CHAPTER

2

Fundamental Chemistry for Environment

2.0   ATOMIC STRUCTURE

An atom is the smallest particle of an element that can take part in chemical reaction. It cannot be further divided. Atom consists of much smaller fundamental particles—nucleus, proton and electron. **Nucleus** contains all the protons and neutrons. **Protons** ($_1^1P$) are positively charged but the **neutrons** do not carry any charge and having the mass almost equal to ($_0^1n$) that of a proton. **Electrons** are extremely small but negatively charged particles ($_1^0e$.). The atom as a whole is a neutral one, i.e. the atom has equal number of protons and electrons. The electrons revolve around the nucleus. **Atomic number** of an element is defined as the number of unit positive charge on the nucleus.

$$\text{Atomic number} = \text{number of protons}$$
$$\text{or}$$
$$= \text{number of electrons}$$

Mosleys' law states that both physical and chemical properties of an element depend on atomic number only. The elements in the periodic table are arranged in the increasing order of atomic number rather than their mass.

2.0.1   The Quantum Theory of Radiation

Planck's quantum theory of radiation states that a black body emits or absorbs the energy such as light and heat not continuously but in whole number of small packet of energy called a **quantum**. The energy of each quantum is expressed as:

$$E = h\nu$$
$$E = \frac{hC}{\lambda} \quad (\because \ \nu = \frac{C}{\lambda}) \quad\quad\quad …(1)$$

2.1.1   Classification of Elements in the Periodic Table Based on their Electronic Configurations

The elements in the periodic table are divided into four types depending on the nature of the atomic orbital into which the last electron enters. This is called differentiating electron.

s-**Block elements:**   In these elements the last electron enters the *s*-orbital of the outermost shell (ns) which is being progressively filled.

p-**Block elements:**   The elements in which *p*-orbitals are being progressively filled called *p*-block elements.

d-**Block elements:**   In these elements, the differentiating electron enters the $(n-1)$th *d*-orbital of $(n-1)$th main shell are called *d*-block elements. These elements are also called **transition elements**.

f-**Block elements (Inner transition elements):**   In these elements, the differentiating electron enters the $(n-2)$th orbitals of the $(n-2)$th main shell.

2.1.2   Periodic Properties

In the periodic table, there is a gradual increase or decrease in a particular property of an element with the increase of atomic number of the elements in the same period or group. Some important properties are discussed below:

Atomic and Ionic radii

The atomic or ionic radius is usually considered the distance from the centre of the nucleus to the outermost shell electrons of an atomic or ionic particle. The atomic and ionic radii are the function of their atomic number.

   (i) The atomic and ionic radii both decrease with the increase of atomic number in the same period because the electrons are added into the same main energy level.

   (ii) The atomic and ionic radii both increase with the increase of atomic number in the same group (moving down in the graph) as the electrons are added to higher main energy level so that they are further away from the nucleus. But simultaneously nuclear charge also increases to increase the electrostatic force of attraction between nucleus and electrons. But the net result is that the former one predominates.
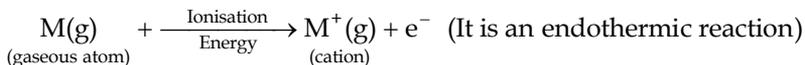
Iso-electronic species are those which have the same number of electrons. In these cases size decreases with increase in atomic number. For example,

   $C^{4-}, N^{3-}, O^{2-} \rightarrow 10$ electrons each—iso-electronic

   size $O^{2-} > N^{3-} > C^{4-}$.
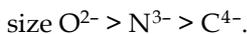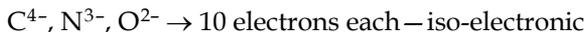
   The size of cation is smaller than of its parent atom while the size of anion is greater than that of its parent atom.

Ionization Potential

Ionization potential is the amount of energy required to remove the outermost electron from an isolated gaseous atom of an element in its lowest energy state to produce a cation.

$$\underset{\text{(gaseous atom)}}{M(g)} + \xrightarrow[\text{Energy}]{\text{Ionisation}} \underset{\text{(cation)}}{M^+(g)} + e^- \quad \text{(It is an endothermic reaction)}$$

The energy required to remove first and second electron known as first and second ionization potential, respectively. The increasing order of ionization potential is

$$I_1 < I_2 < I_3 < I_4 < I_5 < \ ......$$

- The ionization potential increases with the increase in atomic number in the same period because in the same direction size of the atom decreases and nuclear charge increases. The completely and exactly half-filled orbitals have greater ionization potential energy. The decreasing order of ionization potential in the orbitals and period is:
   (i) $s > p > d > f$
    (ii) $Ne > F > O > N > C > B > Be > Li$
- Ionization potential decreases with the increase in atomic number in the group (moving down in a group) as the size of atom increases. Screening effect increases on moving down the group.

    Decreasing order of ionization potential in a group is

    $$Be > Mg > Ca > Sr > Ba.$$

    Screening effect is defined as the decrease in the attractive force exerted by the nucleus on the outermost shell electron due to the presence of the electrons in between the nucleus and outermost shell electrons (Fig. 1).
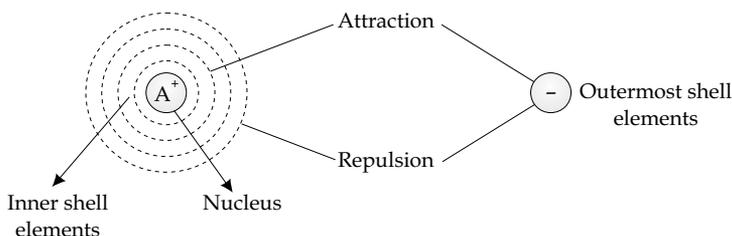

**Fig. 1**   Screening Effect in Atom

- Higher the principal quantum number (*n*) lower is the ionization potential energy. The principal quantum number increases in moving down the group.

Electron Affinity

Electron affinity of an element is defined as the amount of energy released in adding an electron to the outermost shell of an isolated gaseous atom at its ground state to make it an anion. This is an exothermic reaction.

$$Mg + e^- \rightarrow M^- (g) + energy \quad \text{(first electron affinity)}$$
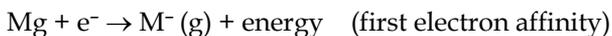
In case of second electron affinity, energy is required to add an electron into the first electron affinity ion.

$$M^- (g) + e^- (g) + \xrightarrow{\text{Energy}} M^{2-} (g) \quad \text{(second electron affinity)}$$
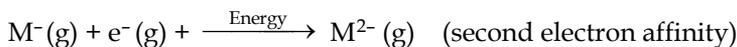
The second electron affinity is an endothermic reaction.

- The electron affinity increases with the increase of atomic number in the same period (moving left to right) as the size of the atom decreases in the same period.
- The electron affinity decreases in moving down the group.

Electronegativity

The electronegativity of a bonded atom is defined as its relative tendency to attract the shared electron pair towards itself. Electronegativity increases in the same period moving left to right and it decreases in moving down in the same group.

- The acidic character of the normal oxides of the elements goes on increasing in the period and it decreases in moving down the group because the higher the electronegativity, the greater is the acidic value and lower is the basic value.
- Higher the electronegative value, lower is the metallic value. Thus, the metallic character decreases and non-metallic character of an element increases in moving from left to right in the same period. Whereas the metallic character increases on moving down the group.

2.2 CHEMICAL BONDING

At ordinary temperatures atoms are rarely capable of free existence. Atoms combine together to form molecules which are more stable and have a lower energy than the individual atom. The attraction between atoms within a molecule is called chemical bond.

The formation of a chemical bond is possible because of the following reasons:

Attainment of a Stable Configuration

The atoms of noble gases do not normally react because of their maximum stability and minimum energy. The atoms of noble gases are having a stable configuration of 8 electrons in the outermost shell called an **Octet**. Only electrons in the outermost shell of an atom are involved in forming bonds, and
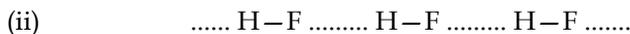
(b) $Mg \rightleftharpoons Mg^{+2} + 2e^-$
        (2, 8, 2)   (2, 8)

$$Mg + :\overset{.}{\underset{..}{Cl}}: \longrightarrow Mg^{+2} (Cl^-) \longrightarrow MgCl_2$$
$$\overset{..}{\underset{..}{.Cl}}: \qquad (Cl^-)$$

Characteristics of Ionic Compounds

The significant features of the ionic compounds are as follows:
   (a) The compounds are the result of electrostatic force of attraction.
   (b) These compounds are polar, so soluble in polar solvents (H_2O, NH_3, etc.) and insoluble in non-polar solvents (C_6H_6, CCl_4, etc.).
   (c) These compounds are ionizable in solution or in fused state.
   (d) The polar linkages are non-directional.
   (e) These are good conductors of electricity.
   (f) They possess high melting points and boiling points.

Conditions for the Formation Ionic Compounds

The three important factors are mainly responsible for the formation of ionic bonds between electropositive and electronegative elements.
   (i) The electropositive elements should have low ionization energy. Ionization potential or ionization energy is the amount of energy required to remove the most loosely bound electron from and isolated gaseous atoms of an element in its ground state.
   Formation of Cation:

$$C(g) + \text{Ionisation energy} \longrightarrow C^+ (g) + e^-$$

   The lower the ionization potential energy the easier is the formation of cation. These are electropositive elements such as alkali metals or alkaline earth metals.
   (ii) The electron affinity of the electronegative atoms should be high. The electron affinity is the amount of energy released when an electron is added to an isolated neutral gaseous atom in its ground state to produce an anion.
   Formation of anion:

$$A \longrightarrow A^-$$
$$Cl(g) + e^- \longrightarrow Cl^- (g) + \text{electron affinity energy}$$

   The greater is the electron affinity value, the easier will be the formation of anion. These are electronegative elements such as halogens or VIIA group elements.
   (iii) The lattice energy of the ionic compound formed should be high.

$$C^+ (g) + A^- (g) \rightarrow CA + \text{lattice energy}$$

atom of a molecule, with an another electronegative atom of some other molecule, e.g.

