CHAPTER - 7

SOLUTIONS AND ELECTROLYTES

INTRODUCTION

Solutions play an important role in many processes. Nutrients are carried in water solution to all parts of a plant; the body fluids of animals are water solutions of numerous substances. The ocean is a vast water solution containing compounds extracted from the minerals of the earth's crust. Medicines and drugs are frequently aqueous or alcoholic solutions of physiological active compounds.

Definition : *"A solution is a homogeneous mixture or single phase mixture of the molecules, atoms or ions of two or more components"* The component that predominates in the solution is usually referred to as the *solvent*. Since there are three states of matter. There are nine types of solutions: *three gaseous solutions, three liquid solutions*, and *three solid solutions*.

7.1 CONCENTRATION OF SOLUTIONS

Concentrations are either expressed in physical units or chemical units. In the former, concentration is expressed in physical units; for example 20 grams of

NaOH per cubic decimetre (dm^3) of solution; a 10% aqueous solution of NaCl contains 10 g NaCl per 100 g solution i.e. 10 g NaCl mixed with 90 g water. What is of interest here that the concentrations expressed in chemical units are more common and frequently used which are discussed below:

Molar Concentration : *"The molar concentration (M) is the number of moles of the soliue contained in one cubic decimetre (dm^3) or litre of solution"*. For example, a 0.5 molar solution of Na_2CO_3 contains 53g of Na_2CO_3 per cubic decimetre of solution, since 53 is half of the molecular mass of Na_2CO_3, 106. A one molar (1M) solution contains 106 g Na_2CO_3 per dm^3 of solution. The term molarity is often used to refer to molar concentration.

Molal Concentration : *"A molal concentration (m) is the number of moles of the solute per kilogram of solvent.* For example, a molal solution (1 m) of Na_2CO_3 contains 106 g Na_2CO_3 dissolved in 1000 g of water, since 106 is the molar mass of Na_2CO_3. 0.5 molal solution contain 53 g Na_2CO_3 per kg of water. The term molality is often used to refer to molal concentration.

7.2 HYDRATION

Water is a universal solvent and its polar nature plays very important part in dissolving substances. It dissolves ionic compounds readily because of the *hydration* of their ions. A hydrated ion is the ion which is surrounded by water molecules. The clustering of ion with water molecules is due to the attraction of a positive ion for the negative end of water molecule, or of a negative ion for the positive end. In solution, the number of water molecules which surround the ions is indefinite. Very often when a water solution of a salt is evaporated, the salt crystallizes with a precise number of water molecules called water of crystallization. Such crystallized salts contain a definite amount of water of crystallization for example, when magnesium chloride is recrystallized from water, the crystallized salt has the composition $MgCl_2.6H_2O$. That is, each magnesium ion in the crystal is surrounded by six water molecules (Fig: 7.1). It is interesting to note that although hydrated salt like $MgCl_2$ $6H_2O$ has water molecule attached to its crystals, yet it appears dry.

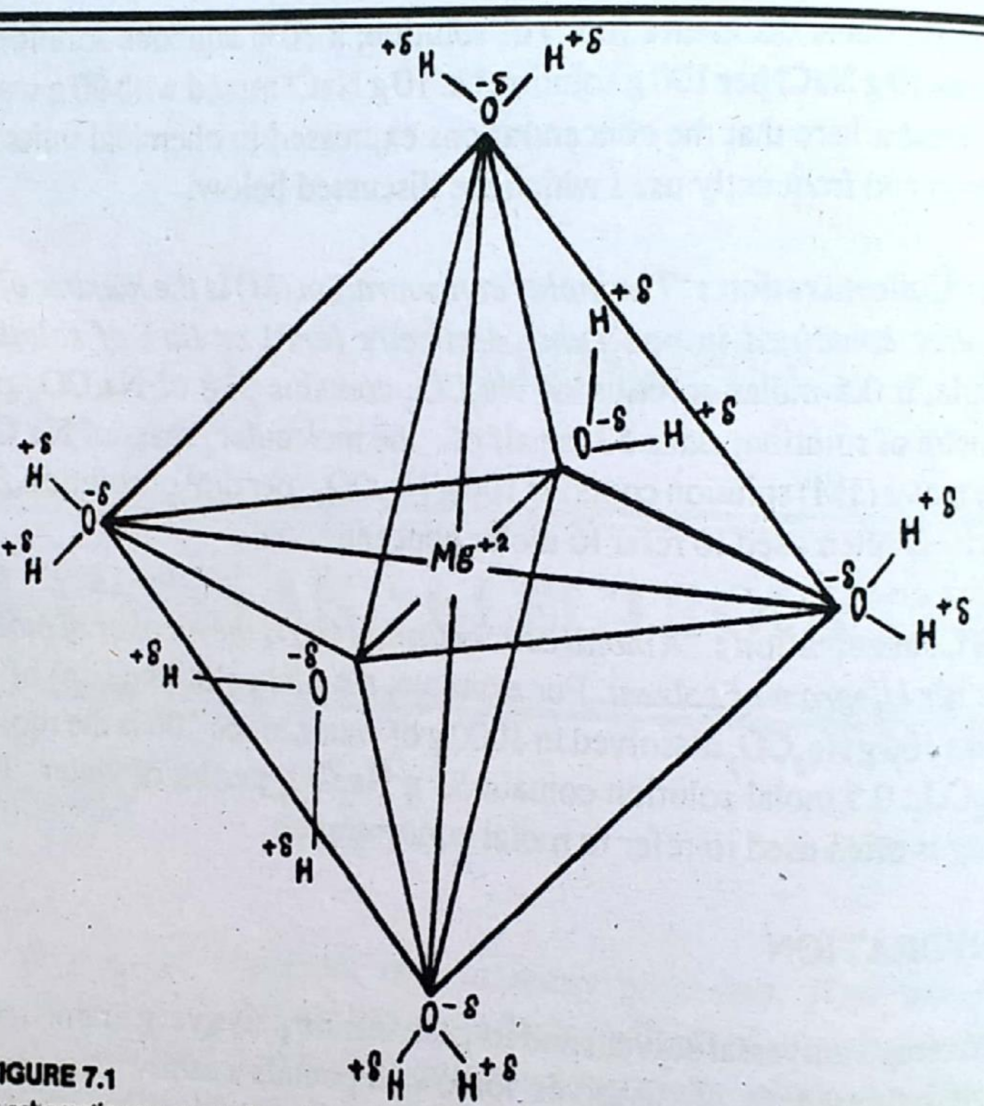

FIGURE 7.1

A schematic representation of the shape of a $[Mg (H_2O)^{2+}_6$ ion, (octahedral). The distance between the metal and oxygen have been exaggerated to show better the special relationship

The ability of an ion to form hydrate depends upon the charge density, that is, size of the ion and its charge. Smaller the size and greater the charge, greater would be the charge density. For example, Al^{+3} has greater charge density than Br because the former is smaller with greater charge than Br^-. Thus small positive ions with multiple charges such as Cu^{2+}, Al^{3+}, Cr^{3+} possess great attraction for water molecules as compared to large negative ions with a single charge such as Br^- or I^-. It is found that usually the water of crystallization is associated with positive ions. For example copper chloride is crystallized with the composition $CuCl_2.4H_2O$, and four water molecules are associated with Cu^{2+} in square planar fashion (Fig. 7.3).

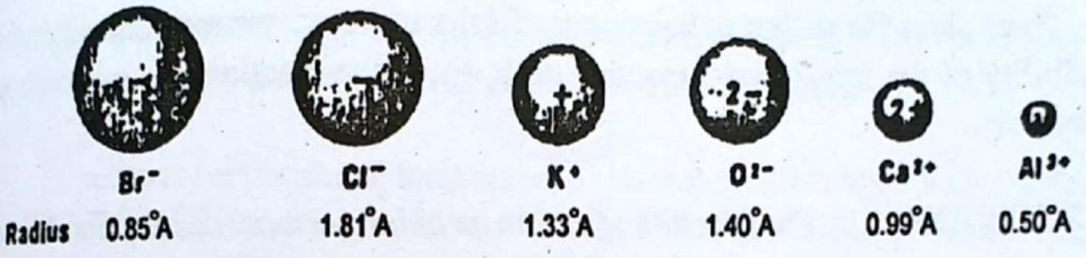

FIGURE 7.2
An arrangement of six ions in the order of their increasing charge density. The large bromide ion with a single charged has the least, the small triply charged aluminium ion the greatest charge density.

