ion or a proton, is present.

Conjugate Acid-Base Pairs

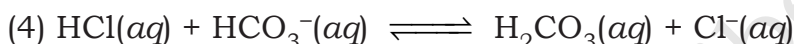
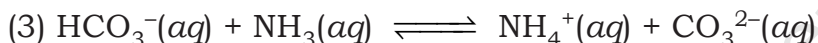
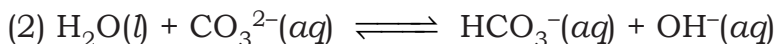
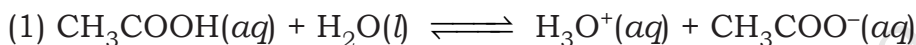
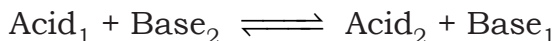
An acid after losing a hydrogen ion or a proton becomes a base whereas a base after accepting the hydrogen ion or a proton becomes an acid. For example, let us consider the reaction between water and ammonia as represented by the following equilibrium:



In the *forward reaction*, water donates a proton to ammonia (base) and acts as acid. In the *reverse reaction*, NH_4^+ ions donate a proton to the OH^- ions (base) and act as acid. A base formed by the loss of proton by an acid is called **conjugate base** of the acid whereas an acid formed by gain of a proton by the base is called **conjugate acid** of the base. In the above example, OH^- is the conjugate base of H_2O and NH_4^+ is conjugate acid of NH_3 . Acid-base pairs such as $\text{H}_2\text{O}/\text{OH}^-$ and $\text{NH}_4^+/\text{NH}_3$ which are formed by loss or gain of a proton are called conjugate acid-base pairs.

A strong acid would have large tendency to donate a proton. Thus, *conjugate base of a strong acid would be a weak base*. Similarly, *conjugate base of a weak acid would be a strong base*.

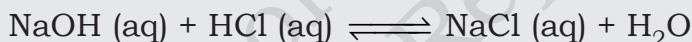
Some more conjugated acid-base pairs have been given in the following equations:



It may be noticed that in equation (1) H_2O is behaving as a base whereas in equation (2) it is behaving as an acid. Similarly, HCO_3^- ion in equation (3) acts as an acid and in equation (4) it acts as a base. *Such substances which can act as acids as well as bases are called amphoteric substances*.

Activities/Lab Work

Write an acid base reaction explaining the concept of Arrhenius theories as well as write an acid base reaction analysing the concept of Bronsted-Lowery theories, identifying conjugate acid base pair.

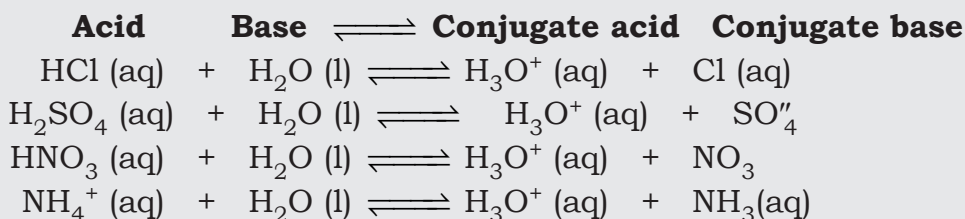


Sodium Hydroxide react with hydrochloric acid to form sodium chloride and water. Here HCl is an acid as it gives H^+ . As per Arrhenius theory an acid is substance which furnishes Hydrogen ion in aqueous solution hence HCl is an acid.

Same way according to Arrhenius theory base is a substance which furnishes OH^- in its aqueous solution. Hence NaOH is a base as it furnishes OH^- .

Concept of Bronsted-Lowery Theory:

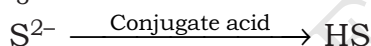
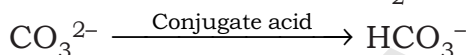
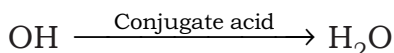
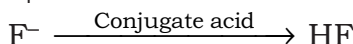
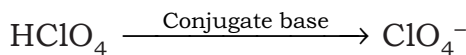
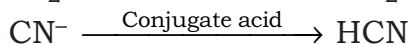
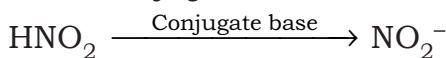
According to Bronsted Lowery Theory acid is a substance which can donate a proton or hydrogen ion. Now let us check with some acids whether these donate hydrogen ion or proton or not.



Here HCl, H₂SO₄, HNO₃ and NH₄⁺ are acids as they donate. Hydrogen ion or Proton and H₂O acts as base as H₂O received H⁺ or proton.

HCl is an acid and Cl⁻ is its conjugate base H₂O here acts as base and H₃O⁺ (aq) is its conjugate acid.

Example 3.1: Write conjugate acid or base for following species.



3.3. LEWIS ACIDS AND BASES

Although Bronsted-Lowry theory was more general than Arrhenius theory of acids and bases but it failed to explain the acid base reactions which do not involve transfer of proton. For example, it fails to explain how acidic oxides such as anhydrous CO₂, SO₂, SO₃, etc., can neutralise basic oxides such as CaO, BaO, etc., even in the absence of solvent.

G.N. Lewis (1923) proposed broader and more general definitions of acids and bases, which do not require the presence of protons to explain the acid base behaviour. According to Lewis concept,

An acid is a substance which can accept a pair of electrons.

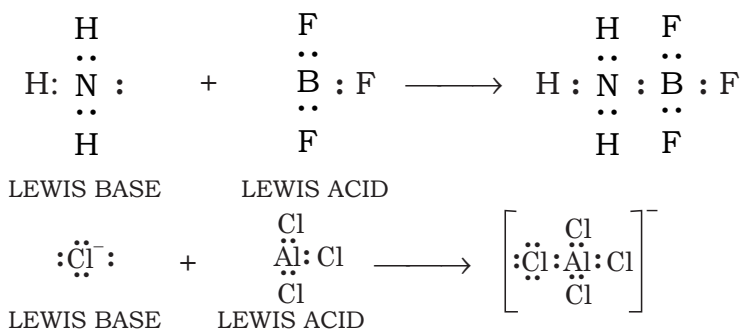
A base is a substance which can donate a pair of electrons.

Acid-base reactions according to this concept involve *donation of electron pair by a base to an acid to form a co-ordinate bond*. Lewis bases

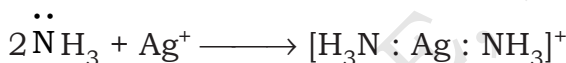
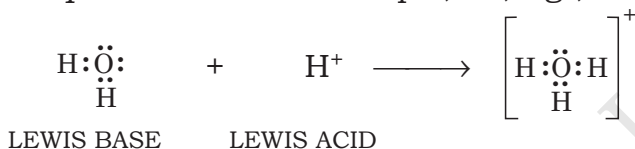
can be neutral molecules such as $\overset{\cdot\cdot}{\text{N}}\text{H}_3$, $\text{CH}_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\text{H}$, $\text{H}_2\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}$, etc., having one or more unshared pairs of electrons, or anions such as CN⁻, OH⁻, Cl⁻, etc.

Lewis acids are the species having vacant orbitals in the valence shell of one of its atoms. The following species can act as Lewis acids.