(i) $\quad\quad\quad$ $-\delta$ $\;+\delta$ $\quad\quad\quad\quad\quad\quad$ $-\delta$ $\;+\delta$

$\quad\quad\quad\quad$ A$-$H $\quad\quad\quad\quad\quad\quad\quad$ B$-$H

Then the existence of hydrogen bond between A$-$H and B$-$H molecules like

$$A-H\ ....\ B-H$$

Here H-atom acts as a bridge between the electronegative atoms A and B.

(ii) $\quad\quad\quad$ ...... H$-$F .... H$-$F .... H$-$F ....

2.3 ACIDS, BASES AND SALTS

According to Lowry and Bronsted (1923) concept of acid base, an acid is defined as a substance which has a tendency to lose proton (H^+) and the base is a substance which has a tendency to gain a proton. Thus, **an acid is a proton donor and a base is a proton acceptor**. For example,

(i) $\quad\quad\quad\quad\quad$ $\left.\begin{array}{l} A \rightleftharpoons H^+ + B \\ HCl \rightleftharpoons H^+ + Cl^- \end{array}\right\}$ Acid

$\quad\quad\quad\quad$ Acid $\rightleftharpoons$ Proton + Conjugate base

(ii) $\quad\quad\quad$ $NH_3 + H^+ \rightleftharpoons NH_4^+$

$\quad\quad\quad$ $HCO_3^- + H^+ \rightleftharpoons H_2CO_3$

$\quad\quad$ Base + Proton $\rightleftharpoons$ Conjugate acid
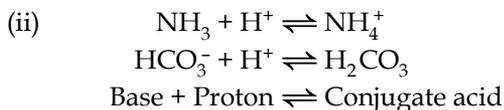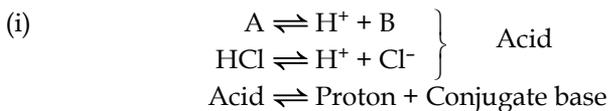
A strong acid reacts with a strong base to produce a weak acid and weak base. But the strong acid and weak base form one conjugate acid-base pair and weak acid and strong base form an another conjugate acid-base pair.

Conjugate Acid-Base Pair

Strong Acid $\;+\;$ Strong Base $\;+\;$ Weak Acid $\;+\;$ Weak Base

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

Conjugate Acid-Base Pair
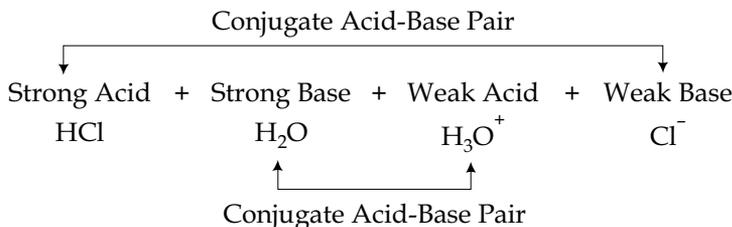
The strong acids and strong bases are considered to be 100% ionized or dissociated in a solvent. An acid is a solute that either by direct dissociation or by reaction with the solvent gives the anionic character to the solvent whereas base is a solute which gives cationic character to the solvent on reaction. For example,

(i) $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

(ii) $HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^-$

(iii) $H_2O + H_2O \rightarrow H_3O^+ + OH^-$
　　　Acid　Base　Acid　Base
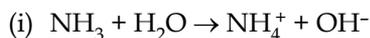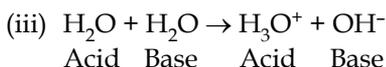
From the equations (i) and (ii) it is evident that water behaves as an acid as well as base. From equation (iii) it is found that all those compounds which produce H_3O^+ ions in H_2O are acids and those produce OH^- ions in H_2O are bases.

In Lewis system, **an acid is an electron pair acceptor and base is an electron pair donor**.

2.3.1 Ionization of Acids and Bases

The strong acids and bases are completely dissociated thus dissociation constant value is very high.

e.g.　　　　　　　　　　$HA \rightleftharpoons H^+ + A^-$

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

In this [HA] is very less or almost negligible, since there will be no undissociated acid in solution. However, the weak acids and bases are partially dissociated, thus equilibrium relationship between the dissociated and undissociated acids or bases existed as:

$$HAc \rightleftharpoons H^+ + Ac^- \quad \text{(weak acid)}$$

$$K_A = \frac{[H^+][Ac^-]}{[HAc]} \quad \text{in terms of concentration}$$

In case of base　　$BOH \rightleftharpoons B^+ + OH^-$

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

In case of polybasic acids there are more than one inosiation stages, thus more than one dissociation constants are obtained, for example,

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_{A1} = \frac{[A^+][HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3{}^{2-} \qquad K_{A2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$
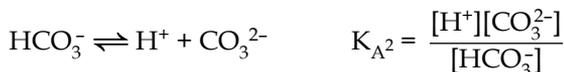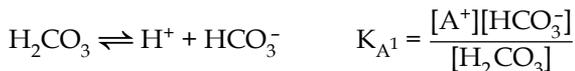
2.3.2 Common Ion Effects

The commonion ion effect states that the presence of a common ion with one of those produced by dissociation will suppress the dissociation reaction i.e. the reaction will move toward reactant side.

$$HAc \rightleftharpoons H^+ + Ac^- \qquad K_A = \frac{[A^+][Ac^-]}{[HAc]}$$

If the solution already contains either {H⁺} or {Ac⁻} ions then dissociation will be less.

2.3.3 Solubility Product

The solubility product of a sparingly soluble salt is the product of ions in the solution. For example,

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$
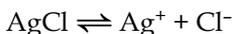
$$L_S = C_{Ag^+} \times C_{Cl^-} \text{ where } L_s = \text{Solubility product.}$$
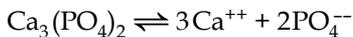
Solubility product of a sparingly soluble salt is constant.

$$Ca_3(PO_4)_2 = 3\,Ca^{++} + 2PO_4^{--}$$

$$L_S = C_{Ca^{++}}^3 \times C_{PO_4^{--}}^2$$

Solubility of a sparingly soluble salt is defined as g moles of the solute present in one liter of solution. It is expressed in g moles per liter.

S represents the solubility.

Then $\quad C_{Ag^+} = S \qquad C_{Cl^-} = S$

$$L_S = S^2 \qquad \text{(Assuming it is completely soluble)}$$

$$Ca_3(PO_4)_2 \rightleftharpoons 3\,Ca^{++} + 2PO_4^{--}$$

$$Ca^{++} = 3S \qquad PO_4^{--} = 2S$$

$$C_{Ca^{++}}^3 C_{PO_4^{--}}^2 = L_S = (3S)^3 \times (2S)^2 = 27S^3 \times 4S^2 = 108S^5$$

2.3.4 Salts

The salts are formed in four different ways and the solutions of these salts are not neutral but depends on how it is formed.

For example,

Salts (ways of formation)	**Solutions** on hydrolysis
Strong acid + weak base	Acidic in nature
Strong base + weak acid	Basic in nature
Weak acid + weak base	Depends on pH value
Strong acid + strong base	No hydrolysis reaction as they are completely dissociated.

pH is defined as the negative logarithm of H⁺ ion concentration.

$$pH = -\log C_{H^+}$$

In pure water (neutral) = $C_{H^+} = C_{OH^-} = 10^{-7}$

pH of neutral water is 7.

pH > 7, the value is basic.

pH < 7, the value is acidic.

pH = 7, the value is neutral.

2.4   THERMODYNAMICS

Thermodynamics concerns itself with the flow of heat and it deals with the relations between heat and mechanical energy (work). It governs not only the transformation of heat into work and *vice versa* but also includes all kinds of inter conversion of one kind of energy into another.

Thermodynamics is based on three empirical laws and nothing contrary to these laws will ever be known. Most of the important laws of physical chemistry, including van't Hoff law of dilute solutions, Raoult's law of vapour pressure lowering, distribution law, law of chemical equilibrium, the phase rule and the laws of thermochemistry can be deduced from the laws of thermodynamics. The laws of thermodynamics cannot be applied to the individual atoms or molecules.

Before we begin with the laws of thermodynamics it is necessary to define some of the terms most commonly used in thermodynamic discussions.

2.4.1   Terminology of Thermodynamics

Work, Heat and Energy

Work, heat and energy are the basic concepts of thermodynamics, and of these concepts the most fundamental is work. Whenever a system changes from one state to another, it is accompanied by energy change. The change in energy may appear in the form of mechanical work, heat, etc. Thus, thermodynamics is concerned with energy changes that accompany a process. A process may be a simple change of state (such as expansion or cooling), a change in physical state (such as melting or freezing), or a complex chemical change in which new substances are produced.

Work: A mechanical work is done whenever the application of a force causes a displacement of a system and the magnitude of the work is measured by the product of the force and the displacement.

Then, $W = F \times \Delta S$, where F is the force and ΔS is the displacement. The usual convention in thermodynamics is that the work done by a system is **positive**, whereas the work done on the system is **negative**.

Heat: Heat is an another form of energy which is different from other forms such as electrical, chemical, etc., because all other forms of energy can be completely transformed into work but heat cannot be wholly converted into work. Any attempt to convert the whole quantity of heat would affect a permanent change in the system or the neighbouring systems. Heat always flows from a region of higher temperature to a region of lower temperature. Hence, heat is energy in transit.

Energy: The energy of a system is its capacity to do work. When the system does work, its energy is reduced because it can do less work than before, so it is negative. But when work done on the system, its capacity to do work is

increased and thus the energy of a system is increased (positive). The process that releases energy as heat is called exothermic and the process that absorbs energy as heat is called endothermic. Energy should, therefore, be defined as a property which can be transformed into or produced from work.

Thermodynamic System

For the purpose of physical chemistry, the universe is divided into two parts, the system and its surrounding. The thermodynamic system may be homogeneous (contains one phase or one kind of matter) or heterogeneous (contains more than one phase, or more kinds of matter).

  (i) **Diathermal walls:** These walls are the boundary walls of a system which allow the transition of heat or matter through them, into or out of the system.