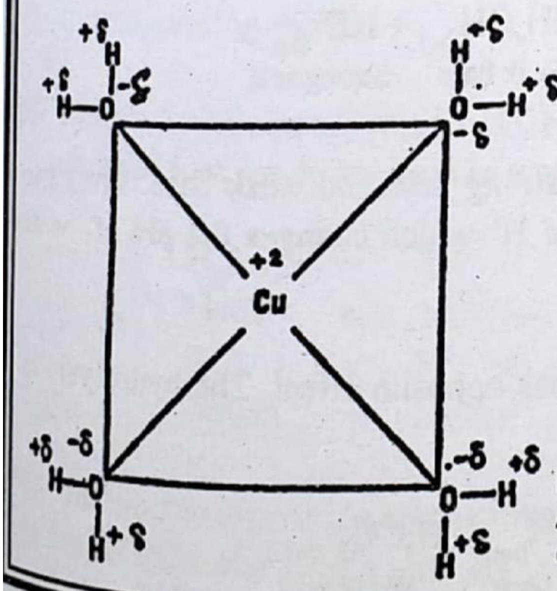

FIGURE 7.3
A Schematic representation of the shape of a $[Cu(H_2O)_4]^{2+}$ ion (square planer).

Many hydrated salts decompose upon heating to give the anhydrous salts.

$$\underset{\text{Pentahydrate}}{CuSO_4.5H_2O_{(s)}} \xrightarrow{\text{Heat}} \underset{\text{Anhydrous salt}}{CuSO_{4(s)}} + 5H_2O_{(g)}\uparrow$$

7.3 HYDROLYSIS

Aqueous solutions of normal salts may be neutral, acidic or alkaline,.

depending on the nature of the salt. For example, an aqueous solution of NH_4Cl is acidic, a Na_2CO_3 solution is alkaline while NaCl solution is neutral.

To explain the different behaviour of salts in water, we must consider the possibility of the ions of salts reacting with water, the reaction being known as hydrolysis.

DEFINITION : *"The reaction of cation or anion (or both) with water so as to change its pH is known as hydrolysis".*

It is interesting here to note that the hydrolysis occurs only when a change in pH takes place. For example, the aqueous solution of NH_4Cl turns blue litmus red because it is acidic in nature:

$$NH_4Cl_{(aq)} + HOH_{(l)} \longrightarrow \underset{\text{Weak base}}{NH_4OH_{(aq)}} + \underset{\text{Strong acid}}{HCl_{(aq)}}$$

In aqueous solution, NH_4Cl forms strong acid and weak base. Thus the solution contains higher concentration of H^+ which changes the pH of water toward acidic.

The aqueous solution of $Na_2\,CO_3$ has opposite effect. The hydrolysis is represented by the following equation:

$$Na_2\,CO_{3(s)} + 2HOH_{(l)} \longrightarrow \underset{\text{Strong base}}{2NaOH_{(aq)}} + \underset{\text{Weak acid}}{H_2CO_{3\,(aq)}}$$

It may be pointed out, the hydrolysis does not occur in case of NaCl because it does not change the pH of water. The aqueous solution of NaCl is, therefore, essentially neutral.

7.4 THEORY OF IONIZATION

The behaviour of the aqueous solutions of electrolytes was found to be quite different than that of non-electrolytes. For example, the electrolytic solutions conduct electricity and the different solutions of acids, bases and salts have different abilities to conduct electricity. Properties like elevation of boiling point, depression of freezing point, osmotic pressure and saturated vapour pressure show marked deviation than similar solutions of the other substances. A relation between the deviation in properties and electrical conductance was also noted. In general, greater the deviation, greater the electrical conductance.

To account for the above facts and to explain the phenomena of electrolysis, the IONIC THEORY was put forward by the Swedish Chemist Svante August Arrhenius about 1880.

(a) The substances called electrolytes are believed to contain electrically charged particles called ions. These charges are positive for H^+ ion or ions derived from metals and negative for the ions derived from non-metals. Number of electrical charges carried by an ion is equal to the valency of corresponding atom.

(b) Molecules of electrolytes (acids, bases and salts) dissociate into oppositely charged ions on dissolution in water, e.g.

$$\begin{aligned} H_2SO_4 &= 2H^+ + SO_4^{2-} \\ NaCl &= Na^+ + Cl^- \\ HCl &= H^+ + Cl^- \\ NaOH &= Na^+ + OH^- \end{aligned}$$

(c) The number of positive and negtive charges on the ions must be equal so that the solution as a whole remains neutral.

(d) In solution, the ions are in state of disorderly motion. Upon colliding they may combine to give unionized molecules. Thus ionization is a reversible process in which the solution contains ions of electrolyte together with unionized molecules.

$$H_2SO_{4(aq)} \rightleftharpoons 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$$

(e) The extent of ionization or to say the degree of ionization depends upon the nature of electrolyte. Strong electrolytes such as NaCl, HCl, etc ionize completely in water. Weak electrolytes such as AgCl, acetic acid (CH_3 COOH) ionize only slightly. For example in 2M solution, only 4 molecules out of 1000 molecules of acetic acid are ionized which mean 996 molecules remain unionized.

(f) Ionization is not affected by electric current. When electric current is passed through an electrolytic solution, the ions begin to migrate towards the opposite electrodes, i.e. positive ions towards negative electrode (cathode) and negative ions towards positive electrode (anode). The ions which are attracted towards cathode are called Cations such as Na^+, H^+ etc., the ions which are attracted towards anode are called Anions, e.g. Cl^-, SO_4^{2-} etc. On reaching the electrodes, the ions lose their charge and change into neutral species (atoms or molecules) by the gain or loss of electrons.

Arrhenius Theory clarified many peculiarities in the behaviour of electrolytic solutions. The presence of ions affords a simple explanation of the deviation in freezing point, boiling point and Osmotic pressure. Since 1 mole of NaCl yields 1 mole of Na^+ (6.02×10^{23} ions) and 1 mole of Cl^- (6.02×10^{23}), the number of these ions is twice that of NaCl. Hence Osmotic pressure must also increase two fold. This is because such properties depend upon the number of particles and not on the nature of compound (colligative properties). However according to the Arrhenius ionic theory, an electrolytic solution is regarded as mechanical mixture of solvent molecules and ions. In no way, it reflected the interaction between these particles. Further development suggested that the ions can interact with water to form *hydrates*. (According to Arrhenius, ions are free to move like isolated atoms).

Despite the good agreement of the electrolytic dissociation theory with facts, it was at first not universally accepted. This was simply due to the concept of atom as being indivisible particle and as such the distinction between atom and ion could not be explained.

(g) The dissociation of electrolyte depends upon (i) nature of electrolyte (ii) degree of dilution (iii) temperature.

(h) The electrical conductivity depends upon (i) the number of ions present in the solution (ii) speed of ions.

7.5 CONDUCTANCE OF ELECTRIC CURRENT THROUGH SOLUTIONS

The existence of ions in solutions of electrolytes was postulated to account for the ability of certain solutions to conduct the electric current. One expects the conductance of an electrolytic solution to vary with (i), dilution (ii), absolute velocities of ions (iii) degree of ionization (iv), temperature (v), pressure etc.

In a concentrated solution, the number of ions per unit volume of solution increases and the distance between ions decreases causing stronger inter ionic attractions. As a result, migration of ions becomes more difficult and the conductance decreases with increase in concentration. As the solution is diluted the inter ionic attraction decreases and the migration of ions becomes easier. As a consequence, the conductance increases with dilution.

As the conduction of electric current is related to the movement of ions, it is obvious that conductance increases with the increase of absolute velocities of ions in solution.

On the basis of electro conductance data, electrolytes are broadly classified into two groups, strong electrolytes and weak electrolytes. The strong electrolytes such as HCl, NaCl etc. show larger conductance which is due to higher degree of ionization ($\propto$)

$$\propto = \frac{\text{Number of dissociated molecules}}{\text{Total molecules dissolved}}$$

Weak electrolytes like CH_3COOH show low conductance due to their low degree of ionization. In both cases, however, conductance increases rapidly with dilution. In fact, the strong electrolytes are almost completely ionized in dilute solutions.

