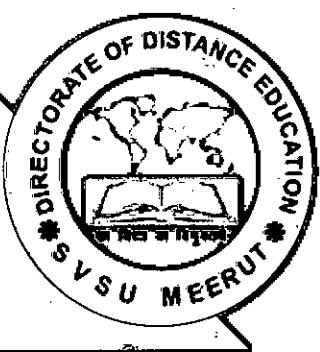


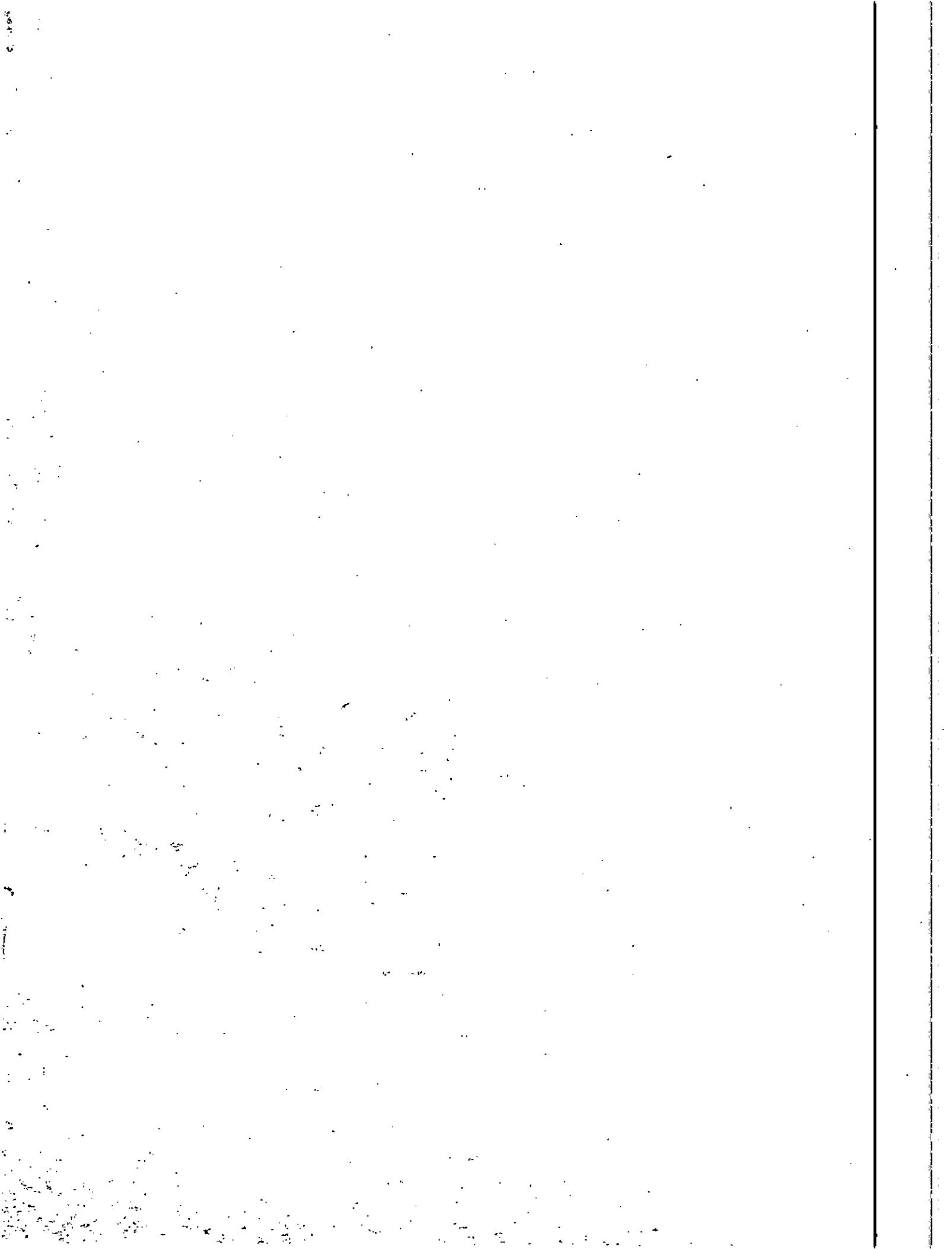
CHEMICAL ENERGETICS, EQUILIBRIA & ORGANIC CHEMISTRY



DIRECTORATE OF DISTANCE EDUCATION

**SWAMI VIVEKANAND
SUBHARTI UNIVERSITY**
Meerut (National Capital Region Delhi)





CHEMICAL ENERGETICS, EQUILIBRIA & ORGANIC CHEMISTRY

B.Sc. PCM-203

Self Learning Material



Directorate of Distance Education

**SWAMI VIVEKANAND SUBHARTI UNIVERSITY
MEERUT-250 005
UTTAR PRADESH**

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Contents

1.	CHEMICAL THERMODYNAMICS	1
2.	THERMOCHEMISTRY	32
3.	CHEMICAL EQUILIBRIA	48
4.	IONIC EQUILIBRIUM	62
5.	BENZENE AND AROMATICITY	84
6.	ALKYL AND ARYL HALIDES	104
7.	ALCOHOLS AND PHENOLS	120
8.	ALDEHYDE AND KETONES (Aliphatic and Aromatic)	138

Syllabus

B. Sc. II Sem.

CHEMISTRY-I : Chemical Energetics, Equilibria & Organic Chemistry

UNIT 1

Chemical Thermodynamics: Intensive and extensive variables; state and path functions; isolated, closed and open systems; zeroth law of thermodynamics.

First law: Concept of heat, q, work, internal energy, U, and statement of first law; enthalpy, H, relation between heat capacities, calculations of q, w, U and H for reversible, irreversible and free expansion of gases (ideal and real) under isothermal and adiabatic conditions.

Thermo Chemistry: Heats of reactions: standard states; enthalpy of formation of molecules and ions and enthalpy of combustion and its applications; calculation of bond energy, bond dissociation energy and resonance energy from thermochemical data, effect of temperature (Kirchhoff's equations) and pressure on enthalpy of reactions. Adiabatic flame temperature, explosion temperature.

Second Law: Concept of entropy; thermodynamic scale of temperature, statement of the second law of thermodynamics; molecular and statistical interpretation of entropy. Calculation of entropy change for reversible and irreversible processes.

Third Law: Statement of third law, concept of residual entropy, calculation of absolute entropy of molecules.

UNIT 2

Chemical Equilibrium: Free energy change in a chemical reaction. Thermodynamic derivation of the law of chemical equilibrium. Distinction between ΔG and ΔG° , Le Chatelier's principle. Relationships between K_p , K_c and K_x for reactions involving ideal gases.