 (ii) **Adiabatic walls:** These walls do not permit any heat or matter to enter into the system or to come out of the system.

(iii) **Isolated system:** The system wholly enclosed by adiabatic walls is called an isolated system.

(iv) **Closed system:** In this system energy exchange with the surrounding is possible but transfer of matter is not permitted.

 (v) **Open system:** In this system exchanging of both matter and energy with the surroundings is possible.

(vi) **Surroundings:** The surroundings are where we make our observations. Surrounding is the rest of the universe around the system. The system and surroundings are separated by a boundary, and to specify these two parts we need to specify the boundary between them, through which matter and energy may be exchanged between the two. Ordinarily, surroundings means water, air, or both.

State of a System

The thermodynamic state of a system is a set of variables such as pressure concentration, temperature, composition, etc., which describe the characteristics possessed by the system. The system in a given state must have definite values assigned to its properties. Thus, when one or more variables undergo change then the system is said to have undergone a change of state. In a homogeneous system, the composition is automatically fixed. The pressure (P), volume (V) and temperature (T) of a system are interrelated with one another in the form of equations of state. If the gas is ideal, it obeys the equation $PV = RT$. Evidently, if only two of these three variables are known, the third one can easily be calculated. The two variables, generally specified, are temperature and pressure. These are called independent variables. The third variable volume is said to be dependent variable.

  (i) **Isothermal process:** When a process is carried out at a constant temperature, it is called an isothermal process.

 (ii) **Adiabatic process:** It is a process in which no heat can enter or leave the system, i.e. it is thermally insulated. In exothermic chemical

system, the temperature of the system may increase and in endothermic chemical system, the temperature of the system may decrease.

(iii) **Isobaric process:**   This process is carried out at constant pressure. In isobaric process, volume change always take place.

(iv) **Isochoric process:**   It is one in which the volume of the system is kept constant.

(v) **Reversible process:**   In an ideally reversible process, that change must occur in successive stages of infinitesimal quantities. The small change should be carried out in such a way that through out the transition, the system must be maintaining virtual thermodynamic equilibrium, at each of the small stages. A process is said to be reversible when the energy change in each step of the process can be reversed in direction by merely a small change in a variable (like temperature, pressure, etc.) acting on a system, i.e. the system may change in the opposite direction back to the initial condition along the same path and the magnitudes of the changes of the thermodynamic quantities in the different stages will be the same as in the forward direction but opposite in sign.

(vi) **Irreversible process:**   Any process which does not take place in the above manner, i.e. a process which does not take place infinitesimally slow, is said to be an irreversible process. Irreversible processes are also called spontaneous processes. Natural processes are, therefore, all irreversible.

2.4.2   Thermodynamic Equilibrium

A system which satisfies all the three (i) thermal equilibrium (ii) mechanical equilibrium and (iii) chemical equilibrium, is said to be in thermodynamic equilibrium.

(i) **Thermal equilibrium:**   A system is said to be in thermal equilibrium if there is no flow of heat from one portion of the system to another, i.e. the temperature at all parts of the system remain same and identical with that of the surroundings.

(ii) **Mechanical equilibrium:**   When there is no unbalanced force existing between different parts of the system or between the system and the surroundings, the system is in mechanical equilibrium.

(iii) **Chemical equilibrium:**   A system is said to be in chemical equilibrium if the composition of the various phases in the system remains the same throughout.

2.4.3   State Function

This is a thermodynamic property which depends only on the state of the system and is independent of the path followed to bring about the change. These properties are like internal energy (ΔE), enthalpy change (ΔH), free energy change (ΔG), entropy change (ΔS), etc.

(i) **Extensive property:** An extensive property of a system is that which depends upon the amount of substance or substances present in the system. For example, mass, volume and energy.

(ii) **Intensive property:** An intensive property of a system is that which is independent of the amount of the substance present in the system. For example, temperature, pressure, viscosity, surface tension, refractive index, specific heat, etc.

(iii) **Internal energy:** Energy system within itself possess a definite quantity of energy called the internal energy or intrinsic energy which is a function of the temperature, pressure, volume and the chemical nature of the substance. In a system of constant composition, the magnitude of internal energy (E) will depend upon the thermodynamic variables (P,V,T), any two of which may be regarded as independent variables.

Thus, $E = f(P,T)$; or $E = f_1 (P,V)$; or $E = f_2 (T,V)$

The internal energy E is a single valued function of the thermodynamic state of the system i.e. whenever the system will be in the thermodynamic state, its internal energy will have the same magnitude.

When a system changes from one thermodynamic state, say A, to another thermodynamic state, say B, its internal energy E will also be changed. Then,

$$\Delta E = E_A - E_B$$

where E_A = internal energy in state A and E_B = internal energy in state B. Thus, internal energy is a state function as it depends only on the initial and final states and not on the path followed between the state, i.e. ΔE independent of the process.

For example, if a system surfers a series of changes so as to come back to the original state, the system is said to have completed a cycle.

Hence, $\qquad\qquad\qquad\qquad\qquad \oint E = 0$

2.4.4 Perfect Differentials

Let $z = \psi (x, y)$, then dz will be a perfect differential when it is found that

(i) z is a single valued function depending entirely on the instaneous values of x and y (or)

(ii) dz between any two specified points or states is independent of the path of transition (or)

(iii) $\oint dz$ for complete cyclic process is equal to zero, or

(iv) $\dfrac{\partial^2 z}{\partial x\, \partial y} = \dfrac{\partial^2 z}{\partial y\, \partial x}$, i.e. the second differentials of z with respect to x and y

carried out in either order become equal to one another.

For example $\partial E, \partial S$, etc. are perfect differentials.

2.4.5 First Law of Thermodynamics

The first law of thermodynamics originates from the relation between heat and work. It has been found that the heat and work are equivalent ways of changing a system's internal energy, i.e. if or whenever, heat is obtained from work the amount of heat produced is proportional to the work spent, or conversely, if heat is transformed into work there is a proportionality between the work obtained and the heat disappeared.

From a number of experimental observation, Helmholtz, Clausius and Kelvin enunciated a generalised law of nature known as the conservation of energy which may be called as first law of thermodynamics. Let 'w' for the work done on a system, 'q' for the energy transferred as heat to a system, and ΔE for the resulting change in internal energy, then from the first law of thermodynamics, i.e. laws of conservation of energy

$$\Delta E = q - w \qquad \qquad ...(1)$$

Work done by the system is taken as positive, while work done on the system is taken as negative. Similarly, the increase in the internal energy of a system is regarded as positive and decrease in the internal energy of a systen is regarded as negative.

For an infinitesimally small change, i.e. in the differential form

$$\partial E = \partial q - \partial w \qquad \qquad ...(2)$$

From this equation some observations can be made for different systems or processes as

(i) **In a cyclic process:** It is already stated that in a cyclic process where the initial and final states are identical, the change of internal energy in this process

$$\Delta E = 0$$

i.e. $\qquad \qquad E_A = E_B$

Where E_A is the internal energy in state A and E_B is the internal energy in state B. Then,

$$\Delta E = q - w = 0 \quad \text{(or)} \quad \oint dE = 0$$

or $\qquad \qquad \oint dq = \oint \partial E + \oint \partial w \quad$ substituting $\oint dE$ value

we get, $\qquad \oint \partial q = \oint \partial w \qquad \qquad ...(3)$

From this equation it is evident that the work done is equal to the heat absorbed in a cyclic process.

(ii) **In isolated system:** In this system there is no heat exchange with surroundings, i.e.

$$\partial q = 0$$

Now $\qquad \qquad \partial E = \partial q - \partial w$

so, $\qquad\qquad \partial E = \partial w$ ...(4)

That is the internal energy of the system is measured by that amount of work done by or on the system.

(iii) In non-isolated system: Internal energy for the system

$$\partial E = \partial q - \partial w$$ ...(5)

For the sourroundings only

$$\partial E^1 = \partial w - \partial q$$ ...(6)

Because, it loses energy ∂q to gain ∂w units of work. Then the net change in the internal energies of the system and surroundings, will be zero i.e.,

$$\partial E = \partial E^1$$

$$\partial E + \partial E^1 = 0$$ ...(7)

2.4.6 Enthalpy

Suppose that the change of a system from state A to B is brought about at constant pressure (P). Let the volume increases form V_A to V_B, then the work done (w) by the system will be

$$W = P(V_B - V_A)$$

$$\Delta E = q - W \qquad \text{(Substituting the value of W)}$$

Then, $\qquad\qquad \Delta E = q - P(V_B - V_A)$

or $\qquad\qquad E_B - E_A = q - P(V_B - V_A)$

or $\qquad\qquad (E_B + PV_B) - (E_A + PV_A) = q$ ...(1)

Then, sum of the two energy terms (E + PV) associated with the system is called enthalpy or heat content of the system, which is denoted as H. It represents the total energy of the system.

Thus, $\qquad\qquad H = E + PV$ ...(2)

From equation (1) $\qquad H_B - H_A = q = \Delta H$

In the differential form

$$\partial H = \partial E + P\partial V + V\partial P$$

Since the system undergoes a change at constant pressure

Then $\qquad\qquad \partial H_P = \partial E_P + P\partial V_P$ ...(3)

Since E depends only on the state of the system and P and V themselves specify the state, then enthalpy depends only on the state, i.e. independent of the path.

From the first law of Thermodynamics

$$\partial Q = \partial E + \partial W \;; \qquad \partial W_P = P\partial V_P$$

At constant volume, there will be no mechanical work

Then $\qquad \partial Q_P = \partial E_P + \partial W_P = \partial E_P + P\partial V_P$ ...(4)

Comparing the equations (2) and (3), we get

$$\partial H_P = \partial Q_P \qquad ...(5)$$

That is, at a constant pressure the increase in enthalpy of a system during a given transformation is equal to the heat absorbed.

At constant volume $\partial V = 0$, then

$$\partial H = \partial E = P\partial V \quad so$$
$$\partial H = \partial E \qquad ...(6)$$

That means enthalpy change is equal to the change in internal energy at constant volume.