(a) *Molecules having an atom with incomplete octet*. For example, BF₃ and AlCl₃



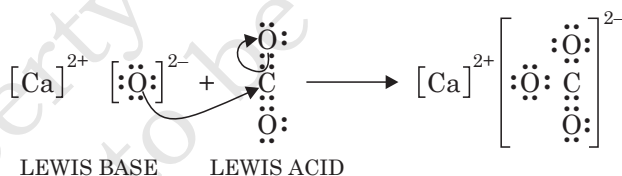
(b) *Simple cations.* For example, H^+ , Ag^+ , etc.



(c) *Molecules in which central atom has vacant orbitals and may acquire more than an octet of valance electrons.* For example, SiF_4 .



(d) *Molecules containing multiple bonds.* For example, CO_2 , SO_2 , etc.



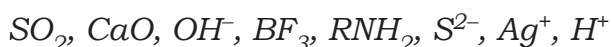
Limitations of Lewis Concept

Though Lewis concept of acids and bases is more general than the Arrhenius as well as Bronsted concepts, yet it has several drawbacks as discussed below:

1. It is too general and includes all the co-ordination compounds and co-ordination reactions.
2. It does not help to assign the relative strengths of acids and bases.
3. It does not explain the behaviour of protonic acids such as HCl , H_2SO_4 , etc., which do not form co-ordinate bond with bases which is the primary requirement of Lewis theory.

- Normally, formation of co-ordination compounds is slow. Therefore, acid-base reactions should also be slow, but in actual practice, acid-base reactions are extremely fast.
- The catalytic activity of many acids is due to $H^+(aq)$ ion. Since a Lewis acid need not contain hydrogen, many Lewis acids will not possess catalytic property.

Example 3.2: Classify following into acids and bases according to Lewis concept.



Solution.

Lewis acid: SO_2, BF_3, Ag^+, H^+

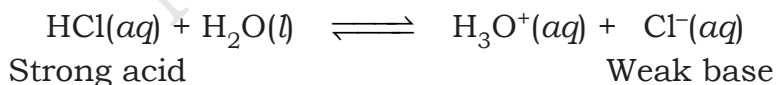
Lewis base: OH^-, CaO, RNH_2, S^{2-}

3.4. DISSOCIATION OR IONIZATION OF ACIDS AND BASES

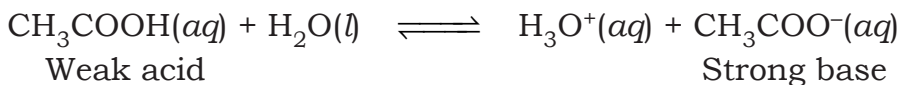
Acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) are termed *strong* because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton (H^+) donors. Similarly, strong bases like sodium hydroxide ($NaOH$), potassium hydroxide (KOH), caesium hydroxide ($CsOH$) and barium hydroxide $Ba(OH)_2$ almost completely dissociate into ions in an aqueous medium giving hydroxyl ions, OH^- . According to Arrhenius concept they are strong bases as they are able to completely dissociate and produce OH^- ions in the medium.

According to Bronsted-Lowry concept of acids and bases, the strength of an acid is measured in terms of its tendency to lose proton whereas strength of a base is measured in terms of its tendency to accept proton. An acid is considered to be strong if it has great tendency to lose proton.

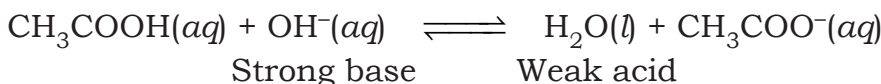
The conjugate base of a strong acid is a weak base.



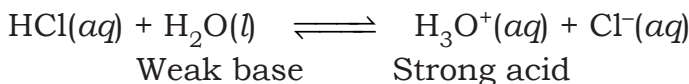
On the other hand, **conjugate base of a weak acid is a strong base.**



A base is considered to be strong if it has great tendency to accept a proton. Therefore, conjugate acid of strong base has little tendency to lose proton and hence is a weak acid.



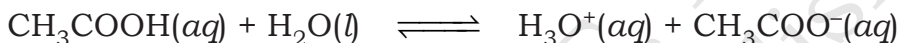
On the other hand, conjugate acid of a weak base is a strong acid.



The strength of acids or bases is experimentally measured by determining its ionization constants or dissociation constants.

Calculation of $[\text{H}_3\text{O}^+]$ and Degree of Dissociation

From the knowledge of K_a it is possible to calculate hydronium ion concentration and degree of ionization of a weak acid. As an example, let us take the case of acetic acid. The following equation represents the ionisation of acetic acid in aqueous solution:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Suppose C moles of CH_3COOH are dissolved per litre of solution and let α be the degree of ionization of CH_3COOH , then at equilibrium the concentration of various species would be as follows:

$$[\text{CH}_3\text{COOH}] = C(1 - \alpha)$$

$$[\text{H}_3\text{O}^+] = C\alpha$$

$$[\text{CH}_3\text{COO}^-] = C\alpha$$

$$\text{Therefore, } K_a = \frac{(C\alpha)(C\alpha)}{C(1 - \alpha)} = \frac{C\alpha^2}{(1 - \alpha)}$$

Since for weak acid α is very small as compared to 1, α in the denominator can be neglected. The expression of K_a then becomes

$$K_a = C\alpha^2$$

Knowing the value of K_a it is possible to calculate the degree of ionization of the acid at any particular concentration C .

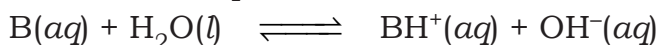
$$\alpha = \sqrt{\frac{K_a}{C}}$$

From the degree of ionization, hydronium ion concentration can be calculated as:

$$[\text{H}_3\text{O}^+] = C\alpha$$

Dissociation Constants of Bases in Water

The **relative strengths of bases** are also compared in terms of their dissociation or ionization constants. The ionization constant K_b for a weak base B can be represented as follows:



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

Smaller the value of ionization constant for a base, weaker is the base.

If C is the molar concentration of base and α is its degree of dissociation, then by similar calculation (as in case of acids) we can derive the relations,

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

and $[OH^-] = C\alpha$.

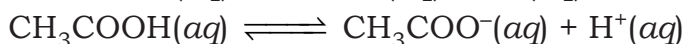
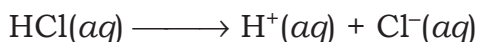
The values of ionization constants for some weak bases are given in Table 3.1.

Table 3.1. The Ionization Constants of Some Bases at 298 K

Base	Ionization Constant, K_b
Ammonia, NH_3	1.8×10^{-5}
Methylamine, CH_3NH_2	4.6×10^{-4}
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}
Trimethylamine, $(CH_3)_3N$	6.5×10^{-5}
Aniline, $C_6H_5NH_2$	4.3×10^{-10}
Pyridine, C_5H_5N	1.8×10^{-9}

Polyprotic Acids and Polyhydroxy Bases

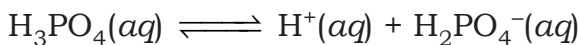
The acids, such as HCl, CH_3COOH , HCN, etc., which have only one ionizable hydrogen are known as **monoprotic acids**.