Conductance of an electrolytic solution is also influenced by the temperature. On raising the temperature by 1°C, conductance increases by 2 to 2.5% which is due to reduced hydration of ions and lower viscosity of solutions.

Pressure has no noticeable effect on conductance. Large increase in pressure will cause a considerable fall in conductance. On raising the pressure to 2000 atmospheres, the electro conductance of acetic acid falls to 0.6% of its original value.

Conductance of a solution plays an important part in the industrial application of electrolysis since it determines to a considerable degree the consumptions of energy in the electrolytic process. Electro-conductivity determinations find extensive use in the control laboratory. Thus the salt contents in various solutions on vaporization of water (for example, in boiler water or on condensing milk) is determined from conductivity measurements.

Electrolysis : As described under the ionization theory, a solution of an electrolyte contains oppositely charged ions. When no electric current is passing, the ions are wandering randomly about in the solution. When electric current is passed through the electrolytic solution, movement of the ions towards their opposite electrodes takes place where they are eventually discharged. "The movement of anions and cations towards their respective electrodes accompanying all chemical changes in an electrolytic solution under the influence of electric current is known as electrolytic conduction of electrolysis".

Electrolysis is performed in what is called an electrolytic cell (see figure 7.4). The essential parts of an electrolytic cell are the positive and negative electrodes which are connected to a source of electricity. The positive electrode is termed an anode and the negative electrode is as cathode. Whether the anode is positive or negative depends upon the definition. The definition we will follow is "The anode is the electrode at which oxidation occurs; the cathode is the electrode where reduction occurs". In electrolytic cell as shown in the diagram anode is positive and cathode is negative. However, in electrochemical or galvanic cell such as battery, the anode is negative and the cathode is positive. The electric current flows into and out of the solution via electrodes. Conventially, the current (flow of electrons) enters the cell at cathode and leaves at anode.

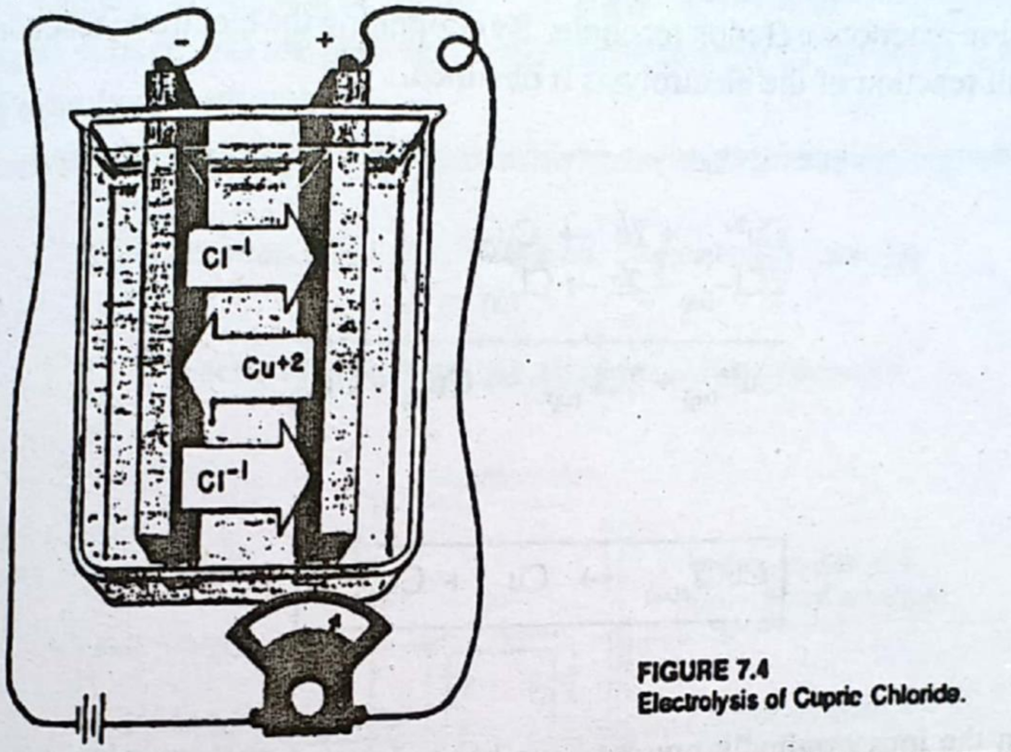

FIGURE 7.4
Electrolysis of Cupric Chloride.

The electrolysis of a moderately concentrated solution of cupric chloride ($CuCl_2$) is illustrated in the fig 7.4. As we are aware of the fact, $CuCl_2$, is composed of ions, it may precisely be represented as Cu^{2+}, Cl^-, Cl^-. On dissolving in water, these ions are separated.

$$CuCl_{2(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

These ions are free to move around randomly among water molecules when no electric current is passing. As soon as the electric current is passed, the movement of these ions begins to take place. Cu^{2+} ions migrate towards cathode and Cl^- ions towards anode. At cathode, Cu^{2+} ions are discharged as copper atoms by the gain of electrons (reduction)

$$Cu^{2+}_{(aq)} + 2e \longrightarrow Cu_{(S)} \text{ ... Reduction at cathode}$$

At anode, Cl^- ions are discharged as Cl_2 gas by the loss of electrons (Oxidation).

$$2Cl^-_{(aq)} - 2e \longrightarrow Cl_{2(g)} \text{ .... Oxidation at anode}$$

Thus the reactions taking place in the electrolytic cell are oxidation - reduction reactions or redox reactions. By combining the electrode reactions, the over all reaction of the electrolysis is obtained.

$$\begin{array}{l} Cu^{2+}_{(aq)} + 2\cancel{e} \rightarrow Cu_{(S)} \\ 2Cl^-_{(aq)} - \cancel{2}e \rightarrow Cl_{2(g)} \\ \hline Cu^{2+}_{(aq)} + 2Cl^-_{(aq)} \rightarrow Cu_{(S)} + Cl_{2(g)} \end{array}$$

$$\boxed{CuCl_{2(aq)} \rightarrow Cu_{(s)} + Cl_{2(g)}}$$

When the ions originally present have been changed to neutral particles, the current can no longer flow.

7.6 ELECTRODE POTENTIAL

The electric current producing appliance known as the Voltaic cell consists of two half cells. In each half cell a metal plate is placed in the solution of its ions.

"The difference of potential created between a metal and solution of its salt is called Electrode potential of the metal". It is the measure of tendency of an electrode to lose (or gain) electrons or to say it serves as a measure of chemical activity during reaction taking place in solution.

Since absolute electrode potential can not be measured, hence it is determined by comparing with the hydrogen electrode which is the reference electrode. Arbitrarily hydrogen electrode has been assigned a potential of 0.000 volts.

A hydrogen electrode consists of a platinum plate immersed in 1 molar solution of sulphuric acid. A current of pure H_2 is passed continuously through the solution under the pressure of 1 atm . (See figure 7.5). The platinum adsorbs H_2 gas on its surface and the platimun coated with hydrogen behaves as if it were made entirely of hydrogen.