2.4.7 Thermochemistry

Most of the chemical reactions are invariably accompanied by energy changes. The study of the heat produced or required by chemical reactions is called thermochemistry. A chemical reaction is said to be exothermic if it is accompanied by evolution of heat and endothermic if it is accompanied by absorption of heat.

The amount of heat evolved or absorbed in a chemical reaction is called the heat of reaction, and the quantities depend in the way the change is carried out, i.e. on the path.

In fact, the reactions are studied usually under two specified conditions either at constant pressure or at constant volume. Heat changes at constant pressure or at constant volume of a reactions are represented as Q_P and Q_V, respectively. We know that,

$$Q_P = \Delta H_P = H_{resultant} - H_{reactant}$$

Assuming work is performed in the process

$$Q_P = \Delta H_P = \Delta E_P + P\Delta V$$

At constant volume

$$Q_V = \Delta E_V$$

Then, $\qquad Q_P - Q_V = \Delta E_P - \Delta E_V + P\Delta V$

Compared to the large heat in other than ideal one, ΔE_P and ΔE_V differ very little extent, thus, $\Delta E_P = \Delta E_V$

Therefore, $\qquad Q_P - Q_V = P\Delta V$

or $\qquad\qquad\qquad Q_P = Q_V + P\Delta V$ ...(1)

$$P\Delta V = \Delta nRT \quad then \quad Q_P = Q_V + \Delta nRT \qquad ...(2)$$

Where Δn is the increase in the number of moles in the chemical reaction. Or it can be represented as

$$\Delta H_P = \Delta E_V + \Delta nRT \qquad ...(3)$$

2.4.8　Second Law of Thermodynamics

The first law establishes definite relationship between the heat absorbed and work performed by a system in a given process. But the first law does not indicate the following points.

- (i) It does not indicate whether the change would occur at all, i.e. whether a specific change or a process including chemical reaction can occur spontaneously.
- (ii) If the change occurs then upto what extent.
- (iii) Also, it does not tell the direction in which the process of transformation would take place.

    The second law of thermodynamics helps us in determining the direction and the extent of change. It will also give us the conditions under which the changes would occur. Therefore, the second law of thermodynamics can be discussed on the following three heads.

Direction of Change

Changes taking place in a system without the external aid are termed as spontaneous processes.

- (i) All spontaneous processes are irreversible and all spontaneous processes tend to equilibrium.
- (ii) Heat will not flow from a lower temperature body to a higher temperature body.

    Thus, the second law can be formulated on account of direction of change as it is impossible for a self-acting machine, unaided by any external agency, to convey heat from a body at a low temperature to one at a high temperature.

Conditions for Change

Generally, there are two conditions under which the heat changes into the direction of work.

- (i) Without the aid of an external agency (Engine) the conversion of heat into work is impossible. The engine must work in a reversible cyclic process.
- (ii) The engine must operate between two temperatures (higher and lower). Hence, under isothermal conditions no engine can convert heat into work. That is why we cannot run our vehicles **with the heat of surrounding air**.

    Thus, the second law account of conditions for change. It is impossible by an external aid (engine), to derive mechanical effect (work) from any portion of matter by cooling it below the temperature of the cooldest of the surroundings.

Extent of Change

Complete conversion of heat into work is impossible without leaving a permanent change elsewhere. Therefore, the second law states that "Only a fraction of a given quantity of heat may be converted into work, when it is allowed to flow from a body at higher temperature to a lower temperature one i.e. the engine would pick-up Q calories from the source (higher temperature), transform only a portion of it into work (W) and return the rest of the heat Q^1 to the sink (lower temperature)". Then,

$$W = Q - Q^1$$

Then the efficiency of the engine as

$$\eta = \frac{\text{Work produced}}{\text{Heat supplied}}$$

$$\eta = \frac{W}{Q} = \frac{Q - Q^1}{Q}$$

$$\eta = 1 - \frac{Q^1}{Q}$$

2.4.9 Entropy

The second law uses the entropy to identify the spontaneous changes among permissible changes. Entropy of a system is a measure of randomness or disorder of the system and is denoted by the symbol 'S'. The thermodynamic definition of entropy derives as the change in entropy 'ds' that occurs as a result of a physical or chemical change. Thus, it is defined as the heat change 'dq' and the temperature 'T' are thermodynamic quantities and this thermodynamic function whose change is measured by (dq/T) is independent of path.

$$\Delta S = S_{final} - S_{initial}$$

The entropy change 'ds' is measured by the ratio of the heat change and the temperature at which the heat change occurs i.e.

$$ds = \frac{dq_{rev}}{T}$$

At different temperatures, then

$$ds = \frac{dq_1}{T_1} + \frac{dq_2}{T_2} + \frac{dq_3}{T_3} + \ldots$$
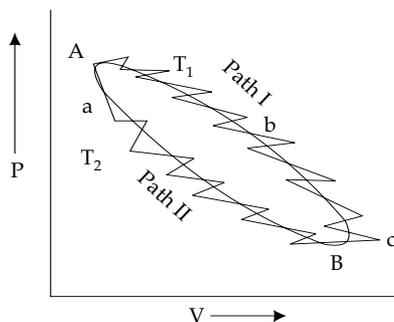
$$\int dS = \int \frac{dq_{rev}}{T}$$

Then we can state that,

(a) Entropy 'S' is a thermodynamic function whose magnitude depends only on the temperatures of the system and can be expressed in terms of P, V, T.

(b) The entropy change 'ds' is a perfect differential. Its value depends only on the initial and final states of the system, independent of the path of the change. The entropy change is measured by the reversible heat change of the system divided by the temperature in absolute state i.e.

$$ds = \frac{dq}{T}$$

(c) Absorption of heat increases the entropy of a system. The rejections of heat by the system leads to a decrease in its entropy. During adiabatic changes (dq = 0) the entropy change is zero. Thus, the adiabatic changes are called isoentropic changes.

Entropy Change in a Reversible Cycle: Let us take a system which undergoes a reversible change in isothermal and adiabatic process, Fig. 2.

Fig. 2 Entroy change in a reversible cycle

Giving positive sign to the heat absorbed (q_2) and negative sign to the heat lost (q_1) by the system, the equation from Carnot cycle $\frac{q_1}{T_1} = \frac{q_2}{T_2}$ can be written as

$$\frac{q_2}{T_2} = -\frac{q_1}{T_1}$$

or

$$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

or
$$\frac{dq_2}{T_2} + \frac{dq_1}{T_1} = 0$$

For other Carnot cycle also $\dfrac{dq_2^1}{T_2} + \dfrac{dq_1^1}{T_1} = 0$

It follows that in Fig. 2 the path ABA comprising a series of Carnot cycles then,

$$\sum \frac{dq}{T} = 0$$

or
$$\int \frac{dq}{T} = 0$$

or
$$\oint ds = 0$$

Hence, in any reversible cyclic process, the net increase in entropy of the system is zero.

2.5   PHASE RULE

The phase rule is a relation between the number of components (C), the number of phases (P), and the variable parameter (F) of a heterogeneous system in equilibrium for a system of any composition. It is expressed as

$$F = C - P + 2 \qquad \qquad ...(1)$$

It is necessary to define appropriately, the terms which are frequently used, namely, Phases, Components and Degrees of Freedom.

Phase: A phase is defined as a physically distinct but homogeneous part of a system separated from other parts by boundary surfaces and is mechanically separable from other parts of a system. A gas or a gaseous mixture is a single phase, a crystal is a single phase, and two completely miscible liquids form a single phase. A system consisting of one phase only is said to be **homogeneous**.

Similarly, the vapours in contact with the solution are two distinct phases, a mixture of two immiscible liquids, e.g. water and benzene will form two distinct phases. Every solid constitutes a separate phase unless a solid solution is formed. So, when calcium carbonate dissociates into calcium oxide and carbon dioxide, there are two solid phases ($CaCO_3$ and CaO) and one gas phase (CO_2).

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

Thus, it is a three-phase heterogeneous system. Two distinct liquid phases with the vapour phase will also form three-phase system. Thus, a heterogeneous system consists of more than one phase.

The phase rule is concerned with the effects that changes in pressure, temperature and concentrations will have on the equilibria of heterogeneous systems. When various phases are in equilibrium with one another in a heterogeneous system, there can be no transfer of energy or mass from one phase to another. Thus, at equilibrium the various phases must have the appropriate pressure and temperature and their respective compositions must be constant all along.

Components: The minimum number of independent chemical constituents necessary to define the composition of all the phases of the system. The composition of every phase can be expressed by means of a chemical equation (when chemical reaction takes place).

When no chemical reaction takes place, the number of components is equal to the number of constituents. Thus, pure water can exist in three phases, i.e. solid (ice), liquid (water) and vapour, but it is a one component system because we need only the species H_2O to specify its composition. Similarly, a mixture of ethanol and water is a two-phase and two-component system, since we need the species H_2O and C_2H_5OH to specify its composition. Sulphur can exist in four phases but is a one component system because we need only the species 'S' to specify its composition.

When a chemical reaction can occur, we need to decide the minimum number of species after completion of the reaction to specify the composition of all phases. For example,
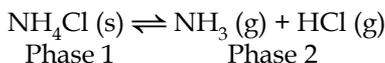
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
Phase 1   Phase 2   Phase 3
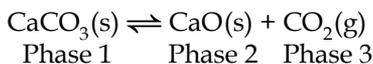
We need the species CO_2 and CaO to specify the composition of the gas (CO_2) and the composition of phase 2 (CaO), respectively. However, additional species is not required to specify the composition of phase 1 ($CaCO_3$) because it can be expressed in terms of the other two constituents by using the chemical reaction.
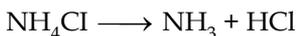
$$CaO + CO_2 \longrightarrow CaCO_3$$
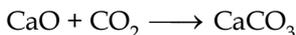
Hence, the it is a two-component system.

Similarly, in case of

$$NH_4Cl (s) \rightleftharpoons NH_3 (g) + HCl (g)$$
Phase 1   Phase 2

Here, NH_3 and HCl can be prepared by the following reaction

$$NH_4Cl \longrightarrow NH_3 + HCl$$

So, it is a one-component system. However, if NH_3 or HCl is in excess, the system becomes a two-component system.