Ionic Equilibria: Strong, moderate and weak electrolytes, degree of ionization, factors affecting degree of ionization, ionization constant and ionic product of water. Ionization of weak acids and bases, pH scale, common ion effect. Salt hydrolysis-calculation of hydrolysis constant, degree of hydrolysis and pH for different salts. Buffer solutions. Solubility and solubility product of sparingly soluble salts – applications of solubility product principle.

UNIT 3

Aromaticity: Hückel's rule, aromatic character of arenes, cyclic carbocations/carbonions and heterocyclic compounds with suitable examples. Electrophilic aromatic substitution: halogenation, nitration, sulphonation and Friedel-Craft's alkylation/acylation with their mechanism. Directing effects of the groups.

Aromatic hydrocarbons : Preparation (benzene): Reactions: (Case benzene): Electrophilic substitution: nitration, halogenation and sulphonation. Friedel-Craft's reaction (alkylation and acylation).

Alkyl Halides Types of Nucleophilic Substitution (S_N1 , S_N2 and S_Ni) reactions.

Reactions: hydrolysis, nitrite & nitro formation, nitrile & isonitrile formation, Williamson's ether synthesis. **Aryl Halides Preparation:** (Chloro, bromo and iodo-benzene case): from phenol, Sandmeyer & Gattermann reactions.

Reactions (Chlorobenzene): Aromatic nucleophilic substitution (replacement by -OH group) and effect of nitro substituent.

UNIT 4

Alcohols: Preparation: Preparation, **Reactions:** With sodium, HX (Lucas test), esterification, oxidation (with PCC, alk. $KMnO_4$, acidic dichromate, conc. HNO_3). Oppeneauer oxidation **Diols:** oxidation of diols. Pinacol-Pinacolone rearrangement.

Phenols: Preparation, **Reactions:** Electrophilic substitution: Nitration, halogenation and sulphonation. Reimer - Tiemann Reaction, Gattermann-Koch Reaction, Houben-Hoesch Condensation, Schotten - Baumann Reaction.

Aldehydes and ketones (aliphatic and aromatic): (Formaldehyde, acetaldehyde, acetone and benzaldehyde)

Preparation: From acid chlorides and from nitriles.