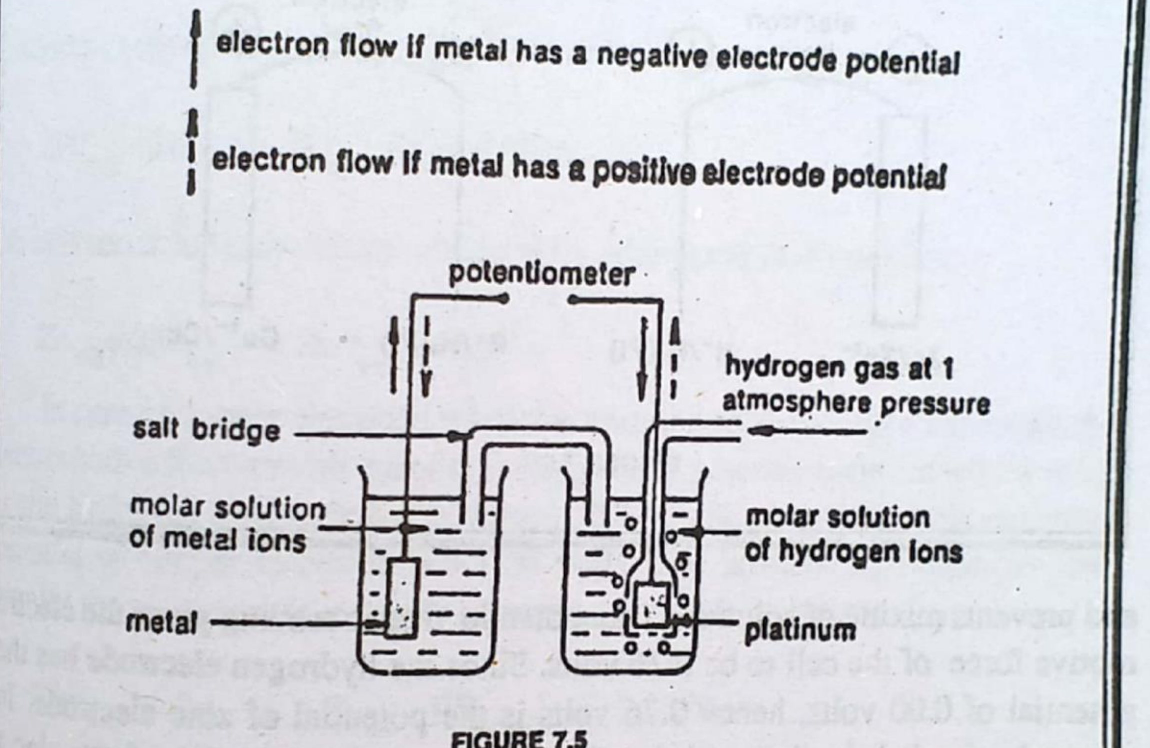

FIGURE 7.5

Since temperature and concentration influence the voltage, these variables are held constant for the comparison. The temperature is held at 25°C, the concentration of ions in contact with elemental electrode is held at 1 molar and the gas pressure at 1 atmosphere. Electrode maintained under these conditions is called standard electrode and its potential as *standard electrode potential*. It is designated as E°. For the purpose of uniformity, since 1953, standard electrode potentials have been expressed in terms of reduction reactions and they are referred to as standard reduction potentials E° Reduction. From these values, standard oxidation potentials are obtained by just reversing their sign.

$$E^{\circ}_{\text{Reduction}} = -E^{\circ}_{\text{oxidation}}$$

To illustrate the method of determining the standard electrode potential, we pick up the example of zinc electrode. For this purpose, we have to construct a voltaic cell made up of zinc (a strip of zinc immersed in IMZnSO$_4$) and hydrogen electrodes. Salt bridge is made of KCl jelly completes the circuit between half cell and prevents mixing of solutions. The potentio metric reading gives the electromotive force of the cell to be 0.76 volts. Since the hydrogen electrode has the potential of 0.00 volts, hence 0.76 volts is the potential of zinc electrode. In external circuit it is observed that flow of electrons takes place from zinc to hydrogen electrode (See fig. 7.6).

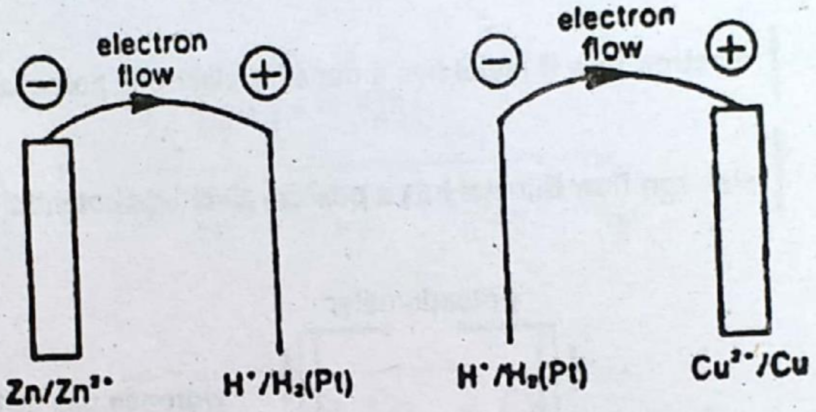

FIGURE 7.6

$$Zn;\ Zn^{2+}_{(aq)}\ (1.0M) \overset{e^-}{\rightarrow}\!\!\! \parallel H^+_{(aq)}\ (1.0M)\ ;\ H_{2(g)}\ (1\ atom);\ Pt.$$

Thus it is believed that electrons must have originated at zinc i.e. it is oxidized, is the anode and is negative with respect to hydrogen electrode. Thus the standard reduction potential of zinc electrode is – 0.76 V.

$$Zn^{2+}_{(aq)} + 2e \rightarrow Zn_{(S)}\ ;\ E^\circ_{Reduction} = -0.76V$$

The standard oxidation potential of zinc is therefore + 0.76 V.

$$E^\circ_{Reduction} = E^\circ_{Oxidation}$$

$$-0.76\ V = +0.76\ V$$

The negative sign signifies that actually the reaction at zinc electrode occurs in the opposite direction, i.e., it is the oxidation rather than reduction which occurs at zinc.

$$Zn_{(S)} - 2e \rightarrow Zn^{2+}_{(aq)}\,;\ E^{\circ}_{Oxidation} = 0.76\ V$$

Reduction takes place at Hydrogen electrode:

$$2H^{+}_{(aq)} + 2e \rightarrow H_{2(g)}\,;\ E^{\circ} = 0.00V$$

The cell reaction is, therefore, obtained by adding the half reaction:

$$Zn_{(S)} + 2H^{+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$$

In case of copper electrode when it is coupled with hydrogen electrode, the electromotive force or voltage of the cell given by potentio meter is +0.34 volts. As the hydrogen electrode has potential of 0.00 volts, therefore, the electrode potential of copper electrode is + 0.34 volts. The positive sign indicates that actually the reduction takes place at copper electrode as written:

$$Cu^{2+}_{(aq)} + 2e \rightarrow Cu_{(s)}\,;\ E^{\circ}_{Reduction} = +0.34\ V$$

From this we predict the oxidation potential to be – 0.34 V

$$E^{\circ}_{Reduction} = -E^{\circ}_{Oxidation}$$

$$+0.34\ V = -0.34\ V$$

In case of copper electrode (a strip of copper immersed in IM Cu SO_4) coupled with hydrogen electrode, the electrons originate at hydrogen electrode i.e. flow of electrons takes place from hydrogen to copper electrode (see fig. 7.6)

$$Cu^{2+}_{(1M)}\quad Cu_{(S)} \underset{||}{\overset{e^{-}}{\leftarrow}} H_2\,(1\ atm)\,;\ 2H^{+}_{(aq)}\,;\ Pt.$$

$$Pt, H_{2(g)}\,;\ H^{+}_{(1M)} \underset{||}{\overset{e^{-}}{\rightarrow}} Cu^{2+}_{(1)}\,;\ Cu_{(s)}$$

Thus copper electrode being cathode, is reduced and is positive with respect to hydrogen as shown above.

Table 7.1 list of more standard reduction potentials at 25°C.