On the other hand, there are many acids, such as phosphoric acid (H_3PO_4), sulphuric acid (H_2SO_4), oxalic acid ($H_2C_2O_4$), which have more than one ionizable hydrogen atoms. Such acids are known as **polyprotic acids**. Thus:

The acids which have more than one ionizable hydrogen atoms are known as polyprotic acids.

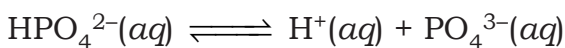
Polyprotic acids are also known as **polybasic acids**. A polybasic acid ionizes stepwise. The stepwise ionization of phosphoric acid, H_3PO_4 is as follows:



$$K_{a_1} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 7.5 \times 10^{-3}$$



$$K_{a_2} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 6.2 \times 10^{-8}$$



$$K_{a_3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 4.2 \times 10^{-13}$$

Here, K_{a_1} , K_{a_2} and K_{a_3} are the first, second and third ionization constants of phosphoric acid respectively. It may be noted that K_{a_1} is greater than K_{a_2} which in turn is greater than K_{a_3} . The reason for this is that it is more difficult to remove a proton (H^+) from a negative ion due to electrostatic forces. For example, it is more difficult to remove a proton from HPO_4^{2-} than from H_2PO_4^- or H_3PO_4 . The ionization constants for some common polyprotic acids are listed in Table 3.2.

Table 3.2. Ionization Constants of Some Common Polyprotic Acids at 298 K

Acid	K_{a_1}	K_{a_2}	K_{a_3}
Carbonic acid	4.3×10^{-7}	5.6×10^{-11}	
Oxalic acid	5.9×10^{-2}	6.4×10^{-5}	
Hydrogen sulphide	1.0×10^{-7}	1×10^{-19}	
Adipic acid	3.7×10^{-5}	3.9×10^{-6}	
Sulphurous acid	1.7×10^{-2}	6.4×10^{-8}	
Sulphuric acid	Strong acid (very large)	1.2×10^{-2}	
Ascorbic acid	7.0×10^{-5}	3.0×10^{-12}	
Phosphoric acid	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Citric acid	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}

Similarly, polyhydroxy or polyacidic bases ionize in steps and have the corresponding dissociation constants such as K_{b_1} , K_{b_2} , etc. For example, $\text{Ba}(\text{OH})_2$ is a diacid base, $\text{Fe}(\text{OH})_3$ is a triacid base. However, these polyhydroxy bases have very less solubility.

Example 3.3: Ionization constant of HF is 3.2×10^{-4} . Calculate the degree of ionization of HF and hydronium ion concentration in 0.02 M solution of HF.

Solutions. $\text{HF}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{F}^-(\text{aq})$
 $(0.02 - x) \text{ M} \qquad \qquad \qquad x \text{ M} \qquad \qquad \qquad x \text{ M}$

$$K_\alpha = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(x)}{(0.02 - x)}$$

$$3.2 \times 10^{-4} = \frac{x^2}{0.02 - x} = \frac{x^2}{0.02} \qquad \qquad \qquad \therefore 0.027x$$

$$x^2 = 3.2 \times 10^{-4} \times 0.02$$

$$x^2 = 6.4 \times 10^{-6}$$

$$x = 6.4 \times 10^{-6}$$

$$x = 2.5 \times 10^{-3} \text{ m}$$

$$\alpha = \frac{2.5 \times 10^{-3}}{0.02} = 0.125$$

3.5. EXPRESSING HYDRONIUM ION CONCENTRATION—pH SCALE

We have seen that concept of ionic product of water enables us to classify solutions as acidic, basic, or neutral by specifying the H_3O^+ ion concentration. For expressing the H_3O^+ ion concentration a logarithmic scale was devised by P.L. Sorensen (1909). This scale is called **pH scale**. The pH of a solution may be defined as negative logarithm of the activity of hydrogen ion (a_{H^+}).

Do You Know?

The symbol pH is derived from *Potenz*, the Danish word for power, pH refers to potency of hydronium ion in solution. The potency of hydroxyl ions of solution is expressed in terms of pOH.

In dilute solutions activity of hydrogen ions is equal in magnitude to the concentration of hydrogen ions in moles per litre *i.e.*, molarity. Activity is a dimensionless quantity and is defined as

$$a_{\text{H}^+} = \frac{[\text{H}^+]}{\text{mol L}^{-1}}$$

From the definition of pH, we can write pH
 $= -\log [\text{H}^+] \quad \text{or} \quad -\log [\text{H}_3\text{O}^+]$

In the present text we shall be using concentration of hydrogen ions or hydronium in place of activity for calculating the pH of solutions. Thus, mathematically, pH may be expressed as

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

From the above relation, the concentration of $[\text{H}^+]$ can be written as

$$[\text{H}^+] = 1 \times 10^{-\text{pH}}$$

This enables us to give alternative definition of pH as the *negative power to which 10 must be raised in order to express the hydrogen ion or hydronium ion concentration of the solution.*

For pure water or neutral solutions, at 298 K, $[\text{H}_3\text{O}^+] = 1 \times 10^{-7} \text{ mol L}^{-1}$. Therefore, pH of such solutions is given as:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [1 \times 10^{-7}] = 7.$$

For acidic solutions, $[\text{H}_3\text{O}^+]$ concentration is more than $1 \times 10^{-7} \text{ mol L}^{-1}$. Therefore, pH of acidic solution is **less than 7**. For basic solutions, the pH value is **greater than 7**. Correspondingly, range of pH is from 0 to 14.

The solutions having pH between 0 and 2 are strongly acidic, those with pH between 2 to 4 are moderately acidic while others having pH between 4 to 7 are weakly acidic. Similarly, the solutions having pH value between 7 to 10 are weakly basic, those having pH 10 to 12 are moderately basic whereas others which have pH range between 12 to 14 are strongly basic.

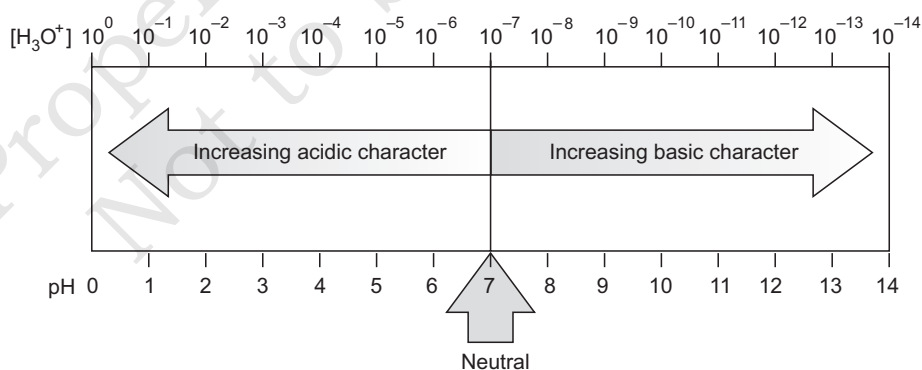
The complete range of $[\text{H}_3\text{O}^+]$ and pH has been illustrated in Fig. 3.4.

The approximate pH of a solution can be determined with the help of **pH papers**. pH papers have different colours in solutions of different pH. A pH paper can determine pH of a solution with an accuracy of about 0.5. However, for accurate measurement of pH (upto accuracy of 0.001 units) **pH metres** are used.