Reactions: Reaction with HCN, ROH, $NaHSO_3$, NH_2 -G derivatives. Iodoform test. Aldol Condensation, Cannizzaro's reaction, Wittig reaction, Benzoin condensation. Clemensen reduction and Wolff Kishner reduction.

Meerwein-Ponndorf-Verley reduction.

1

CHEMICAL THERMODYNAMICS

LEARNING OBJECTIVES

- Terms Used in Chemical Thermodynamics
- Zeroth Law of Thermodynamics
- Nature of Work and Heat
- Internal Energy
- Enthalpy
- First Law of Thermodynamics
- Heat Capacity
- Work Done in an Isothermal Reversible Expansion of a Gas
- Work Done in Adiabatic Reversible Expansion of a Gas or Deduction of $PV^\gamma = \text{Constant}$
- Second Law of Thermodynamics
- Entropy
- Entropy Changes for Different Processes
- Criteria of Spontaneity of a Reaction
- Molecular and Statistical Interpretation of Entropy
- Thermodynamic or Kelvin Scale of Temperature
- Nernst Heat Theorem
- Third Law of Thermodynamics
 - Summary
 - Student Activity
 - Test Yourself

Thermodynamics is that branch of natural science which deals with energy transformations accompanying the physical and chemical processes. Thermodynamics shows the quantitative relations between various forms of energy and heat. The subject is of theoretical nature but has proved of immense importance in physics, chemistry and engineering. The **advanced physical chemistry** is now often studied from the standpoint of thermodynamics. It also helps us to lay down the criteria for predicting feasibility of a process including a chemical reaction under a given set of conditions. In the other words, it helps us to predict whether a given process or a chemical reaction is possible under given conditions of pressure, temperature and concentration. Thermodynamics also helps us to determine the extent to which a process including a chemical reaction, can proceed before attainment of equilibrium.

• 1.1. TERMS USED IN CHEMICAL THERMODYNAMICS

In the study of thermodynamics, few terms are frequently used. These are described as follows:

1. **Thermodynamic system.** It is defined as *any specified portion of matter under study which is separated from the rest of the universe with a bounding surface*. A system may consist of one or more than one substance.

2. **Surroundings.** *The rest of the universe which might be in a position to exchange matter and energy with the system is called the surroundings.* For example, when a chemical reaction is carried out between two aqueous solutions in a beaker, the contents of the system form the surroundings.

3. **Types of systems (Open-, Closed- and Isolated systems).**

(a) A system which can exchange matter as well as energy with its surroundings is said to be an **open system**.

(b) A system which can exchange energy but not matter with its surroundings is called a **closed system**.

(c) A system which can exchange neither energy nor matter with its surroundings is called an *isolated system*.

If a system is maintained at a constant temperature, it is termed an *isothermal system*. If a system is so insulated from its surroundings that no heat flows in or out of the system, it is termed an *adiabatic system*.

4. **Homogeneous and heterogeneous systems.** A system is said to be *homogeneous* if it is completely uniform throughout. In such a system, there is **only** one phase, e.g., a pure solid, pure liquid or a mixture of gases.

A system is said to be *heterogeneous*, when it is not uniform throughout. In **such** a system there are two or more phases, e.g., a system consisting of two immiscible solvents.

5. **Macroscopic systems.** A system is said to be *macroscopic* when it consists of a large number of molecules, atoms or ions. (The word macroscopic means *on a large scale* and is, therefore, used to convey the sense of appreciable quantities). The properties associated with macroscopic system are known as *macroscopic properties*, e.g., pressure, temperature, volume, density, viscosity, surface tension etc.

6. **State of a system.** When macroscopic properties of a system have fixed **values**, the system is said to be in a **definite state**. When there is any change in the **property**, the system changes into a different state. Therefore, the state of a system is fixed by its macroscopic properties.

7. **Thermodynamic variables or state variables.** The quantities whose **values** determine the state of a system are called its thermodynamic variables or **state variables**. The most important state variables are mass, composition, **pressure**, temperature and volume. It is, however, not necessary that we should always specify all the variables, because some of them are inter-dependent. For a single pure **gas**, composition may not be one of the variables, as it remains only 100%. For one mole **of an ideal gas**, the gas equation $PV = RT$ is obeyed. Evidently, if only two out of the **three variables** (P, V, T) are known, the third can be easily calculated. The two variables generally specified are pressure and temperature. These are known as *independent variables*. The third variable, viz., volume is known as *dependent variable*, as its value depends upon the values of pressure and temperature.