Degrees of Freedom: The degree of freedom of a system is defined as the number of independent variables (temperature, pressure and concentration) that can be changed independently without disturbing the number of phases in equilibrium. This can also be defined in an another way as the number of variables that must be specified in order to define the system completely.

In a single component, single phase systems, the two variables (temperature and pressure) must be specified to get the same number of phases, so F = 2. Such a system is called **bivariant**. In a single component, two-phase systems, if temperature is specified, pressure becomes known automatically and *vice versa*. Only one variable, either temperature or pressure will have to mention. So, here F = 1 and it is called **Monovariant**. Similarly, in a single component, three-phase system F = 0 and it is called as **non-variant or invariant**.

2.5.1 One Component System

The water system, H_2O: One component systems must comprise of a pure substance only. For a one component system, the simplest example is pure water. Under ordinary circumstances, the water system consists of three phases, viz. ice, water and water vapour.

$$\text{Ice (s)} \rightleftharpoons \text{water (l)} \rightleftharpoons \text{water vapour (g)}$$
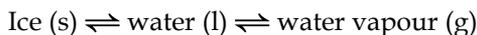
1. If the system consists of only one phase, say water vapour, then, according to the phase rule,

$$F = C - P + 2 = 1 - 1 + 2 = 2 \ \ \text{(bivariant)}$$

   Here, both pressure (P) and temperature (T) can be varied independently without changing the number of phases, i.e. a single phase is represented by an area on a phase diagram.

2. If a one component system has two phases in equilibrium say water and water vapour, or ice and water, or ice and water vapour, then the degree of freedom is,

$$F = C - P + 2 = 1 - 2 + 2 = 1 \ \ \text{(monovariant)}$$

   It implies that pressure is not freely variable if the temperature is fixed and *vice versa*. Thus, the system consisting of a liquid in contact with its vapour. The equilibrium of two phases is represented by a line in the phase diagram.

   (a) when a liquid in contact with its vapour,

      water (l) $\rightleftharpoons$ water (g)

   (b) when a solid in contact with its liquid then,

      ice (s) $\rightleftharpoons$ water (l).

   (c) a solid in contact with its vapours.

      ice (s) $\rightleftharpoons$ water vapour (g).

3. When all the three phases are in equilibrium of one component system then the degree of freedom is

$$F = C - P + 2 = 1 - 3 + 2 = 0 \ \ \text{(invariant)}.$$

   Here, no external condition has to be specified to define the system. The equilibrium of three phases is, therefore, represented by a point called **triple point**, on the phase diagram. Since F cannot be negative, in one component system, more than three phases cannot coexist in true equilibrium.
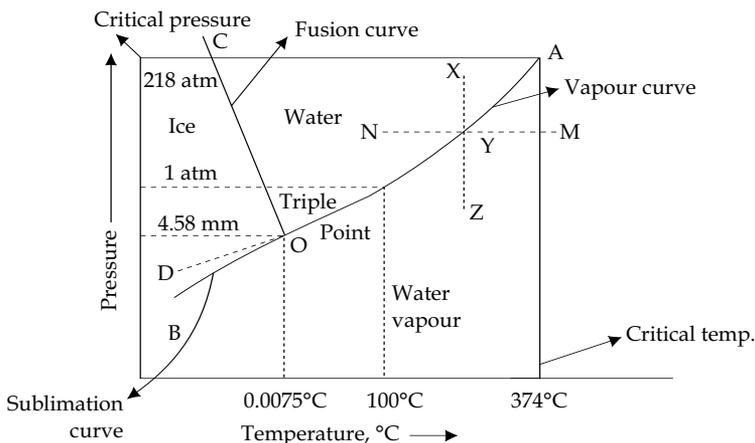
Fig. 3 Phase Diagram of Water System (Invariant)

The phase diagram of the water system is represented in Fig. 3.

Every equilibrium involves in two phases as

(1) liquid ⇌ vapour   (2) solid ⇌ liquid   (3) solid ⇌ vapour

1. As it is mentioned that a single phase is represented by an area on a phase diagram, the areas AOC, BOC and AOB are the areas of existence of liquid, solid, and vapour phase, respectively. Within this area, the system is bivariant, i.e. F = 2.

2. Similarly, a boundary line in a phase diagram represents the equilibrium of two phases. Thus, any point on boundary line is a monovariant (F = 1). These boundary lines in the phase diagram are OA, OB and OC. The curve OA represents the equilibrium between water (l) and water vapour (g) at different temperatures (vapour pressure curve). It is evident that for any given temperature, equilibrium vapour pressure is fixed, i.e. there is only one variable. Thus, the degree of freedom of the system is one, i.e. univariant or monovariant as

$$F = C - P + 2 = 1 - 2 + 2 = 1 \text{ (monovariant)}$$

For any point X and N above OA the system would be water. Similarly, any point Z and M below OA the system would be vapour. Hence, OA in the phase diagram is the boundary line between two phases (water and vapour). However, the line OA terminates at the critical point 'A' (t = 374°C and P = 218 atm) beyond which the liquid phase is no longer distinguishable from vapour phase.

Similarly, the curve OB represents the equilibrium between ice and vapour (sublimation curve). Here, for each temperature there can be one and only one pressure and vice versa. The curve OC represents the equilibrium between ice and water. The line has a negative slope, i.e. melting point is lowered with increase in pressure.

The triple point O, where the three lines meet, all the three phases, i.e. ice, water and vapour, should co-exist in equilibrium. The vapour pressure at this point is 4.58 mm and temperature is 0.0075°C. The system is non-variant at the triple point.

$$F = 1 - 3 + 2 = 0 \quad \text{(non-variant)}.$$

If either the temperature or the pressure is changed, the three-phase would not co-exist, one of the phases would disappear.

A liquid below its freezing point is said to remain in supercooled state, which is not normally stable and usually described as metastable state. The vapour pressure of the supercooled water also changes with temperature. The curve OD represents the supercooled state of water which lies above the curve OB. Thus, the vapour pressure of the metastable phase is greater than that of the stable phase.

2.6   THE COLLOIDS

Thomas Graham in 1861 found that a Colloid is a dispersion of small particles (< 500 mm diameter) of one material in another (solvent). In a colloid system, dispersion rate of one material in another is very slow. When this dispersion rate is more than enough then it is called as crystalloids and the materials exist in crystalline state. These solutions of *crystalloids* can readily percolate through parchment or cellophane papers. But in case of colloidal solution, it cannot pass through the parchment or cellophane paper.

When substances like sand, powdered glass, barium sulphate, charcoal, etc. are added to water, some remain floating or sink as a distinct phase and are called heterogeneous course suspensions. The solution which percolate through the parchment or cellophane paper easily is called a **true solution**. The solute particles in the true solutions are molecularly dispersed and are invisible. The diameter of the solutes in true solution is approximately 10^{-8} cm.

The systems with properties intermediate between those of heterogeneous course suspensions and homogeneous true solution are called colloidal systems. In general, colloidal particles are aggregate of numerous atoms or molecules, but are too small (diameter between $10^{-7} - 10^{-4}$ cm approximately) to be seen with an ordinary optical microscope but can be detected by light scattering (Tyndall effect), sedimentation, and osmosis.

A colloidal solution is a two-phase heterogeneous system in which a finely divided particles of any substance (approximately $10^{-7} - 10^{-4}$ cm diameter) dispersed in another continuous or dispersion medium. Generally, colloidal particles are charged either positively or negatively.

The colloidal system, is often called a **sol**. The ratio of colloid surface area to their volume is so large that their properties are dominated by events at their surfaces.

Table 1 Different Colloidal Systems

S. No.	Dispersed phase	Dispersion medium	Colloidal System	Examples
1.	Solid	Solid	Solid sol.	Rock salt, coloured precious stones.
2.	Solid	Liquid, water/benzene	Sol, hydrosol/benzosol	Starch, proteins, gold ink, paints, etc.
3.	Solid	Gas	Solid aerosol	Smoke, volcanic dust, fumes, etc.
4.	Liquid	Solid	Gel	Jellies, gels, cheese, curd, butter, etc.
5.	Liquid	Liquid	Emulsion	Milk, cod-liver oil
6.	Liquid	Gas	Liquid aerosol	Mist, fogs, clouds
7.	Gas	Liquid	Foam or froth	Whipped cream, foam detergent sud, etc.
8.	Gas	Solid	Solid foam	Adsorbed gases or occluded gases cake, rubber, etc.

2.6.1 Classification of Colloidal System

The name given to the colloid depends on either of the two phases involved. The colloidal system is often called as solution and is classified in two ways. These are:

(1) Mode of dispersion of the dispersed phase in dispersion medium, i.e. reversible solutions and irreversible solutions.

   (a) **Reversible solutions:** In this type of solutions, the dispersed phase is dispersed spontaneously in the dispersion medium because of thermal energy. In this type of solutions, redispersion also occurs easily.

   (b) **Irreversible solutions:** In these solutions, no spontaneous dispersion occurs and are thermodynamically unstable. The irreversible sols will be throwing out of the dispersion medium from the colloidal state to the macrostate.

(2) The other type of classification based on solvent affinity of the dispersed phase. These are (a) lyophilic and (b) lyophobic.

   (a) **Lyophilic sols:** Lyophilic sols are those which have spontaneous tendency to pass into the colloidal state, hence these solutions are reversible. The other characteristics are like

      (i) The surface tension of these solutions is lower than that of the dispersion medium in which the particles are dispersed.

      (ii) These sols show very weak Tyndall scattering effect.

      (iii) Viscosity is much higher than that of the dispersion medium.

      (iv) These sols are thermodynamically stable.

      (v) They are not easily precipitated by addition of electrolytes.

      (vi) These sols are solvent loving. Due to the presence of a number of polar groups in the molecules of lyophilic sols, these are extensively hydrated. Examples are starch, gelatin, glue, etc.