ELECTRODE	HALF-REACTION	E° (V)	ELECTRODE	HALF-REACTION	E°(V)
Li^+/Li	$Li^+ + e^- \rightarrow Li$	-3.05	$Ag(NH_3)_2^+/Ag$	$Ag(NH_3)_2^+ + e \rightarrow Ag + 2NH_3$	$+0.37$
K^+/K	$K^+ + e^- \rightarrow K$	-2.93	O_2/OH^-	$O_2 + 2H_2O + 4e \rightarrow 4OH$	$+0.40$
Ba^{2+}/Ba	$Ba^{2+} + 2e^- \rightarrow Ba$	-2.90	$NiO_2/Ni(OH)_2$	$NiO_2 + 2H_2O + 2e \rightarrow Ni(OH)_2 + 2OH$	$+0.49$
Ca^{2+}/Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87	Cu^+/Cu	$Cu^+ + e^- \rightarrow Cu$	$+0.52$
Na^+/Na	$Na^+ + e^- \rightarrow Na$	-2.71	I_2/I^-	$I_2 + 2e^- \rightarrow 21$	$+0.54$
Mg^{2+}/Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37	O_2/H_2O_2	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	$+0.68$
Al^{3+}/Al	$Al^{3+} + 3e^- \rightarrow Al$	-1.66	Fe^{3+}/Fe^{2+}	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$+0.77$
$Fe(OH)_2/Fe$	$Fe(OH)_2 + 2e^- \rightarrow Fe + 2OH^-$	-0.88	Hg_2^{2+}/Hg	$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	$+0.79$
H_2O/H_2	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83	Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag$	$+0.80$
$Cd(OH)_2/Cd$	$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$	-0.81	$O_2/H_2O(pH7)$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$+0.82$
Zn^{2+}/Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76	Hg^{2+}/Hg	$Hg^{2+} + 2e \rightarrow Hg$	$+0.85$
Cr^{3+}/Cr	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74	NO_3^-/NO	$NO_3^- + 4H^+ + 3e \rightarrow NO + 2H_2O$	$+0.96$
Fe^{2+}/Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44	Br_2/Br^-	$Br_2 + 2e^- \rightarrow 2Br^-$	$+1.07$
H_2O/H_2 (pH 7)	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.42^*	O_2/H_2O	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$+1.23$
Cd^{2+}/Cd	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40	MnO_2/Mn^{2+}	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	$+1.28$
$Ag(CN)_2^-/Ag$	$Ag(CN)_2^- + e^- \rightarrow Ag + 2CN^-$	-0.40	$Cr_2O_7^{2-}/Cr^{3+}$	$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow$	$+1.33$
$PbSO_4/Pb$	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.36		$2Cr^{3+} + 7H_2O$	
Ni^{2+}/Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25	Cl_2/Cl^-	$Cl_2 + 2e^- \rightarrow 2Cl^-$	$+1.36$
Sn^{2+}/Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14	PbO_2/Pb^{2+}	$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	$+1.46$
Pb^{2+}/Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13	MnO_4^-/Mn^{2+}	$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$	$+1.51$
Fe^{3+}/Fe	$Fe^{3+} + 3e^- \rightarrow Fe$	-0.036	$PbO_2/PbSO_4$	$PbO_2^+ + 4H^+ + SO_4^{2-} + 2e^- \rightarrow$	$+1.69$
H^+/H_2	$2H^+ + 2e^- \rightarrow H_2$	0.000		$PbSO_4 + 2H_2O$	
$AgCl/Ag$	$AgCl + e^- \rightarrow Ag + Cl^-$	$+0.22$	H_2O_2/H_2O	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	$+1.78$
Hg_2Cl_2/Hg	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	$+0.27$	$S_2O_8^{2-}/SO_4^{2-}$	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	$+2.00$
Cu^{2+}/Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	$+0.34$	F_2/F^-	$F_2 + 2e^- \rightarrow 2F^-$	$+2.87$

*The potential at pH 7 is not E°

This is known as electro chemical series or E.C.S.

Few important facts about the electrochemical series are summarized as :

(i) Metals above hydrogen in ECS undergoes oxidation in the comparison cell i.e. they are anodes. Metals placed below hydrogen undergoes reduction i.e. they are cathodes.

(ii) Whether or not the electrode reaction will occur spontaneously when electrode is connected to hydrogen electrode can be inferred from the sign of electrode potential. If it is positive, the reaction will occur as written and the electrode will act as anode. If the sign is negative, the reverse reaction will occur and it will be cathode and hydrogen electrode as anode.

(iii) In the ECS, there is decreasing tendency from top to bottom to lose electrons (undergo oxidation) and increasing tendency to gain electrons (undergo reduction). In other words, the reducing strength decreases and the oxidizing strength increases from top to bottom. Thus lithium is the strongest reducing agent and F_2 the strongest oxidizing agent.

(iv) In E.C.S, the metals are placed in the order of reactivity and shows the displacement order. Metals displace metals lying below them in the list from solution of their salts. All metals above hydrogen have negative electrode potentials.

7.7 OXIDATION NUMBER (O.N.)

Definition :

"The formal charge (i.e. not real) on the atom in the compound or ion under consideration is known as oxidation number or state."

In defining the oxidation number, the term 'formal charge' is used which means it is not the actual charge on the atom in a molecule or ion. While using the concept of O.N., all the compounds (including all the covalent compounds) are imagined to be completely ionic, although no compound, is completely ionic. In covalent compounds, therefore, the bonding electrons (that are present in a bond) are considered to be "owned" by the more electronegative atom e.g. in $H:\ddot{\underset{..}{O}}:H$, oxygen is more electronegative than hydrogen, therefore two electrons, one from each hydrogen, are considered to be owned by oxygen giving rise to two negative charges on oxygen. Therefore, oxidation number of oxygen in water would be 2^- Each hydrogen is considered to have lost one electron giving rise to one positive charge on each hydrogen. Therefore, oxidation number of hydrogen would be 1^+.

Guiding rules that have been established to determine the oxidation number of atoms are mentioned below :

1. The oxidation number of all the elements in free state is zero.

$$Br^\circ_2,\ Na^\circ,\ H_2^\circ,\ P^\circ,\ O_2^\circ\ ,\ N^\circ_2$$

2. In a compound, the more electronegative elements are assigned negative oxidation numbers, and the less electronegative elements are assigned the positive oxidation numbers.

$$Cl^{1+}F^{1-},\ H^{1+}Cl^{1-}$$

3. In a neutral species, the sum of oxidation numbers is Zero:

$$^{2+}NO^{2-}\ ,\quad ^{1+}HBr^{1-}\ ,\quad ^{4+}SO_2{}^{(2-)}{}_2$$

4 The oxidation number of oxygen in most of its compounds is 2 .

$$^{2+}SrO^{2-}\ ,\quad ^{(1+)_2}H_2O^{2-}\ ,\quad ^{4+}CO_2{}^{(2-)}{}_2$$

The exceptions are few :

$^{(1+)_2}O\overset{(1-)_2}{F_2}$,
Oxygen is less E.N.

$^{(1-)_2}Na_2O_2{}^{(1-)_2}$,
per oxide
(0-0 bond)

$\overset{1+}{K}O_2{}^{(\frac{1}{2}-)_2}$
super oxide.

5. **The oxidation number of hydrogen when combined with a non-metal is 1^+.**

$\overset{4-}{C}\overset{(1+)_4}{H_4}$, $\overset{3-}{N}\overset{(1+)_3}{H_3}$, $\overset{1+}{H}\overset{1-}{F}$

When combined with a metal of lower E.N, O.N of Hydrogen is 1^-.

${}^{1+}NaH^{1-}$, ${}^{2+}CaH_2{}^{(1-)_2}$, ${}^{1+}KH^{1-}$

This is due to the electronegativity of hydrogen being intermediate between metals and non-metals.

6. **The oxidation number of fluorine in its compounds is always 1^- because it is the most electronegative element and can not form more than one bond.**

${}^{2+}OF_2{}^{(1-)_2}$, ${}^{6+}SF_6{}^{(1-)_6}$, ${}^{1+}ClF^{1-}$

The oxidation number of the other halogens in binary compounds is usually 1^-

$\overset{1+}{K}\overset{1-}{Br}$, $\overset{1+}{Na}\overset{1-}{Cl}$, $\overset{2+}{Mg}\overset{(1-)_2}{Cl_2}$

Few exceptions are there

$\overset{1+}{H}\overset{2-}{O}\overset{1+}{Cl}$, $\overset{1+}{H}\overset{3+}{Cl}\overset{(2-)_2}{O_2}$, $\overset{1+}{H}\overset{5+}{Cl}\overset{(2-)_3}{O_3}$, $\overset{1+}{H}\overset{7+}{Cl}\overset{(2-)_4}{O_4}$

HOCl	HClO$_2$	HClO$_3$	HClO$_4$
Hypochlorous acid	Chlorous acid	Chloric acid	perchloric acid

7. **In polyatomic ions, the sum of the oxidation states of all the atoms present in them equals the ionic charge:**

$\overset{5+}{P}\overset{(2-)_4}{O_4^{3-}}$, $\overset{4+}{C}\overset{(2-)_3}{O_3^{2-}}$, $\overset{6+}{S}\overset{(2-)_4}{O_4^{2-}}$

8. Group I, II and III elements show the oxidation state of 1+, 2 + and 3+ respectively in their compounds:

$$\underset{\text{1 group}}{\underset{\uparrow}{\overset{1+}{\text{K}}\overset{1-}{\text{Cl}}}} \quad , \quad \underset{\text{II group}}{\underset{\uparrow}{\overset{2+}{\text{Ca}}\overset{(1-)_2}{\text{F}_2}}} \quad , \quad \underset{\text{III group}}{\underset{\uparrow}{\overset{3+}{\text{Al}}\overset{(1-)_3}{\text{Br}_3}}}$$

It may be pointed out that the oxidation number is simply an imaginary number and it reflects the extent to which an element has been oxidized or reduced. In an oxidized form of the element, the O.N. is more positive, and in reduced form, it is more negative.