The approximate pH of some common substances are given in Table 3.3.

Table 3.3. The pH of Some Common Substances

<i>Name of the Fluid</i>	<i>pH</i>
Saturated solution of NaOH	~ 15
0.1 M NaOH solution	13
Lime water	10.5
Milk of magnesia	10
Egg white, sea water	7.8
Human blood	7.4
Tears	7.4
Milk	6.8
Human saliva	6.4
Black coffee	5.0
Tomato juice	~ 4.2
Soft drinks and vinegar	~ 3.0
Lemon juice	~ 2.2
Gastric juice	~ 1.2
1 M HCl solution	~ 0
Concentrated HCl	~ -1.0

**Fig. 3.2.** Range of pH and $[H_3O^+]$.

Add to Your Knowledge

- **pOH of the solution**

Like pH, pOH may be defined as the negative logarithm of hydroxyl ion concentration of the solution in moles per litre

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

- **Relationship between pH and pOH of solution**

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}, \text{ at } 25^\circ\text{C}$$

$$\log K_w = \log [\text{H}_3\text{O}^+] + \log [\text{OH}^-] = -14$$

or $-\log K_w = -\log [\text{H}_3\text{O}^+] + (-\log [\text{OH}^-]) = 14$

or $\text{p}K_w = \text{pH} + \text{pOH} = 14$ at 25°C

- As the temperature increases K_w increases and $\text{p}K_w$ decreases. Consequently, pH and pOH of solution also decrease.
- pH of neutral water is < 7 at high temperatures. For example, the pH of neutral water at 37°C , the body temperature, is 6.98.
- It is more appropriate to express the strengths of acids and bases in terms of their $\text{p}K_a$ or $\text{p}K_b$ values

$$\text{p}K_a = -\log K_a; \text{p}K_b = -\log K_b$$

- Lower the value of $\text{p}K_a$, stronger will be the acid.

EXPERIMENT NO. 2

Aim: To measure the pH of a solution using pH paper and universal indicator.

Requirements: Test tubes, measuring cylinders, glass rod, pH paper, universal indicator solution, 0.1 M HCl, 0.01 M HCl, 0.001 M HCl and 0.0001 M HCl.

Procedure: 1. Using pH paper. Put 2–3 drops of sample solution on pH paper by means of a glass rod and observe the colour on pH paper. Now compare the shades of colour formed with various colours given on “pH indicator chart”. Note down the approximate pH of sample colour and record in the table.

2. **Using universal indicator solution.** Take clean and dry test tube. Take 5 ml of each of given solution in different test tubes with the help of measuring cylinder. Put 2–3 drops of universal indicator in each test tube by means of a dropper. Note the colour of solution in each test tube and compare its colour with different colour shades as given in “pH indicator chart” after comparing the colour in each tube, note the pH of solution and record in the table.

3. **Using pH meter.** Take a pH meter, turn it on. Put meter on pH mode. Now place the electrode in the appropriate solution and begin reading. Press the measure button to begin reading pH once your electrode is placed in the solution. Take four readings and record in the table.

Observations:

Sample No.	Molarity of acid sol.	For pH paper		For universal indicator		For pH meter	Calculated pH $-\log (H_3O^+)$
		colour	pH value	colour	pH	pH	
1.							
2.							
3.							
4.							
5.							

Example 3.4: How many grams of NaOH must be dissolved in one litre of the solution to have a solution of pH = 12?

Solution.

$$pH = -\log [H_3O^+] = 12$$

$$\log [H_3O^+] = -12$$

$$\therefore [H_3O^+] = 1 \times 10^{-12} \text{ mol L}^{-1}$$

We know that $K_w = [H_3O^+][OH^-]$

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

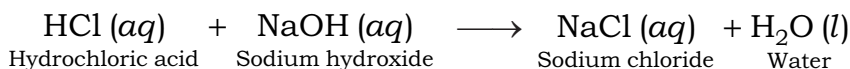
3.6. ACID-BASE PROPERTIES OF SALTS

A **salt** is a compound formed by replacement of either all or a part of the ionisable hydrogen atoms of an acid by some other cation.

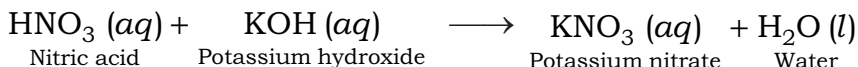
A salt is formed by neutralization of an acid by a base.



For example, sodium chloride (NaCl) is formed by neutralization of hydrochloric acid with sodium hydroxide.



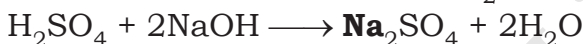
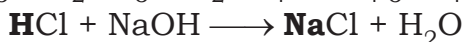
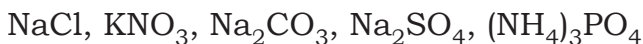
Similarly, potassium nitrate (KNO_3) is formed by neutralization of nitric acid with potassium hydroxide.



Types of Salts

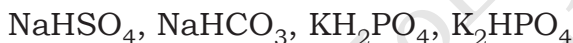
1. **Normal salts** are the salts formed by complete replacement of all the ionisable hydrogen atoms of an acid by metallic or ammonium ions.

Some **examples** of normal salts are:



2. **Acid salts** are the salts formed by partial replacement of ionizable hydrogen atoms by metal or ammonium ions.

For example,



Because there is still some replaceable hydrogen present in this type of salts, these salts behave as an acid as well as a salt and hence are known as **acid salts**.

Acid salts ionize in water to yield hydrogen ions.



3. **Basic salts** are the salt formed by partial replacement of hydroxyl groups of a base by some other anion.

For example,

Basic lead chloride, $\text{Pb}(\text{OH})\text{Cl}$, basic magnesium bromide, $\text{Mg}(\text{OH})\text{Br}$.

Chemicals from Common Salt

Sodium chloride (NaCl) is known as common salt. It is present in sea water along with many other salts. Sodium chloride is separated from these salts. Sodium chloride also exists as solid salt, in the form of rocks, in several parts of the world. The large crystals of sodium chloride obtained from rocks are generally brown in colour due to impurities present in them. This is known as **Rock salt**. Rock salt is mined just like any other mineral. Common salt is an important component of our food. It is also used for the extraction of sodium metal.

The common salt is an important raw material for many materials of daily use. Some of these compounds are : Caustic soda (NaOH), Washing

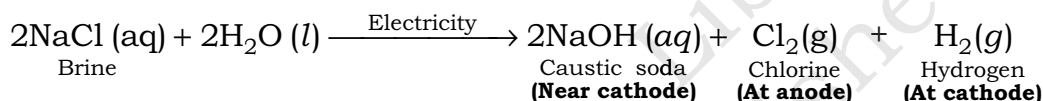
soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), baking soda (NaHCO_3) and bleaching powder (CaOCl_2).

Now let us study preparation and uses of some of these compounds.

Sodium Hydroxide, Caustic Soda (NaOH)

Preparation

Sodium hydroxide is prepared by passing electricity through an aqueous solution of sodium chloride (also known as brine) in a specially designed cell. As a result of electrolysis chlorine gas is given off at anode and hydrogen gas at the cathode. Sodium hydroxide solution is formed near the cathode.