(b) **Lyophobic sols:** These sols are solvent repelling sols. These sols do not have spontaneous tendency to pass into the colloidal state and are irreversible in character. The other characters of these sols are stated as

(i) Surface tension is usually the same as that of the dispersion medium.

(ii) The lyophobic sols are often coloured. They show the Tyndall effect.

(iii) Viscosity is about the same as that of the dispersion medium.

(iv) They are thermodynamically unstable.

(v) They are precipitated more easily by addition of even a little electrolyte.

(vi) The colloidal particles are not hydrated to a large extent. For example: Gold solution, silver solution, etc.

2.7   ELECTROCHEMISTRY

Substances like metals viz. iron, copper, silver, mercury and non-metals like water, solutions of salts, acids, etc., allow the current to flow through them. These are called **conductors**. But there are other substances, most of the non-metals do not allow the current to flow through them, so these are called non-conductors or **insulators**. The conductors are broadly divided into two classes:

1. **Metallic conductors or electronic conductors** in which electricity passes through without producing a chemical change.
2. **Electrolytes or electrolytic conductors** in which electricity causes a chemical reaction.

The substances in their aqueous solutions are called non-electrolytes when they do not allow the current to flow through them. For example, alcohols, oils, sugar solution, starch solution, etc.

The main differences between electronic conductors and the electrolytic conductors are as follow:

Electronic conductors	Electrolytic conductors
1. In electronic conductors the electricity is carried exclusively by the transport of electrons without the transfer of matter at all.	1. It involves the actual transfer of matters (ions).
2. There is no chemical change when current is passed.	2. By the passage of electricity there occurs a chemical change i.e. decomposition of matter. It is called electrolysis. Electrolysis occurs only on the electrodes and not throughout the bulk of electrolyte.
3. The electrons flow from a higher negative potential to a lower one.	3. The current enters into the electrolyte through positive electrode or anode and leaves through negative electrode or cathode.
4. With increase in temperature the conductivity of electronic conductors decreases.	4. With increase in temperature the conductivity increases.

2.7.1 Electrode Potential

When a chemical equilibrium is not reached in the overall cell reaction, then there can be an electrical work as the reaction drives electrons through an external circuit. The flow of electricity from one electrode to another electrode is possible only when there is a potential difference between the two electrodes. This potential difference is called the electrode potential or cell potentials. It is shown in Fig. 4(a).

The electrochemical cell consists of two electrodes (metal) and the electrolyte. Generally, the negative electrode (anode) is placed at the left and positive electrode (cathode) on the right of the cell. When the metal electrode is in contact with an electrolyte, some metal ions enter into the electrolyte solution due to a tendency called Nernst electrolytic solution tension, leaving behind electrons on the electrode as

$$M \longrightarrow M^{+n} + ne^-$$

This electrode is negative and called **anode**. On the other hand, the positive metalic ions from the solution enters into the electrode by taking electrons from the electrode. So, it is now positive electrode and called **cathode**.

$$M^{n+} + ne^- \longrightarrow M$$

Due to electrostatic force in the vicinity of the electrode any further transference of metal ions does not take place. Thus, the positive charge and negative charge remain close to the metal surface forming a double layer. This is called **Helmholtz electrical double layer**. Because of the Nernst's electrolytic solution tension there is a difference in electrode potentials.

$$E = E^o - \frac{RT}{nF} \ln \frac{a_{Red}}{a_{Oxd}}$$

Where,
- R is the uviversal gas constant, equal to 8.314510 JK^{-1} mol^{-1}
- T is the temperature in kelvin. (Kelvin = 273.15 + °C)
- a the chemical activities on the reduced and oxidized side, respectively
- F is the Faraday constant (the charge per a mole of electrons), equal to 9.6485309 $* 10^4$ C mol^{-1}
- n is the number of electrons transferred in the half-reaction.
- [Red] is the concentration of oxidizing agent (the reduced species).
- [Ox] is the concentration of reducing agent (the oxidized species).
- E is the electrode potential
- E^o is the standard electrode potential

The electrode potential difference depends on the rates of transfer of ions from the metal to the solution and the discharge of ions from the solution on

the metal. The electrode which has the tendency to lose electrons (oxidised) is called **oxidation potential** and the tendency of the electrode to gain electrons (reduced) is called **reduction potential**. This is shown in the Fig. 4(a).

Measurement of electrode potentials: The potential difference of the double layer formed at an electrode is known as **single electrode potential**. For example, let us take an oxidation electrode potential, say Zinc-Zinc ion electrode.

Then,
$$Zn \rightarrow Zn^{++} + 2e^-$$

Let E_{Zn} is the electrode potential of Zn electrode.

Then,
$$E_{Zn} = E^o_{Zn} - \frac{RT}{nF} \ln \frac{a_{Zn^{++}}}{a_{Zn}}$$

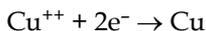where E^o_{Zn} is constant and is equal to $\frac{RT}{nF} \ln k$

where K is the equilibrium constant.

or
$$E_{Zn} = E^o_{Zn} - \frac{RT}{nF} \ln \frac{a_{oxidant}}{a_{reductant}}$$

since $a_{Zn} = 1$ (Solid Zinc).

Then,
$$E_{Zn} = E^o_{Zn} - \frac{RT}{nF} \ln a_{Zn^{++}}$$

Similarly, for reduction electrode potential copper-copper ion electrode
$$Cu^{++} + 2e^- \rightarrow Cu$$

$$E_{Cu} = E^o_{Cu} - \frac{RT}{nF} \ln \frac{a_{Cu}}{a_{Cu^{++}}} \frac{Reductant}{Oxidant}$$

or
$$E_{Cu} = E^o_{Cu} + \frac{RT}{nF} \ln \frac{a_{Cu^{++}}}{a_{Cu}} \quad (a_{Cu} = 1)$$

Then,
$$E_{Cu} = E^o_{Cu} + \frac{RT}{nF} \ln a_{Cu^{++}}$$

In the electrochemical series the elements are arranged in decreasing order (downwards) of their standard electrode potential. In the electrochemical series negative sign indicates that the reduced form has a greater tendency to get oxidised and leave electrons. For example,

$$Zn^{+2} + 2e^- \rightleftharpoons Zn \text{ (s)} \qquad E^0 = -0.76$$
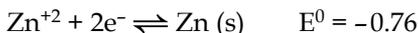
Positive sign indicates that the oxidised form has greater tendency to get reduced and take electron.

$$Cu^{+2} + 2e^- \rightleftharpoons Cu \qquad E^0 = 0.80$$

Hence, Zn has the greater tendency to lose electrons.

2.7.2 Electrochemical Cell

The redox reactions in solution is studied in terms of electrical measurement in a device called electrochemical cell. This electrochemical cell consists of two electrodes in contact with an electrolyte. The electrochemical cells are mainly two types (a) Galvanic cell, and (b) Electrolytic cell.

(a) **Galvanic Cell:** A galvanic cell is an electrochemical cell in which the free energy of a chemical process is converted into electrical energy, i.e. electricity is produced due to spontaneous reaction occurring inside it.

Direction of Electron Flow
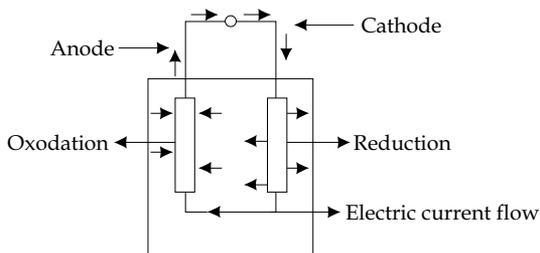
Fig. 4(a) Galvanic Cell

The chemical equation of the redox reaction in Galvanic cell is

$$Zn \mid Zn^{++} \parallel Cu^{++} \mid Cu.$$

(b) **Electrolytic Cell:** The electrolytic cell is one in which external electrical energy is used to carry out a chemical reaction, i.e. non-spontaneous reaction is occurring inside it.
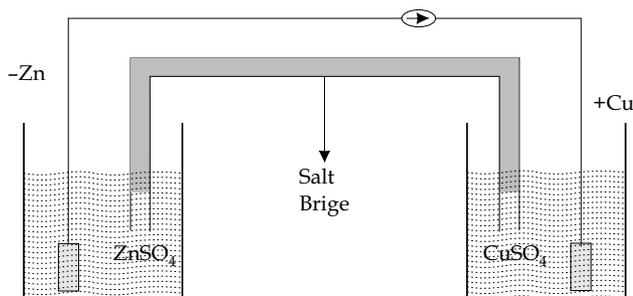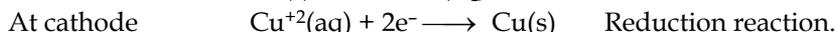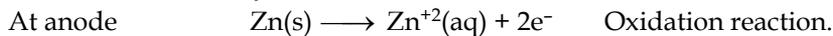
In both the electrochemical cells, if the two electrodes share the same electrolyte (single compartment) then salt bridge is not required, but in case of different electrolytes (two compartments) the salt bridge is required to complete the electrical circuit and cell reaction proceeds. To illustrate this cell reactions we may take Daniel cell (Galvanic cell) which consists of a Zn electrode immersed in a $ZnSO_4$ electrolyte solution and a copper electrode dipping in $CuSO_4$ solution. These two are kept in two separate chambers and connected by a salt bridge. Now, each chamber, i.e. one electrode and its electrolyte is regarded as a half-cell.

The electrode reactions in the Daniel cell are shown in Fig. 4(b).

$$Zn \rightleftharpoons Zn^{+2} + 2e^-$$

$$Cu \rightleftharpoons Cu^{+2} + 2e^-$$

Zinc has a greater tendency to ionize to Zn^{+2} than copper so that Zn^{+2} ion goes into solution leaving behind two electrons on the Zn electrode. Thus, Zn electrode is –ve, called anode. On the other hand, at the copper electrode,

copper ions from the solution are deposited by accepting two electrons each from the electrode so they are +ve, called cathode.

At anode $Zn(s) \longrightarrow Zn^{+2}(aq) + 2e^-$ Oxidation reaction.