8. **Extensive variable.** The variable of a system which depends upon the **amount** of the substance or substances present in the system is known as **extensive variable**, e.g., mass, volume, energy, etc.

9. **Intensive variable.** The variable of a system which is independent of the amount of the substance present in the system is known as **intensive variable** e.g., pressure, temperature, viscosity, refractive index.

10. **State functions and path functions.** State variables which are determined by the initial and final states of the system **only** and not by the path followed are called **state functions**. These depend upon how the change from initial to the final **state is carried out**.

State variables, on the contrary which are determined or depend on the **path followed** are called **path functions**.

Consider the expansion of a gas from P_1, V_1, T_1 to P_2, V_2 and T_2 (i) in steps and (ii) adiabatically. In adiabatic expansion, let the work done by the system be W and **heat absorbed** is zero.

In stepwise expansion, heat absorbed = Q and work done = W . Here $W \neq Q$ and the heat absorbed in the two cases are also different even though the system has undergone the same net change. Thus, W and Q are path functions and not the state functions. However, the change in internal energy (heat absorbed-work done) in the two cases will be seen to be constant. This is possible only if E_1 and E_2 have the same values in the **two states of the system**. Internal energy of a system is thus a **state function**. Entropy, free energy, enthalpy are other state functions.

11. **Thermodynamic equilibrium.** A system in which the macroscopic properties do not undergo any change with time is said to be in **thermodynamic equilibrium**. When an isolated system is left to itself and the pressure and temperature are measured at different points of the system, it is seen that although these quantities may initially change with time, the rate of change becomes smaller and smaller until no

further observable change occurs. In such a state, the system is said to be in thermodynamic equilibrium.

Thermodynamic equilibrium means the existence of three kinds of equilibria in the system. These are termed *thermal equilibrium*, *mechanical equilibrium* and *chemical equilibrium*.

(a) **Thermal equilibrium** : A system is said to be in thermal equilibrium if there is no flow of heat from one part of the system to another. This is possible when the temperature remains the same throughout in all parts of the system.

(b) **Mechanical equilibrium**. A system is said to be in mechanical equilibrium if there is no mechanical work done by one part of the system to the other. This is possible when the pressure remains the same throughout in all parts of the system.

(c) **Chemical equilibrium** : A system is said to be in chemical equilibrium if the concentration of the various phases remain the same throughout in all parts of the system.

12. Thermodynamic process : A thermodynamic process is a path or an operation by which a system changes from one state to another. Four different thermodynamic processes are known which are as follows :

(a) **Isothermal process** : A process is said to be isothermal if the temperature of the system remains constant throughout the whole process. This is obtained by making a perfect thermal contact of the system with a thermostat of a large heat capacity.

(b) **Adiabatic process** : A process is said to be adiabatic if no heat is allowed to enter or leave the system during the whole process. In such a process, therefore, the temperature gets altered because the system is not in a position to exchange heat with the surroundings. It is obtained by having the wall of the system made of perfect heat insulating substance.

(c) **Isobaric process** : A process is said to be isobaric if the pressure remains constant throughout the whole process.

(d) **Isochoric process** : A process is said to be isochoric if the volume remains constant throughout the whole process.

13. Reversible and irreversible processes : A process which is carried out infinitesimally slowly so that the driving force is only infinitesimally greater than the opposing force is called a reversible process. In a reversible process, the direction of the process can be reversed at any point by making a small change in a variable like pressure, temperature etc.

Any process which does not take place in the above way, i.e., a process which does not occur infinitesimally slowly, is termed an irreversible process.

A reversible process cannot be realised in practice, it would require infinite time for its completion. Hence, all those reactions which occur in nature or in laboratory are irreversible. A reversible process is thus *theoretical* and *imaginary*. The concept of reversibility can be understood as follows :

Consider a gas cylinder provided with a frictionless and weightless piston upon which is kept some sand. At the beginning, when an equilibrium exists between the inside pressure of the gas and outside pressure of atmosphere plus sand, the piston is motionless. If we remove a grain of sand, the gas will expand slightly, but the equilibrium will be restored almost instantaneously. If the same grain of sand is replaced, the gas will return to its original volume and the equilibrium remains unchanged.

14. Exact and inexact differentials : An exact differential is one which integrates to a finite difference, $\int_A^B dE = E_B - E_A$, where E_A and E_B are the internal energy of the system in the initial and final states, respectively. It is independent of the path of integration. In a cyclic process, the final state is the same as the initial state, i.e., $E_B = E_A$, the cyclic integral of an exact differential, $\oint dE = 0$. The difference, $E_B - E_A$ is denoted by ΔE .