This process is known as **chlor-alkali process** due to the formation of chlorine and sodium hydroxide (an alkali) as the products.

All the three products formed in chlor-alkali process are used for variety of purposes.

For example,

- **Sodium hydroxide** is used in the manufacture of soaps, detergents, paper and artificial silk. It is used for degreasing metals and for purification of bauxite. It is also used in the preparation of many other compounds such as sodium chlorate, sodium hypochlorite, etc.
- **Hydrogen** is used in the manufacture of important compounds such as ammonia, hydrochloric acid, methyl alcohol, etc. It is also used for hydrogenation of oils. Hydrogen is also used as a fuel.
- **Chlorine** is used for disinfection of drinking water and swimming pools. It is used in the preparation of insecticides and pesticides. It is also used in the preparation of many chloro compounds such as CCl_4 , CHCl_3 , sodium chlorate, hydrochloric acid, sodium hypochlorite, etc.

Bleaching Powder, CaOCl_2

Bleaching powder is prepared on industrial scale by passing chlorine gas through dry slaked lime. Chemically it is **calcium oxychloride** and is represented by the formula, **CaOCl_2** .

It is also known as chloride of lime.



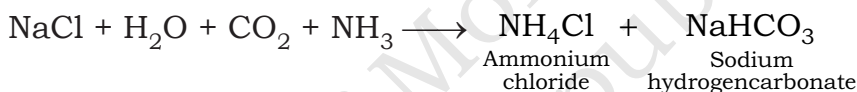
Uses of Bleaching Powder

1. Bleaching powder is chiefly used for bleaching cotton and linen textiles, wood and paper pulp. Delicate articles like silk, wool, straw, etc., are not bleached by it, *as these are likely to be damaged*.
2. It is a strong disinfectant and is therefore, used for sterilization of water.
3. It is employed for making wool unshrinkable.
4. It is also used as an oxidizing agent in the manufacture of many chemicals.

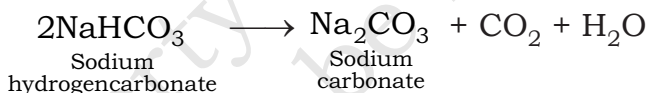
Washing Soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)

Preparation

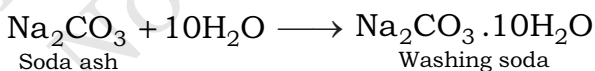
Washing soda is prepared from sodium chloride by **Ammonia-soda process** or **solway process**. In this process carbon dioxide gas is bubbled through a brine solution saturated with ammonia. It results in the formation of sodium hydrogencarbonate.



Sodium hydrogencarbonate so formed precipitates out in the presence of excess of sodium chloride. The precipitated sodium hydrogencarbonate is filtered off and then ignited to get sodium carbonate (Na_2CO_3).



Anhydrous sodium carbonate thus formed is called **soda ash**. When soda ash is dissolved in water and subjected to crystallisation, the crystals that separate out are of sodium carbonate decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) which is also known as **washing soda**.



Uses of Sodium Carbonate

1. Large quantities of sodium carbonate are used in the manufacture of glass, borax, soap and caustic soda.
2. It is used in paper, paints and textile industries.
3. It is used for softening hard water. It removes temporary as well as permanent hardness.

- It is used for washing purposes in laundry.
- As an important laboratory reagent both in qualitative and quantitative analysis.

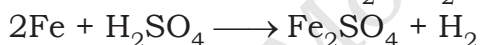
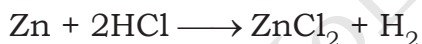
Preparation of Salts in Laboratory

Salts are generally the outcome of neutralization reaction between acids and bases. When an acid react with a base, results in the formation of salts and water. **For example**, hydrochloric acid reacts with sodium hydroxide to form sodium chloride and water.



Salts can be prepared in laboratory by following processes:

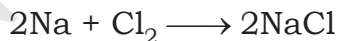
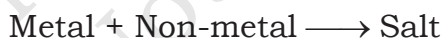
1. **Reaction of active metal with acid:** The metals which are more active than hydrogen as per activity series react with dilute acid solutions to form salt and hydrogen.



2. **Reaction of strong acid and strong base:** Strong acids like HCl, H_2SO_4 , or HNO_3 react with strong base like NaOH, KOH; for corresponding salt and water.

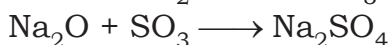
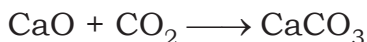


3. **Reaction between a metal and a non-metal:** Metal and a non-metal combine to form a salt. For example: sodium reacts with chlorine gas to form sodium chloride.



Ferrous Sulphide

4. **Reaction between acidic oxide and basic oxide:** Basic oxide like CaO and Na_2O undergo a combination reaction with acidic oxides like CO_2 and SO_3 to form their corresponding salts.



5. **Reaction between metal and a base:** A strong base react with less active metal and form salt and water. When zink is heated with aqueous

solution of NaOH, sodium zincate is formed, sodium zincate (Na_2ZnO_2) is a complex salt.

Manufacturing of Salts in Industries

The common salt NaCl which is used in our kitchens is prepared in industries by various methods.

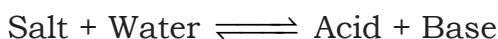
1. **Manufacture from rock salts:** Beds of rocks are mined and rock salt so obtained if of high degree of purity, is grounded, screened and marketed without much processing. The salt is mined in large lumps that are first crushed, then move finely ground and screened by size into various grades. The salt is then bulk loaded into bags and sent to market.

2. **Manufacture of salt from sea water:** Sea water contains common salt NaCl and so many other salts. Sea water is stored in series of shallow ponds. In these ponds solution is concentrated to a specific gravity of about 1.22 which means that it is 1.22 times more dense as a given volume of pure water. Here suspended impurities like sand, clay and less soluble salt such as calcium carbonate or chalk and calcium sulphate are removed. Solar evaporation of dead sea water is increased by adding dye to the water. Dye permits more heat to be absorbed from sunlight in thinner layers of brine so that shallow ponds may be used and penetration of the brine to the ground is reduced.

When concentrated the brine is passed through a series of crystallizing pan when salt is deposited as evaporation proceeds. The specific gravity of salt increases from 1.22 to 1.26 finally. The crystallizing pans are racked in two rows those are allowed to drain for several days. After that salt is collected into heaps, drained again lifted from pans and finally dried. In many countries, the industries the salt is harvested mechanically and washed with saturated brine. It is then dewatered, washed with fresh water and stored for further processing or direct sale.

Hydrolysis of Salts

Hydrolysis may be defined as the process in which water reacts with salt to form an acid and a base.



$$K = \frac{[\text{Acid}] [\text{Base}]}{[\text{Salt}] [\text{Water}]}$$

$$K [\text{Water}] = \frac{[\text{Acid}] [\text{Base}]}{[\text{Salt}]}$$

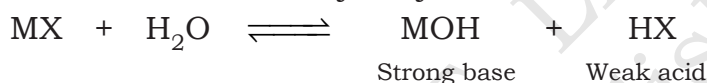
Since [Water] remains practically constant during hydrolysis we can write

$$K_h = \frac{[\text{Acid}][\text{Base}]}{[\text{Salt}]}$$

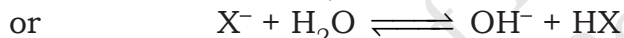
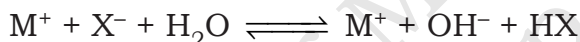
where K_h is the hydrolysis constant of the salt.