At cathode $Cu^{+2}(aq) + 2e^- \longrightarrow Cu(s)$ Reduction reaction.

Overall reaction $Zn(s) + Cu^{+2}(aq) \longrightarrow Zn^{+2}(aq) + Cu(s)$.

Fig. 4(b)   Danial Cell

The electrochemical cell may be reversible or irreversible. In a reversible cell, the chemical reaction inside the cell proceeds in either direction depending on the direction of electric current flow but in an irreversible cell chemical reaction cannot be reversed under the same condition as earlier said. In a reversible cell each half-cell is also a reversible. The thermodyamic relations are only applicable to the reversible cell.

2.7.3   EMF of a Cell and Free Energy Change

The thermodynamic relations are applicable to reversible cell only. The chemical process occurring in any galvanic cell is exothermic. The electrical energy of a reversible cell was measured by the decrease of free energy of the cell, i.e. equivalent to the heat of chemical reaction occurring in the cell.

$$\Delta H = -nFE \quad \text{or} \quad E = -\frac{\Delta H}{nF}$$

where,   E is the electrical energy (EMF), ΔH is the heat of reaction.

nF is the charge of 1 gm mole of the substance.

In the Daniel cell, the cell reaction is

$$Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$$

$$Zn + Cu^{++} \longrightarrow Zn^{++} + Cu$$

Helmholtz found that the output of the electrical energy is not equivalent to the heat of reaction but equivalent to the net available work of the process i.e., to the decrease of free energy $(-\Delta G)$. Then,

$$-\Delta G = nFE \qquad \qquad \qquad ...(1)$$

As a result of one successful initiation, many reactant molecules might be consumed. The overall quantum yield (ϕ) is the number of reactant molecules that react for each photon absorbed.

$$\phi = \frac{\text{number of molecules reacting}}{\text{number of quanta of radiation absorbed}}$$

Energy $E = N_0 h\upsilon$ or $\dfrac{N_0 hc}{\lambda}$

$N_0 \rightarrow$ Avogadro number $= 6.02 \times 10^{23}$

$h \rightarrow$ Planck's constant $= 6.625 \times 10^{-27}$ ergs/sec.

$C \rightarrow$ Velocity of light $= 2.998 \times 10^{10}$ cm/sec.

Then $\qquad\qquad E = \dfrac{1.196 \times 10^8}{\lambda}$ ergs/mole

The energy E which activates one mole of the reactant, i.e. the energy corresponding to Avogadro number of photons is called **one einstein**.

### Primary Processes in Photochemical Reactions

This process follows the steps like:

1. The first step in a photochemical process is the absorption of energy of the radiation by the molecule. $A + h\upsilon \rightarrow A^*$ (excitation)

2. The energy obtained from a photon leads to an electronic transition. $A^* + A \rightarrow A_2$ (dimerisation), $A^* \rightarrow A + h\upsilon'$ (fluorescence).

3. The excited molecule re-emits the absorbed energy in order to come to stable state, fluorescence (single excited state) phosphorescence (triplet excited state) may occur. $A_2 \rightarrow 2A$ (thermal).

   Broadly, there are four distinct possibilities of the excitation of the molecules:

   (a) $NOCl + h\upsilon \longrightarrow NOCl^*$

   $NOCl^* + NOCl \longrightarrow 2NO + Cl_2$
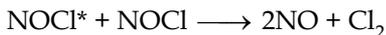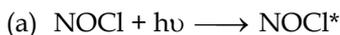
   The molecule is excited by the photon energy and it may retain its energy until it can be used chemically by combination with another molecule.

   (b) $HI + h\upsilon \rightarrow H + I$

   $H + HI \rightarrow H_2 + I$

   $I + I = I_2$
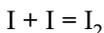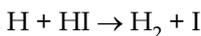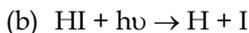
   This is due to the direct decomposition of the molecule.

   (c) By ionization process, i.e. when the molecules are in excited state (unstable), the molecule would dissociate producing atoms or radicals.

(d) At the unstable state, the molecule breaks up into atoms or radicals. The fragments of dissociation are produced with different kinetic energy. The products of dissociation may start secondary chemical changes or chain reactions as

$$Cl_2 + h\upsilon \longrightarrow 2Cl$$

$$Cl + H_2 \longrightarrow HCl + H$$

$$H + Cl_2 \longrightarrow HCl + Cl \text{ and so on.}$$
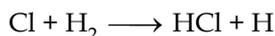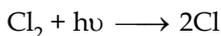
Photochemical equilibrium: The absorption of light by the reactant in the forward process will increase the speed of the forward reaction, but will not influence the rate of reverse thermal process.
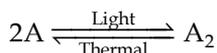
$$2A \underset{\text{Thermal}}{\overset{\text{Light}}{\rightleftharpoons}} A_2$$

The dimerization is carried out photochemically with light and the opposite change, the conversion of dimers into monomers is a thermal process.

Fluorescence: In this process the emitted radiation has a frequency less than that of the absorbed radiation. The absorbed energy is released within 10^{-8} seconds but it may come out in successive stages.

$$A + h\upsilon \rightarrow A^*$$

$$A^* \rightarrow A^1 + h\upsilon'$$

$$A^1 \rightarrow A + h\upsilon''$$
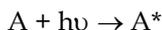
The emission in fluorescence shall cease as soon as the light source is removed.

Phosphorescence: The absorbed energy released in more than 10^{-8} seconds and the emission in phosphorescence will continue for some time even if the source of light is removed.

Chemiluminescence: The light is emitted as a result of chemical reaction at ordinary temperature. The emission occurs at the expense of some amount of heat of reaction.

2.9 FUNDAMENTAL REACTIONS AND THEIR MECHANISM

All types of chemical reactions involve the existing bond breaking and formation of new bonds. The reactions of the inorganic compounds are the reactions of the ions and are characterised by their reversibility. On the other hand, reactions of organic compounds are molecular in nature, and the atoms of the molecules are firmly bound by covalent bonds. Generally, the organic reactions are based on the fundamental concepts of energetics or thermodynamics. The organic chemical reactions may be stepwise reaction or a concerted reaction. Both these reactions may proceed through intermediates or transition state, respectively. The detailed path under taken by the reactants in order to get converted into products is the mechanism of the reaction. Thus,

–I Effect

The atoms or groups having greater electron affinity (greater electro-negativity) than hydrogen atom are said to have -I effect.

For example, $-NO_2$, $-OH$, $-OCH_3$, $-Br$, $-CI$, $-F$, $-CN$, $-I$, $-COOH$, etc.

Let the compounds like

$$-C_2^{++\delta} - C_1^{+\delta} - Cl^{-\delta}$$
$$-C_3^{+++\delta} - C_2^{++\delta} - C_1^{+\delta} - Cl^{-\delta}$$
$$-C_4 - C_3^{+++\delta} - C_2^{++\delta} - C_1^{+\delta} - CI^{-\delta}$$
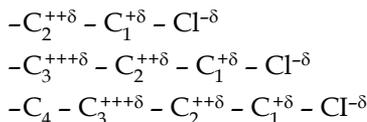
At $-C_4$, the inductive effect is almost negligible and at $-C_1$ it is more.

+I Effect

The atoms or groups having lesser electron affinity than hydrogen, i.e. the atoms or groups those can release the electrons (more electropositive) to the adjacent carbon atom are said to have +I effect. For example,

$$-H, -D, -CH_3, -CH_2-CH_3, -CH (CH_3)_2 - C (CH_3)_3, \text{etc.}$$
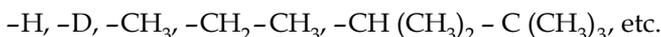
The +I effect of these groups is due to electron releasing nature of alkyl groups.

Application of Inductive Effect

(i) Strength of acid: Increase of +I effect will decrease the acid strength

+I effect increases

$$\overrightarrow{H\ COOH < CH_3COOH < C_2H_5COOH < C_3H_7COOH}$$

decrease in acid strength.

Increase in –I effect will increase in acid strength

Increase in –I effect

$$\overrightarrow{\text{Acetic acid} < \text{Iodoacetic acid} < \text{bromoacetic acid} < \text{chloroacetic acid}}$$
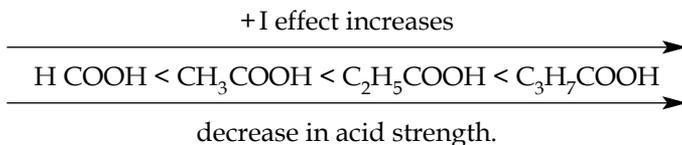
increase in acid strength.
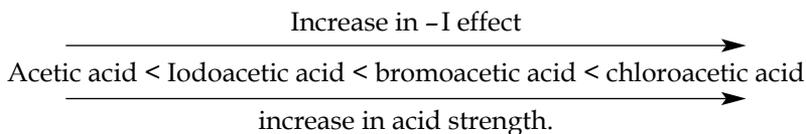
(ii) Strength of base: Increase in +I effect will increase in base strength.

+I effect increases

$$\overrightarrow{NH_3 < CH_3 NH_2 < (CH_3)_2 NH < (CH_3)_3 N}$$

Base strength increases
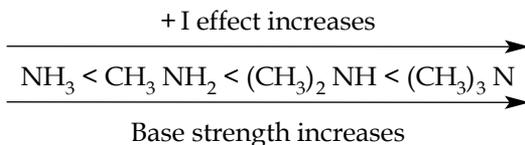
Increase in –I effect will decrease in base strength.

(iii) Effect on bond length: Usually the bond length decreases with increase in both inductive effect.