Example 1. Give the oxidation number of tin in $SnCl_2$ and $SnCl_4$.

Solution: Since oxidation number of each chlorine atom is 1^-, hence total negative charge in $SnCl_2$ is 2–. To balance the negative and positive oxidation number, the O.N. of Sn must be 2+.

$$\overset{2+}{\text{Sn}}\overset{(1-)_2}{\text{Cl}_2} \qquad \therefore \quad \text{Sn} = 2+$$

Similarly in $SnCl_4$, the O.N. of Sn = 4+

$$\overset{4+}{\text{Sn}}\overset{(1-)_4}{\text{Cl}_4} \qquad \therefore \quad \text{Sn} = 4+$$

Example 2. Give the oxidation number of Nitrogen in HNO_3.

Solution: In HNO_3, each of the three oxygen has O.N.=2 $^-$, for a total of 6$^-$. Since hydrogen is 1^+, therefore O.N. of Nitrogen is 5^+.

$$\overset{1+}{\text{H}}\overset{5+}{\text{N}}\overset{(2-)_3}{\text{O}_3} \qquad \text{N} = 5+$$

Example 3. Determine the oxidation number of S in SO_3^{2-}

Solution: The total oxidation number of the three oxygen atoms, is 6^-. 2^- is to be left as the charge on the whole ion. Therefore, the oxidation number of sulphur is $4+ \left[\overset{4+}{S}\overset{(2-)_3}{O_3}\right]^{2-}$.

7.8 OXIDATION AND REDUCTION REACTIONS

Definition I : Oxidation is a chemical change in which electrons are lost by an atom or group of atoms, and reduction is a chemical change in which electrons are gained by an atom or group of atoms. Consider the following examples.

$$Fe^{o} \rightarrow Fe^{2+} + 2\bar{e} \quad \text{(Oxidation)}$$

In this reaction neutral iron atom has lost 2 electrons and has changed to ferrous ion, so it is oxidation.

$$Cl_2 + 2e \rightarrow 2\,Cl \qquad \text{(Reduction)}$$

In this reaction, Cl_2 gains two electrons and charges to $C\bar{l}$ ions, it is therefore reduction. These definitions of oxidation and reduction are based on electron transfer.

Definition II : The most comprehensive definitions of oxidation and reduction are in terms of oxidation numbers:

Odixation is a process in which the oxidation number of an element is increased: reduction is a process in which the oxidation number of an element is decreased. For example $C^{o} + O^{o}_2 \rightarrow C^{4+}O_2^{(2-)}{}_2$ is an oxidation of carbon, since its oxidation number increases from zero to 4^+ (Total change of four units).

Similarly, $H_2^{o} + Br^{o}_2 \longrightarrow 2H^{+}Br^{-1}$ is the reduction of bromine as its oxidation number decreases from O to 1–. It may be pointed out that oxidation and reduction occur simultaneously and such reactions are referred to as redox. reactions.

Oxidation number is the concept that is helpful in diagnosing quickly the state of oxidation or reductions of particular atoms in various compounds.

7.9 BALANCING OXIDATION-REDUCTION EQUATIONS (ION-ELECTRON METHOD)

In this method of balancing the redox equations, only those reactants and products are balanced that contain the elements undergoing a change in oxidation state. That is to say, only those reactants and products are balanced which are actually oxidized or reduced. For this purpose it is important to transform molecular equation into ionic equation. Following key points must be kept in mind while writing down an ionic equation:

(a) Ionic substances are written in the ionic form only if the ions are separated from each other in the reaction medium. For example solid NaCl, Na^+ and Cl^- are not written because these ions are held together in its crystal. When present in solution, however, NaCl would be indicated by Na^+ and Cl^-, or either of these ions alone if only the sodium or the chlorine undergoes a change in oxidation state. Insoluble salts such as $BaSO_4$ are always written in the neutral form.

(b) Partially ionized substances are written in the ionic form only if the extent of ionization is appreciable. Thus water which is very little ionized, is written as H_2O. Strong acids such as HCl, HNO_3, are written in the ionized form but weak acids such as nitrous acid, sulphurous acid (HNO_2, H_2SO_3) are always written in the molecular form. Strong bases such as NaOH, KOH may be written in the ionic form as Na^+ and OH^- or K^+ and OH^-. A weak base like NH_3 is written as NH_3.

(c) Complex ions such as ferrocyanide $[Fe(CN)_6]^{4-}$ or ferricyanide, $[Fe(CN)_6]^{3-}$ which are stable and are written as such and never as separate ions like Fe^{3+} and CN^-.

Rules for Balancing by Ion-Electron Method :

1. Write a skeleton equation which includes those reactants and products that contain the elements undergoing a change in oxidation state.
2. Transform the molecular skeleton equation into ionic form. If the given equation is already in the ionic form, then this step is omittted.

3. The ionic equation is split in to two partial equations i.e. the oxidation and reduction equation.

4. Balance each partial equation in terms of atoms. In neutral or acidic medium, H_2O and H^+ are added for balancing oxygen and hydrogen respectively. The oxygen atoms are balanced first.

   In case of basic medium, OH^- and H_2O are added to balance oxygen and hydrogen respectively.

5. Balance the charge in each partial equation by adding electrons to either the left or right side of the equation. It will be found that electrons are added to the left in the partial equation for the reduction equation and to the right in the partial equation for oxidation reaction.

6. Multiply each partial equation by a number so that the electrons in both the partial equations become equal in number.

7. Add the two partial equations after cancelling the electrons. In the sum equation, cancel out any species common to both sides.

Example 1. Balance the oxidation of H_2S with HNO_3 by ion electron method.

Step 1 :- Write the skeleton equation

$$HNO_3 + H_2S \longrightarrow NO + S + H_2O$$

Step 2 :- Transform the molecular equation into ionic form:

$$NO^-_3 + H_2S \longrightarrow NO + S$$

The oxidizing agent is the nitrate ion, NO^-_3, since its Nitrogen changes the oxidation state (undergoes decrease in oxidation state). The reducing agent is H_2S, since sulphur undergoes an increase in oxidation state. It could have been written as sulphide ion (S^{2-}), but H_2S is preferable because of the very slight degree of ionization of the acid in nitric acid solution.

Step 3:- Split the ionic equation into two partial equations (Oxidation, reduction)

$$\overset{5+}{NO_3} \longrightarrow \overset{2+}{NO} \quad \text{...} \quad \text{Reduction (Nitrogen from 5+to 2}^{+}\text{)}$$

$$H_2S^{2-} \longrightarrow S^{o} \quad \text{...} \quad \text{Oxidation (Sulphur from 2}^{-}\text{ to O)}$$

Step 4 :- Balance the partial equations. Since the medium is acidic, oxygen and hydrogen atoms are balanced by adding H_2O and H .