The fraction of the total salt that is hydrolysed at equilibrium is called degree or extent of hydrolysis. It is denoted by 'h'.

1. Hydrolysis of Salt of a Weak Acid and a Strong Base. This type of salts includes salts of sodium and potassium except halides, nitrates and sulphates. For example, sodium carbonate, potassium cyanide, sodium acetate, etc. This type of salts produce **alkaline solutions** on hydrolysis. Let us discuss the hydrolysis of a salt MX of this type.



In solution MX and the strong base MOH undergo complete dissociation whereas acid HX being weak acid remains almost undissociated. Therefore, we can write,



Applying law of mass action,

$$K_h = \frac{[\text{OH}^-][\text{HX}]}{[\text{X}^-]}$$

For the dissociation of weak acid, we can write

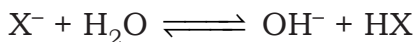


$$K_a = \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}]}$$

Multiplying with K_h

$$\begin{aligned} K_a \times K_h &= \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}]} \cdot \frac{[\text{OH}^-][\text{HX}]}{[\text{X}^-]} \\ &= [\text{H}_3\text{O}^+][\text{OH}^-] \\ &= K_w \end{aligned}$$

$$\therefore K_h = \frac{K_w}{K_a} \quad \dots(3.1)$$

Degree of Hydrolysis

Suppose initial conc. of salt is C and h is the degree of hydrolysis, then

$$[X^-] = C(1 - h), [OH^-] = Ch, [HX] = Ch$$

$$\begin{aligned} K_h &= \frac{[OH^-][HX]}{[X^-]} = \frac{(Ch)(Ch)}{C(1-h)} \\ &= Ch^2 \quad (\because 1-h \approx 1) \\ h &= \sqrt{\frac{K_h}{C}} \quad \dots(3.2) \end{aligned}$$

Thus, degree of hydrolysis of salt of this type is inversely proportional to the square root of conc. of the salt. Substituting the value of K_h from equation (3.1) in equation (3.2)

$$h = \sqrt{\frac{K_w}{K_a \times C}}$$

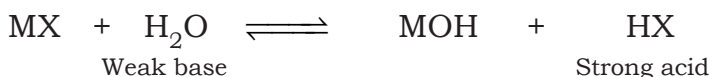
Hydronium ion conc. and pH

$$\begin{aligned} [OH^-] &= Ch = C \sqrt{\frac{K_w}{K_a \times C}} = \sqrt{\frac{K_w \times C}{K_a}} \\ [H_3O^+] &= \frac{K_w}{[OH^-]} = \frac{K_w}{\sqrt{\frac{K_w \times C}{K_a}}} = K_w \sqrt{\frac{K_a}{K_w \times C}} \\ &= \sqrt{\frac{K_w \times K_a}{C}} \end{aligned}$$

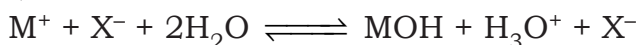
$$pH = \frac{1}{2} (-\log K_w - \log K_a + \log C)$$

$$pH = \frac{1}{2} (pK_w + pK_a + \log C)$$

2. Hydrolysis of Salt of a Strong Acid and a Weak Base. This type of salts includes halides, nitrates and sulphates of all metals except that of sodium and potassium. For example, zinc nitrate, copper sulphate, aluminium sulphate, ferric chloride etc. This type of salts produce **acidic solutions** on hydrolysis. Let us discuss the hydrolysis of a salt MX of this type



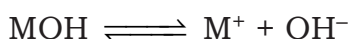
In solution MX and the strong acid HX undergo complete dissociation whereas the weak base MOH remains almost undissociated. Therefore, we can write,



Applying law of mass action

$$K_h = \frac{[MOH][H_3O^+]}{[M^+]}$$

For the dissociation of weak base we can write



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

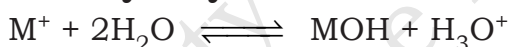
Multiplying with K_h

$$K_b \times K_h = \frac{[M^+][OH^-]}{[MOH]} \cdot \frac{[MOH][H_3O^+]}{[M^+]}$$

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

or
$$K_h = \frac{K_w}{K_b} \quad \dots(3.3)$$

Degree of Hydrolysis



Suppose initial conc. of salt is C and h is the degree of hydrolysis. Then at equilibrium

$$[M^+] = C(1 - h), [H_3O^+] = Ch, [MOH] = Ch$$

$$K_h = \frac{[MOH][H_3O^+]}{[M^+]} = \frac{(Ch)(Ch)}{C(1 - h)} = Ch^2$$

$$(\because 1 - h \approx 1)$$

$$h = \sqrt{\frac{K_h}{C}} \quad \dots(3.4)$$

Thus, degree of hydrolysis of salts of this type increases with dilution (or decrease in conc.). Substituting the value of K_h from equation (3.3) in equation (3.4)

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

Hydronium ion conc. and pH

$$\begin{aligned}
 [\text{H}_3\text{O}^+] &= Ch = C \sqrt{\frac{K_w}{K_b \times C}} \\
 &= \sqrt{\frac{K_w \times C}{K_b}} \\
 -\log [\text{H}_3\text{O}^+] &= \frac{1}{2} [-\log K_w - \log C + \log K_b] \\
 \text{pH} &= \frac{1}{2} [\text{p}K_w - \log C - \text{p}K_b]
 \end{aligned}$$

3.7. BUFFER SOLUTIONS

Generally, pH of the solution changes on addition of small amounts of acids or bases to it. But if the solution contains a weak acid and its conjugate base, or a weak base and its conjugate acids, such a solution can resist change in pH and is called a buffer solution.

A buffer solution is the solution which can resist the change in pH on addition of small amount of acid or base. The ability of buffer solution to resist change in pH on addition of acid or base is called buffer action.

Depending upon pH values, buffer solutions are divided into two classes. If the pH of the buffer solution is *less than 7*, it is called **acidic buffer** and if it is *more than 7*, it is called **basic buffer**.

1. **Strong Acid Buffers:** A strong acid such as nitric acid or hydrochloric acid can act as a buffer with a low pH. Strong acids are completely ionized in aqueous solution and there the concentration of hydrogen ions is high. The addition of a small amount of acid or base to the acid will have negligible effect on the pH of the solution.

2. **Strong Base Buffers:** A strong base such as NaOH, KOH etc., can act as a buffer with a high pH. The addition of small amount of acid or base has negligible effect on pH of solution of such bases. For example, when 1 cm³ of 0.1 M HCl is added to 100 cm³ of 0.01 M NaOH solution, the pH changes from 12.00 to 11.96, which is negligible change.

3. **Weak Acid Buffers:** Buffer solutions with pH range 4 to 7 can be prepared from weak acids and their salts with strong bases. For example, acetic acid and sodium acetate are commonly used for this purpose.

4. **Weak Base Buffers:** Buffer solutions with pH values between 7 and 10 can be prepared from weak bases and their salts with strong acids. For example, a solution containing NH_4OH and NH_4Cl acts as a buffer.