(i) $> C = C <$ $\xrightarrow{\text{Br} - \text{Br}}$ $> \overset{\displaystyle \text{Br} \atop |}{C} - \overset{| \atop \displaystyle \text{Br}}{C} <$

(ii) $> C = O <$ $\xrightarrow{\text{HCN}}$ $> \overset{\displaystyle \text{CN} \atop |}{C} - \text{OH}$
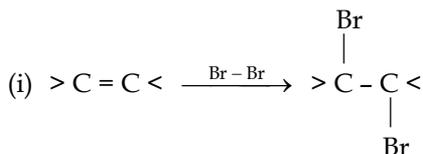
2.9.5 Resonance and Resonance Effect and Tautomerism

In many cases, it is not possible to describe the electronic structure of a species adequately with a single Lewis structure. As examplified by dinitrogen oxide N_2O.

$$: \ddot{N} = \overset{+}{N} = \ddot{O} : \longleftrightarrow : N \equiv \overset{+}{N} - \ddot{O} :$$

Resonance: If for any given compound two or more structures can be written diferring only in distribution of electrons or lone pair of electrons neither anyone of the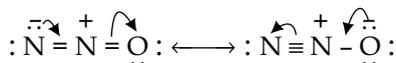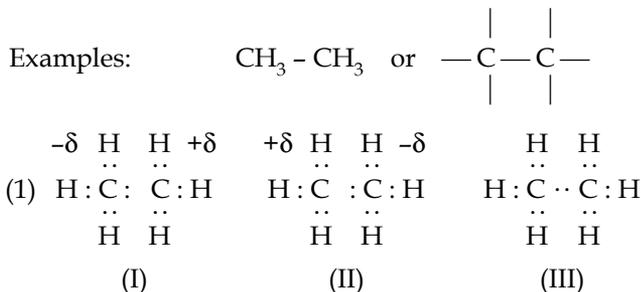 structures would explain the behaviour of that compound rather a hybrid of them explains the behaviour of that compound and that hybrid compound possess less energy than anyone. This phenomenon is know as *resonance*.

Examples: $CH_3 - CH_3$ or $-\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} -$

(1)
$$\begin{array}{ccc}
-\delta \;\; H \;\;\; H \; +\delta & +\delta \; H \;\;\; H \; -\delta & H \;\;\; H \\
\quad\;\; \overset{..}{} \;\; \overset{..}{} & \quad \overset{..}{} \;\; \overset{..}{} & \overset{..}{} \;\; \overset{..}{} \\
H : C : \; C : H & H : C \; : C : H & H : C \;\cdot\cdot\; C : H \\
\quad\;\; \underset{..}{} \;\; \underset{..}{} & \quad \underset{..}{} \;\; \underset{..}{} & \underset{..}{} \;\; \underset{..}{} \\
\quad\;\; H \;\;\; H & \quad H \;\;\; H & H \;\;\; H \\
(I) & (II) & (III)
\end{array}$$

Thus, it is a case of functional isomerism. It is considered dynamic isomerism.

Inter conversion of tautomers is hetrolytic in nature, involving the migration of an atom or group from a carbon to anouther atom with necessary rearrangement of linkages. If the migrating group is a cation, tautomeric transformations are known as **cationotropic** if an anion it is **anionotropic** the most common tautomerism involve the migration of a proton and are known as **prototropic** transformation.

If the hydrogen atom travels from one to another of the two polyvalent atoms linked together, the system is dyed. If the hydrogen atom travels from first to third in a chain, the system is a triad and so on. e.g.,

(1) Dyad System $H - C \equiv N \rightleftharpoons C \stackrel{\leftharpoonup}{=} N - H$

                Hydrogen cyanide   Hydrogen isocyanide

    Two polyvalent atoms (C and N) $\longrightarrow$ Dyad

(2) Triad System

$$
\begin{array}{ccc}
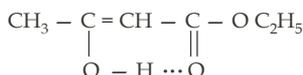R - CH - C - R^{1} & & R - CH - C - R^{1} \\
\quad | \quad\ \ || & \rightleftharpoons & \quad\quad\ | \\
\quad H \quad\ O & & \quad\quad O - H \\
\text{Keto form} & & \text{enol form}
\end{array}
$$

Acetoacetic Ester

$$
\begin{array}{cc}
CH_3 - C - CH - COOC_2H_5 - & CH_3 - C = CH - COOC_2H_5 - \\
\quad\ \ || \quad\ | & \quad\ \ | \\
\quad\ \ O \quad\ H & \quad\ \ OH \\
\text{Keto form (92\%)} & \text{enol form (8\%)}
\end{array}
$$
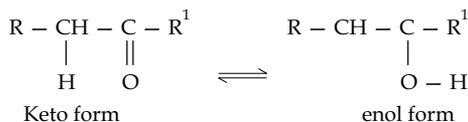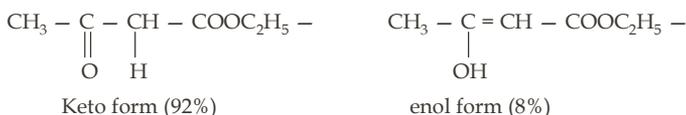
Stability of enolic form is ascribed to the formation of intramolecular hydrogen binding.

$$
\begin{array}{c}
CH_3 - C = CH - C - O\,C_2H_5 \\
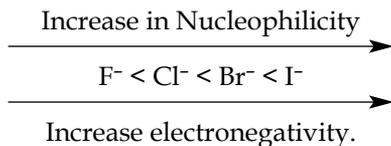\quad\quad | \quad\quad\quad\ \ || \\
\quad\quad O - H \cdots O
\end{array}
$$

Characteristics of tautomerism

(1) Tautomers are discrete chemical entities, capable of isolation under suitable conditons, frequently the give rise to separate series of stable derivatives.

(2) Tautomerism if caused by the migration of a group or atoms between two polyvalent atoms of the same molecule. It is thus reversible intramelecular transformation.

(3) Tautomers differ from each other in stability. The less stable form is called Labile form.

(4) It is a dynamic equilibrium.

2.9.6   Reaction Intermediates

Energy is needed to break bonds, while energy is released during bond formation. When reactants collide with sufficient enthalpy of activation and with the proper orientation, they pass through a hypothetical transition state in which some bonds are breaking while others may also be forming. The energy of a reaction *Vs.* the progress of the reaction is plotted on a potential energy diagram. The progress of the reaction is expressed as reaction coordinate and is measured in terms of bond breaking and bond forming.

If the product releases more energy than reactant, then the reaction is exothermic; while, in case, the product releases less energy than the reactant, then the reaction is endothermic. That is, if ΔH is negative then reaction is exothermic and ΔH is positive, the reaction is endothermic. From the diagram

$$\xrightarrow{\text{Increase in Nucleophilicity}}$$

$$F^- < Cl^- < Br^- < I^-$$
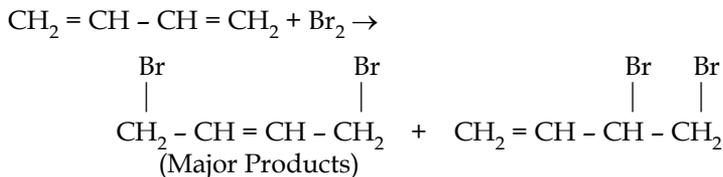
$$\xrightarrow{\text{Increase electronegativity.}}$$

2.9.9 Conjugation and Hyperconjugation

Conjugation: If the single and double bonds are present alternately in a molecule, it is said to contain double bonds in conjugation and the molecule is called conjugated molecule.
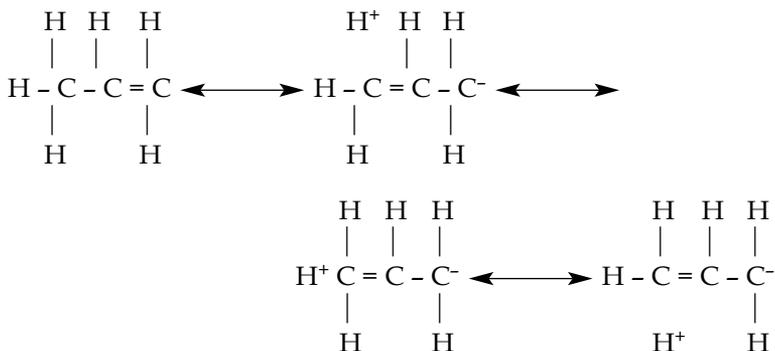
$$CH_2 = CH - CH = CH_2 \qquad (1, 3, \text{Butadiene})$$

The double bonds in a conjugated system do not behave as an isolated double bonds. In case of addition with Br_2 molecule they result in a mixture addition products, as

$$CH_2 = CH - CH = CH_2 + Br_2 \rightarrow$$

$$
\begin{array}{ccc}
\text{Br} & \text{Br} & \quad \text{Br} \quad \text{Br} \\
| & | & \quad | \quad | \\
CH_2 - CH = CH - CH_2 & + & CH_2 = CH - CH - CH_2 \\
\text{(Major Products)} & &
\end{array}
$$

Thus, conjugation effect in molecules results in large deviations from their usual behaviour.

Hyperconjugation: Hyperconjugation is defined as the conjugation ability of sigma (σ) electrons of α-hydrogen atom with unsaturated system when a $H-C$ bond is attached to an unsaturated system.

$$
\begin{array}{ccc}
\text{H} \ \ \text{H} \ \ \text{H} & & \text{H}^+ \ \text{H} \ \text{H} \\
| \ \ \ | \ \ \ | & & \ \ \ | \ \ | \\
\text{H} - \text{C} - \text{C} = \text{C} & \longleftrightarrow & \text{H} - \text{C} = \text{C} - \text{C}^- \longleftrightarrow \\
| \ \ \ \ \ | & & \ \ \ | \ \ \ \ | \\
\text{H} \quad \ \ \text{H} & & \ \ \text{H} \quad \ \ \text{H}
\end{array}
$$

$$
\begin{array}{ccc}
\text{H} \ \text{H} \ \text{H} & & \text{H} \ \text{H} \ \text{H} \\
| \ \ | \ \ | & & | \ \ | \ \ | \\
\text{H}^+ \ \text{C} = \text{C} - \text{C}^- & \longleftrightarrow & \text{H} - \text{C} = \text{C} - \text{C}^- \\
| \ \ \ \ | & & \ \ \ | \ \ \ \ | \\
\text{H} \quad \ \text{H} & & \text{H}^+ \quad \text{H}
\end{array}
$$

Since σ electrons are less polarizable than π or n electrons, the contribution of the ionic forms involving σ bonds will be less significant than that of ionic forms involving π and n electrons.