In the first partial equation, 2 H_2O must be added to the right side to balance the oxygen atoms. Then $4H^+$ are added to the left to balance Hydrogen.

$$NO_3^- + 4H^+ \longrightarrow NO + 2H_2O$$

In the second partial equation, $2H^+$ are added to the right to balance tw hydrogen atoms on the left:

$$H_2S \longrightarrow S + 2H^+$$

Step 5 :- Charge is balanced in the partial equations by adding electrons. In th first equation, the net charge on the left is 4+ (1–) = 3 + and on the right it is zer Hence 3 electrons are added to the left side:

$$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$$

In the second equation, the net charge on the right is 2+, hence 2 electro are added to make it zero as on the left:

$$H_2S \longrightarrow S + 2H^+ + 2e^-$$

Step 6 :- In order to equate the electrons lost and gained, first partial equation multiplied by 2 and the second by 3 (cross multiplied):

$$2NO_3^- + 8H^+ + 6e \longrightarrow 2NO + 4H_2O$$

$$3H_2S \longrightarrow 3S + 6H^+ + 6e^-$$

Step 7 :- Cancel out the electrons and add the partial equations:

$$2NO_3^- + 3H_2S + 8H^+ \longrightarrow 2NO + 3S + 4H_2O + 6H^+$$

Since $6H^+$ are common to both sides, hence they are cancelled

$$2NO_3^- + 3H_2S + 2H^+ \longrightarrow 2NO + 3S + 4H_2O \text{ (Balanced)}$$

This equation may be converted back to molecular form by combining NO_3^- and H^+.

$$\underline{\overline{2HNO_3 + 3H_2S \longrightarrow 2NO + 3S + 4H_2O}}$$

This is properly balanced equation.

Example 2: The oxidation of $FeSO_4$ by $KMnO_4$ in acidic solution

Step 1 :- The skeleton equation:

$$KMnO_4 + H_2SO_4 + FeSO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

Step 2 :- Transform into ionic form:

$$MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$$

Step 3 :- Make partial equations :

$$MnO_4^- \longrightarrow Mn^{2+}$$

$$Fe^{2+} \longrightarrow Fe^{3+}$$

Step 4 :- Balance the partial equations :

$$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+}$$

Step 5 :- Balance the charge by adding electrons.

$$MnO_4^- + 8H^+ + 5\bar{e} \longrightarrow Mn^{2+} + 4H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+} + 1\bar{e}$$

Step 6 :- To equate the electrons lost and gained, multiply second equation by 5:

$$\begin{array}{l} MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \\ 5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^- \end{array}$$

Step 7 :- After cancelling electrons, add the two partial equations:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \text{ (Balanced)}$$

To convert back to the molecular form:

$$2KMnO_4 + 10\,FeSO_4 + 8H_2SO_4 \rightarrow 2MnSO_4 + 5\,Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$$

7.10 INDICATORS

The end point of an acid-base titration is often detected by means of an indicator. Indicators are complex molecules that are themselves weak acids or weak bases.

A large number of indicators are known and each undergoes its colour change over a particular pH range. The following table lists some of the common indicators along with their colour change:

Table 7.2 colours of some indicators in acid, base and neutral condition.

Indicator	Colour in acid	Colour in base	Colour when neutral
Litmus	Red	Blue	Purple
Methyl orange	Red	yellow	Orange
Phenolphthalein	Colourless	pink	Colourless
Universal Indicator	Red	Purple	Green

For a strong acid and weak base, methyl orange is often used. For a strong base and weak acid, Phenolphthalein is commonly chosen.

The behaviour of indicators can be explained by the fact that the unionized molecule of an indicator and its anion possess different colours. Alternatively, one may be coloured and the other colourless. The indicator HIn, for instance, dissociates to give its anion In^- as shown by the following equilibrium.

$$\underset{\text{(Red)}}{HIn} \rightleftharpoons \underset{\text{(Yellow)}}{H^+ + In^-}$$

The undissociated molecule HIn, say is red and the anion In^- yellow. It can be seen that the equilibrium position of the indicator will be affected by the hydrogen ion concentration $[H^+]$. If the hydrogen ion concentration, is high, the equilibrium will move to the left and the undissociated HIn will predominate the solution will be red. If a base is added which reduces the hydrogen ion concentration, the equilibrium position will move to the right and the solution will become yellow. When there is equal concentration of HIn and In^-, the indicator will be in its neutral position and it will give mixture of red and yellow and it will appear orange.

7.11 STRENGTH OF ACIDS AND BASES

All the acids and bases, according to the Arrhenius, ionize in aqueous solutions to yield H^+ and OH^- respectively. The extent to which these substances ionize, is however, not same in all the cases. The extent of ionization is expressed in terms of degree of dissociation or percentage dissociation.

The degree of dissociation ($\propto$) is the ratio of the number of molecules ionized to the total number of dissolved molecules.

$$\propto = \frac{\text{Number of molecules dissociated}}{\text{Total number of dissolved molecules.}}$$

This ratio when multiplied by 100 gives the percentage dissociation. For example, the degree of dissociation of HCl is 0.9 – 0.95 and its percentage dissociation is 90–95% i.e. out of every 100 molecule, 90–95 molecules of HCl get ionized in equeous solution. The acids and bases having high percentage dissciations are strong and those with low percentage dissociation are weak. The following table 7.3 lists some strong and weak acids and base alongwith their percentage dissociation.

Table 7.3 Some strong and weak acids

Acids		Bases	
Strong	**Weak**	**Strong**	**Weak**
HCl 90-95%	H_2S 0.1%	$NaOH$ 90-95%	NH_4OH 1.4%
HNO_3 90-95%	CH_3COOH 1.4%	KOH 90-95%	
H_2SO_4 60% (1 stage)	H_2CO_3 0.17%	$Ba(OH)_2$ 77% (1 stage)	

Thus strong acids or bases ionize almost completely and the weak acid or bases ionize partially in aqueous solutions.

According to Bronsted-Lowry theory, an acid is a proton donor and a base is a proton acceptor.

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \bar{A}_{(aq)}$$

The formation of acid-base theory in terms of equilibrium suggests a way of measuring the strength of acids and bases. For the above equilibrium the dissociation constant (Ka) of the acid HA is given by:

$$Ka = \frac{[H_3O^+_{(aq)}][\bar{A}_{(aq)}]}{[HA_{(aq)}]\ [H_2O]}$$

Larger the value of dissociation constant (Ka), stronger is the acid. Same is true for bases. Some typical dissociation constants for acids are given in the following table 7.4

Table 7.4 Some typical dissociation constants for acids

Acid	Ka(mol dm^{-3}) at 298°K.
Hydrocyanic acid	4.8×10^{-10}
Formic acid	1.8×10^{-4}
Acetic acid	1.8×10^{-5}
Chloroacetic acid	1.4×10^{-3}

Thus chloroacetic acid is stronger than formic acid which in turn is stronger than acetic acid.

In term of pH, acids with-low pH values, such as hydrochloric acid, nitric acid and sulphuric acid are strong acids. Similarly bases with high pH values such as solution of potassium hydroxide, sodium hydroxide are strong alkalis. These substances are strong electrolytes and are nearly completely ionized in aqueous solutions. Weak acids and bases have pH value nearer to 7, they are partially ionized in aqueous solution and are weak electrolytes. Example are acetic acid and ammonia solution (NH_4OH).

7.12 pH

The small values of the concentration of hydrogen ion(H^+) that we have encountered with solutions of slightly dissociated acid led Sorensan in 1909 to introduce the conception of pH.

Water acts as an acid as well as a base. For example, if we add NH_3 to H_2O, water acts as a proton donor or acid forming NH^+_4 . It also acts a proton acceptor or base forming H_3O^+, if an acid is added to it :

$$H_2O + \ddot{N}H_3 \longrightarrow NH^+_4 + OH^-$$
$$H_2O + H^{\delta+} - Cl^{\delta-} \longrightarrow H_3O^+ + Cl^-$$

Careful measurements have shown that pure water ionizes slightly to produce ions of H_3O^+ and OH^-. Electrical conductance measurements of water at 25°C has indicated the concentration of 1.0×10^{-7} M each of H^+ and OH^- The ionic product of water is therefore

$$K_w = [H_3^+O]\,[OH^-] = 1.0 \times 10^{-14} M$$

In acidic solution, the concentration of H_3O^+ is always greater than that of OH^- and in basic solutions, the concentration of H_3O^+ is less than that of OH^-

pH is a convenient way of expressing the acidity and basicity of dilute aqueous solutions.

The pH of a solution is the negative. logarithm of the hydrogen ion concentration:

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

Thus for water in which $[H^+] = 1 \times 10^{-7}$,
$pH = -\log (10^{-7}) = (-\log 1.0) + (-\log 10^{-7})$
$= 0.00 + 7.00 = 7.00$

The pH of 7.00 represents the point of neutrality. Clearly acidic solutions will have pH values which are low i.e. less than 7, basic solutions will have pH values which are high i.e. greater than 7.