Importance of Buffer Solutions

Buffer solutions play an important role in many industrial processes such as electroplating, manufacture of medicines, dyes, photographic materials, etc. Many biological fluids such as blood, urine, etc., have a definite pH which is maintained by buffer action of many substances. The pH of human blood is maintained between 7.35 and 7.45 by buffer action of carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-) and carbon dioxide (CO_2). The pH values of some biological fluids and other systems are given in Table 3.3.

pH of a Buffer Solution

pH of a buffer solution is calculated by applying **Henderson-Hasselbalch equation**. In order to derive this equation let us consider an acidic buffer consisting of weak acid HA and its salt NaA



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Since HA is weakly dissociated, the concentration of HA in solution can be taken equal to the initial concentration of the acid. Since NaA is completely dissociated, concentration of A^- can be taken equal to the concentration of NaA (salt)

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Salt}]}{[\text{Acid}]}$$

$$[\text{H}_3\text{O}^+] = \frac{K_a [\text{Acid}]}{[\text{Salt}]}$$

Taking the logarithm on both the sides, we get

$$-\log [\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

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

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

From the above equation, it is clear that the pH of an acidic buffer solution consisting of a weak acid and its salt depends on the pK_a of the acid, and the concentrations of the salt and acid in the buffer solution.

A buffer solution containing equimolar concentrations of the salt and acid has $pH = pK_a$.

Similarly, for basic buffers,

$$pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Further, the pH of the basic buffer solution can be calculated from pOH using the relation:

$$pH + pOH = 14$$

or

$$pH = 14 - pOH$$

3.8. ACID-BASE TITRATIONS

An acid-base titration is a method of quantitative analysis for determining the concentration of an acid or base by exactly neutralizing it with a standard solution of acid or base having known concentration. The progress of titration (process of neutralization) is monitored by using pH indicator.

The acid-base titration is useful in case of strong or weak acid or base. Objective of acid-base titration is to know

1. The concentration of acid or base
2. Whether the unknown acid or base is strong or weak.
3. pK_a of unknown acid or pK_b of the unknown base

In titration acid is treated with base and a base is treated with acid. End point of titration is decided by an indicator. Acid-base titration are in use to calculate the amount of known acidic or basic substance through acid base reactions. Hence implies the determination of concentration of solution with respect to water whose pH is 7. A standard solution is added from an apparatus known as burette. The process of adding a standard solution until the reaction is complete is known as titration. All reactions are not titrations. A reaction is a titration if it satisfies following conditions.

- (a) The reaction has to be fast.
- (b) The change in free energy during the reaction must be large enough for spontaneity of reaction.

(c) It should be possible to decide the completion of reaction very clearly.

End point of titration: End point of titration is a stage that shows the completion of reaction. The end point is detected by a physical change that is either produced by solution itself or by addition of a reagent known as **indicator**.

The **end point** or the **equivalence point** reaches when the stoichiometric amount of acid has been added to the alkali solution. At this point all the alkali has been neutralised and the solution contains salt and water only.

From the end point we can find the volume of the base (V_b) having molarity M_b required to neutralize a certain volume of the acid (V_a) of molarity M_a . Now, number of moles in V mL of a solution of molarity M is given by $M \times V/1000$. For the titrations involving monobasic acid and monoacid base, one mole of base is required to completely neutralize one mole of the acid.

Therefore,

$$\frac{M_a V_a}{1000} = \frac{M_b V_b}{1000} \text{ or } M_a V_a = M_b V_b$$

For titration involving polyacid bases and polybasic acids the above equation takes the form

$$n_a M_a V_a = n_b M_b V_b$$

where n_a is the basicity of the acid while n_b is the acidity of the base.

Thus, for the titration of sulphuric acid with sodium hydroxide, the equation applicable is

$$2M_a V_a = M_b V_b$$

Similarly, for the titration of barium hydroxide (a diacid base) against hydrochloric acid (a monobasic acid) the equation becomes

$$M_a V_a = 2M_b V_b$$

The end point is indicated by colour change of the indicator or a sudden rise or fall in pH. The pH of the reaction mixture changes during the course of titration.

The equivalent point: The equivalent point is a stage of titration, where the amount of reagent added is exactly equal to the amount of the reacting substance in the titrated solution.

End point and equivalent point are supposed to be same. But most often they are not identical as the end point is detected only after addition of a slightly excess amount of titrant. If there is a difference between

end point and the equivalent point, then it amounts to an error in the experiment.

Indicator: Acid-base indicators are substances change colour or develop turbidity at a certain pH. This indicates the equivalence point as well as the pH. They are soluble in acid and base and are organic in nature. Phenolphthalein is used to titrate strong acid with strong alkali or weak acid with strong alkali. Phenolphthalein is pink in alkaline medium and colourless in acidic medium. Methylene orange is used to treat strong acid with weak alkali. Methylene orange has yellow colour in alkaline medium and pink or red colour in acidic medium. Phenolphthalein changes colour between 8.3–10 in a pH range hence suitable indicator. Methylene orange changes colour between pH range 2.5–6.5.

Table 3.4. Indicators and their pH ranges

Indicator	Colours		pK_{In}	pH Range
	Acid	Base		
Thymol blue (first change)	Red	Yellow	1.5	1.2 – 2.8
Methyl orange	Red	Yellow	3.7	3.2 – 4.4
Bromocresol green	Yellow	Blue	4.7	3.8 – 5.4
Methyl red	Yellow	Red	5.1	4.8 – 6.0
Bromothymol blue	Yellow	Blue	7.0	6.0 – 7.6
Phenol red	Yellow	Red	7.9	6.3 – 8.4
Thymol blue (second change)	Yellow	Blue	8.9	8.0 – 9.6
Phenolphthalein	Colourless	Pink	9.4	8.2 – 10.0

Titrant or Titrator: Titrant is a standard solution of known strength. During titration it is taken in the burette.

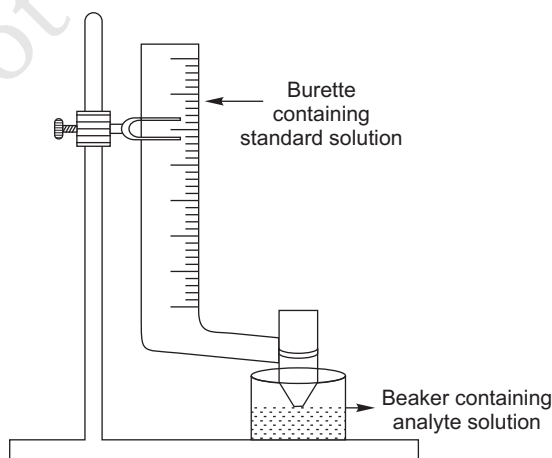


Fig. 3.3

Titrand: Titrand is the sample or the **analyte** whose concentration and volume are unknown. It is the solution to which a titrant reacts.

Titration Volume: Titration volume is the volume of titrant reacted with the titrand.

Acid-base titration are of four types:

1. Strong acid – strong alkali
2. Weak acid – strong alkali
3. Strong acid – weak alkali
4. Weak acid – weak alkali

Titration curves: Titration curve is the plot between volume of titrant dripped into the analyte or titrand versus the pH of analyte solution.

X-cordinate: Volume of titrant added or used during the course of titration is taken on X-cordinate.

Y-cordinate: pH of the analyte solution is taken on Y-cordinate.

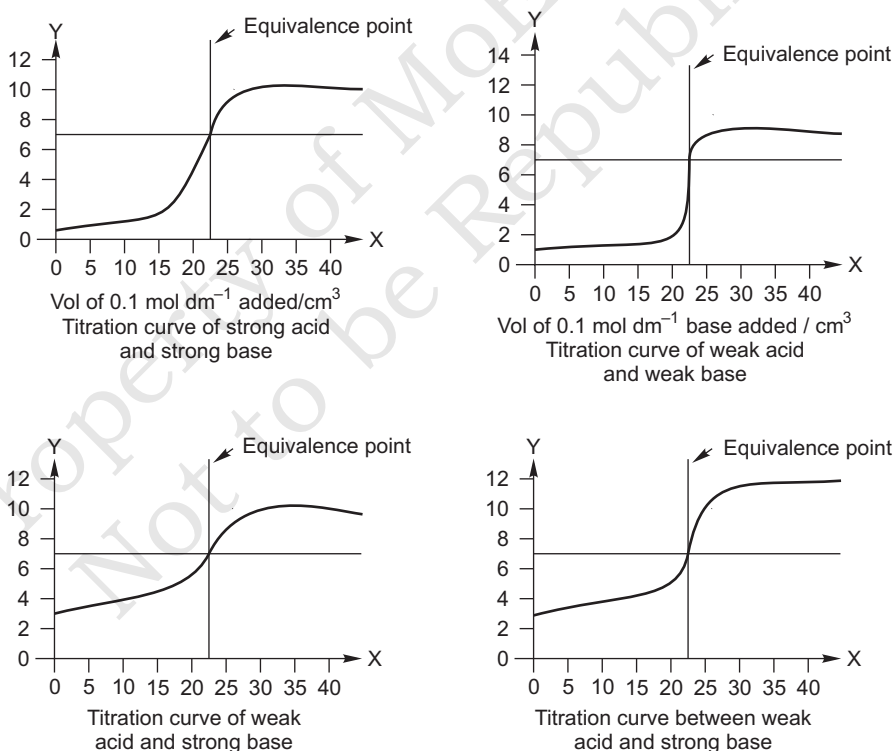


Fig. 3.4

During titration pH of the analyte solution does not change in a regular manner as alkali is added. Horizontal section of curve shows that there is a very small change in pH even if large amount of alkali is added. The

steep portion of each curve shows that even a single drop of alkali can change the pH considerably except in case of weak acid and weak base. At equivalence point there is a large change of pH even though it is not centred on pH7.

SUMMARY

- **Acid.** A substance which furnishes H^+ ions in aqueous solution (*Arrhenius concept*) proton donor (*Bronsted concept*) and acceptor of electron pair (*Lewis concept*).
- **Base.** A substance which gives OH^- ions in aqueous solution, (*Arrhenius concept*); acceptor of proton (*Bronsted concept*) and donor of electron pair (*Lewis concept*).
- **pH of Solution.** Potency of H^+ in solution. It is negative logarithm of H_3O^+ ion concentration in solution.
- **pOH of Solution.** It is negative logarithm of OH^- ion concentration of the solution.

- **Hydrolysis.** It is reverse of neutralisation. It involves the interaction of the ions of electrolyte with H_2O molecules in solution to give acidic or basic solution.

Salts of strong acids and strong bases do not undergo hydrolysis and their aqueous solutions are neutral.

Salts of strong acids with weak bases undergo cationic hydrolysis and give acidic solutions.

Salts of strong bases with weak acids undergo anionic hydrolysis and yield basic aqueous solutions.

Salts of weak acids with weak bases undergo complete hydrolysis and yield almost neutral solutions.

- **Buffer Solution.** A solution which resists the change in its pH value on addition of small amount of acid or a base.

A buffer solution is generally a mixture of weak acid and its conjugate base or weak base and its conjugate acid.

- pH of Buffer solution is given by Henderson-Hasselbalch equation.

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} \quad \dots \text{for acidic buffers}$$

$$pOH = pK_b + \log \frac{[Salt]}{[Base]} \quad \dots \text{for basic buffers}$$

$$pH = pK_a \text{ when } [Salt] = [Acid]$$

$$pOH = pK_b \text{ when } [Salt] = [Base]$$



EVALUATION

I. Multiple Choice Questions

- Which of the following is the strongest base?
(a) Cl^- (b) SO_4^{2-}
(c) CH_3COO^- (d) NO_3^- .
- Which of the following is the weakest base?
(a) OH^- (b) HCOO^-
(c) CH_3O^- (d) Br^- .
- H_2O acts as a base according to
(a) Arrhenius concept only (b) Lewis concept only
(c) Bronsted concept only (d) Lewis as well as Bronsted concept.
- The pH of 0.1 M solution of the following compounds increases in the order:
(a) $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$
(b) $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$
(c) $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$
(d) $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$.
- The pH at the equivalence point of a titration may differ from 7.0 because of:
(a) the self ionization of water
(b) hydrolysis of the salt formed
(c) the indicator used
(d) the concentration of the standard solution.
- Which of the following aqueous solutions will have highest pH?
(a) Sodium acetate (b) Sodium chloride
(c) Ammonium phosphate (d) Calcium chloride.
- Among the following, the weakest Bronsted base is
(a) F^- (b) Cl^-
(c) Br^- (d) I^- .
- Which of the following is least likely to behave as a Lewis base?
(a) OH^- (b) H_2O
(c) NH_3 (d) BF_3 .
- For a buffer solution, which of the following is true?
(a) pH does not change at all on addition of acid or base
(b) pH change is very little on addition of acid or base
(c) It is a mixture of strong acid and its salt
(d) It is a mixture of strong base and its salt.

10. Buffer solutions have constant acidity and alkalinity because:
- acids and alkalies in these solutions are shielded from attack by other ions
 - they have large excess of H^+ or OH^- ions
 - they have fixed value of pH
 - these give unionised acid or base on reaction with added acid or alkali.

II. Descriptive Questions

- Which is more acidic, a solution having a pH of 4 or one having pH of 3?
- State the formula and the name of the conjugate base of each of the following acids:
 - H_3O^+
 - HSO_4^-
 - NH_4^+
 - HF
 - CH_3COOH
 - $CH_3NH_3^+$
 - H_3PO_4
 - $H_2PO_4^-$
- State the formula and name of the conjugate acid of each of the following bases:
 - OH^-
 - HPO_4^{2-}
 - $H_2PO_4^-$
 - CH_3NH_2
 - CO_3^{2-}
 - NH_3
 - CH_3COO^-
 - HS^-
- pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained by diluting the given solution a 100 times?
- Decide whether solutions of the following salts are acidic, basic or neutral
 - Sodium acetate
 - Ammonium acetate
 - Ferric nitrate
 - Sodium carbonate
 - Potassium sulphate.
- Write the conjugate acids for the following Brønsted bases: NH_2^- , NH_3 and $HCOO^-$.
- Classify the following species into Lewis acids and Lewis bases and show how these act as such:
 - HO^-
 - F^-
 - H^+
 - BCl_3