Table : pH Scale

$[H^+]$	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14} mol dm^{-3}
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

← Acidic ← Neutral → Basic →

Thus acidity is measured on a scale from O (very acidic) to 14 (very alkaline). This is the pH scale. pH scale should be thought of simply as numbers which indicate acidity.

pH of a solution is determined using universal indicator. By mixing together various indicators which change colour at slightly different acidities, chemical manufacturers have developed a universal indicator which goes through a spectrum of colours as the acidity changes. pH numbers are related to universal indicator colours as follows :

Red	Orange	yellow	Green	Blue	Deep blue	Purple
0	3	6	7	8	10	14

pH of a solution can be determined by adding a few drops of universal indicator solution, the reading off the pH number from the corresponding colour. Colour charts are provided by the manufacturer for this purpose.

For more precise measurements, pH meters are available. These are used with a delicate glass electrode which, when dipped into a solution, will give a direct reading of pH on the meter.

Below is given the chart which gives the pH of some common matter:

1.0	1.2	2.9	6.6	7.0	7.3	7.9-8.4	10.5	11.6	13
HCl	H_2SO_4	CH_3COOH	Milk	Distilled water	Blood	Sea Water	Milk of Magnesia	Na_2CO_3	NaOH

← Acidic — **Neutral** — Basic →

Worked Example 1: What is the pH of 0.004 mol dm^{-3} HCl (fully dissociated) at 25°C.

Solution: The fully dissociated HCl has $[H^+] = 4.0 \times 10^{-3}$ mol dm^{-3}, so

$$
\begin{aligned}
pH &= -\log(4.0 \times 10^{-3}) \\
&= (-\log 4.0) + (-\log 10^{-3}) \\
&= -0.60 + 3 = 2.40
\end{aligned}
$$

Worked Example 2: The pH of a solution is 9.63. Compute its hydrogen ion concentration.

Solution: The pure exponential number is $10^{-9.63}$. Converting this number to a mixed number, we have,

$$
\begin{aligned}
10^{-9.63} = 10^{0.63} \times 10^{9} &= 10^{0.37} \times 10^{10} \\
&= 2.34 \times 10^{-10}
\end{aligned}
$$

Therefore the concentration of hydrogen ion in this solution is 2.34×10^{-10} mol dm^{-3}.

7.13 BUFFERS

Normally the pH of a solution does not remain essentially constant: for example the pH of distilled water is 7. This pH of water alters either by absorbing CO_2 from atmosphere (forming H_2CO_3) or by absorbing silicates of glass.

The control of pH in living systems is essential for health. It is found, for instance, that the blood has a pH of about 7.3. The pH remains constant although the concentration of carbon dioxide and hence carbonic acid, varies considerably. If acid is added to a sample of blood its pH is found to change very little unless an excess of acid is added.

A solution which tends to resist changes in pH is called a buffer solution.

Buffer solutions of specified pH values are prepared easily by half neutralizing a solution of a weak acid with a strong base, or a weak base with a strong acid. An example of buffer solution is acetic acid (a weak acid) mixed with sodium acetate (its salt with strong base). Similarly ammonia solution, NH_4OH (a weak base) mixed with ammonium chloride (its salt with strong acid) is another example of buffer solution.

$$CH_3\,COOH_{(aq)} + CH_3\,COO^{-}\ Na^{+}\,(aq) = \text{Buffer solution}$$

$$NH_4OH_{(aq)} + \overset{+}{NH_4}\overset{-}{Cl}_{(aq)} = \text{Buffer solution.}$$

In practice, more sophisticated buffer solutions have been developed for use, particularly in the field of Bio-chemistry. The buffer in blood is the carbonic acid, it self a weak acid, in conjuction with protein molecules. We can illustrate the functioning of a buffer system by the dissociation equilibrium of a weak acid.

$$CH_3\,COOH_{(aq)} \rightleftharpoons CH_3\,COO^{-}_{(aq)} + H^{+}_{(aq)}$$

The buffer also contains the salt sodium acetate which is fully dissociated to furnish acetate ions.

$$CH_3\,CO\bar{O}Na^{+}_{(aq)} \rightleftharpoons CH_3\,COO^{-}_{(aq)} + Na^{+}_{(aq)}$$

Due to the increase in the concentration of acetate ions, the acetic acid equilibrium is pushed to the left there by reducing the H^+ concentration and forming undissociated acetic acid. Thus there is no appreciable change in pH. Even if small amount of acid or alkali are added, there is very little change in pH of the mixture. In case of added acid, the additional H^+ in the solution will combine with CH_3 COO to produce undissociated acetic acid.

$$CH_3\,COO^{-}_{(aq)} + H^{+}_{(aq)} \longrightarrow CH_3COOH_{(aq)}$$

and the pH will remain at about original level.

Small amounts of base (NaOH) added to the buffer solution will be neutralized by reactions with weak acid.

$$OH^{-}_{(aq)} + CH_3\,COOH_{(aq)} \rightleftharpoons H_2O_{(l)} + CH_3\,COO^{-}_{(aq)}$$

7.14 NEUTRALIZATION

When two substances (acid and base) having opposed properties are allowed to react, salt and water are produced. The reaction is known as neutralization.

$$\text{Acid} + \text{Base} \longrightarrow \text{Salt} + \text{Water}$$

For example, Hydrochloric acid is completely neutralized by sodium hydroxide.

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

In this reaction strong acid neutralizes strong alkali. Instead of complete neutralization, there may be partial neutralization; for example sulphuric acid reacts with sodium hydroxide to form sodium hydrogen sulphate:

$$H_2SO_{4(aq)} + NaOH_{(aq)} \longrightarrow NaHSO_{4(aq)} + H_2O_{(aq)}$$

In this reaction, only one hydrogen ion of sulphuric acid is neutralized by sodium hydroxide.

In all these neutralization reactions, hydrogen ion of the acid combines with hydroxide ion of base to form water.

The reaction in which hydrogen ion of acids ard hydroxide ions of alkalis to produce water is known as Neutralization.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

It may be pointed out that the salts formed as a result of complete neutralization are normal and those produced by partial neutralization are either acidic or basic.

NaCl	$NaHSO_4$	Mg(OH)Cl
Normal salt	Acidic salt	Basic salt

PROGRESS TEST 7

1(a) "The ability of an ion depends upon its charge density". Comment on the statement.

(b) What is essential difference between hydration and hydrolisis.

2. What is ionization theory? How does it explain the conductance of electric current through solutions?

3. What is electrolysis? Explain by giving the example of $CuCl_2$. Give all necessary electrode reactions.

4. Write detailed note on Electrode potential. What do you infere from the Electro chemical series?

5.(a) Define oxidation number; oxidation, reduction.
(b) Give the oxidation number of:
(i) Cr in $K_2Cr_2O_7$ (ii) S in $Na_2S_2O_3$ (iii) C in C_2H_6O (iv) Mn in MnO^-_4
(v) N in NCl_3. (vi) O in OF_2

6. Enumerate the rules for balancing the Redox equations by Ion Electron method.

7. Balance the following equations by ion electron method.

(i) $Cr_2O_7^{2-} + \overset{+}{H} + I_2 \longrightarrow Cr^{3+} + I\bar{O}_3 + H_2O$

(ii) $MnO_4^{-1} + SO_3^{2-} + \overset{+}{H} \longrightarrow Mn^{+2} + SO_4^{2-}$

(iii) $Cr(OH)_3 + SO_4^{2-} \longrightarrow CrO_4^{2-} + SO_3^{2-}$ (Basic)

(iv) Oxidation of Cl^{-1} by MnO_4^{-1} in acid solution
($KMnO_4 + KCl + H_2SO_4 \rightarrow MnSO_4 + K_2SO_4 + H_2O + Cl_2$)

(v) $MnO_4^- + SO_3^{2-} + OH^- \rightarrow Mn^{2+} + SO_4^{2-}$

8. What are the indicators? How can you explain their behaviour?

9. Write notes on:
(i) pH (ii) Neutralization (iii) Buffers

10. Define pH? What is pH of 0.1M HCl at 25°C?

11. What are strong and weak acids and bases? Give appropriate examples.