An inexact differential is one which integrates to a total quantity depending upon the path of integration, e.g.,

$$\int_A^B \delta W = W$$

where W is the total quantity of work appearing during the change from initial state A to the final state, B . Small changes in path, independent of state functions are represented by symbols like dE , dEm , etc., while small changes in path dependent functions are represented by symbols like δq , δW etc. Finite changes in the former are represented by symbols like ΔE , ΔF etc., but symbols like Δq , ΔW are meaningless when we deal with path dependent functions. This is so, because the system in the two states is not associated with any heat or work. Heat and work appear during the process only. Moreover, the cyclic integral of an inexact differential is generally not zero.

• 1.2. ZEROTH LAW OF THERMODYNAMICS

We know that temperature is one of the quantities necessary to define the state of a thermodynamic system. In other words, every thermodynamic system must possess a temperature. *This postulate of the existence of temperature is sometimes called the zeroth law of thermodynamics.* In other words, this law states that, *if body A is in equilibrium with body C and body B is also in equilibrium with body C, then bodies A and B are in equilibrium with each other.*

Energy manifests itself not only in the form of mechanical work, but also as heat energy, electrical energy and chemical energy. Energy is composed of two factors viz., intensity factor and capacity factor. The product of these two factors gives the energy.

Heat energy is measured by the product of temperature (intensity factor) and heat capacity (capacity factor) of the system. The product gives the energy of the system. If a substance of mass m kg and specific heat is s kJ per kg is heated through t , the heat energy involved is given by mst kJ.

The precise experimental basis for this assumption is the law of thermal equilibrium from which it can be shown that in a thermodynamical system for every participant in equilibrium, there exists a certain single valued function f of the state variables, P and V , which have the same values for all participants. Mathematically, it can be expressed as,

$$f_1(P_1, V_1) = f_2(P_2, V_2) = f_3(P_3, V_3) = \dots = T$$

where the subscripts 1, 2, 3 refer to different participants. The identical numerical value has been put down as T , which may be called the *temperature*, any one of the bodies being used as a thermometer reading the temperature T on a suitable scale. The above equation thus defines an empirical temperature. It is true that it has not been found possible to express the last equation in finite or closed form for most substances. Its existence for most substances will, however, be taken for granted.

• 1.3. NATURE OF WORK AND HEAT

It has been seen that when a system changes from one state to another, it is accompanied by change in energy. The change in energy may appear in the form of work, heat, light etc.

In CGS system, the unit of energy is *erg*. In SI system, the unit of work, heat and energy is *joule* (1 calorie = 4.184 joules = 4.184×10^7 ergs). An erg is defined as the *work done when a resistance of 1 ohm is moved through a distance of 1 cm*. As erg is a small quantity, a bigger unit, called joule (1 joule = 10^7 erg) is used. Joule (1850) showed that there is a definite relationship between mechanical work done W and heat produced, q , i.e.,

$$W \propto q \text{ or } W = Jq$$

where J is known as *Joule mechanical equivalent of heat*.

Energy is made up of two factors, viz., (i) *Intensity factor* and (ii) *Capacity factor*. The product of these two factors gives the energy. Heat energy is measured by the product of temperature (*intensity factor*) and the heat capacity (*capacity factor*) of the system. The product gives the energy of the system. If a substance of mass m kg and specific heat s kJ per kg is heated through t° , the heat energy involved is given by mst kilo joules.

Similarly, when a body of mass m kg is moved through a height h m, the work done against gravity is obtained by multiplying the *intensity factor* (mg newtons) and

capacity factor (h metres). The work done is mgh joules. This work is stored in the body as potential energy and is released when the body falls to its original position.

• 1.4. INTERNAL ENERGY (U)

Every substance is associated with a certain amount of energy, which depends upon its chemical nature, temperature, pressure and volume. This energy is known as **internal** or **intrinsic energy**. The exact value of this energy is unknown because the chemical nature includes several indeterminant factors, e.g., translational, rotational and vibrational motion of the molecules, the manner in which the molecules are put together, the nature of individual atoms, the energy possessed by the nucleus and the arrangement and number of electrons. Internal energy of a substance or system is, however, a definite quantity, and it is a function of the state of the system at the given instant, irrespective of the manner in which that state has been brought about. The absolute value of internal energy cannot, thus, be determined. However, in thermodynamics, it is the change in internal energy (ΔU) accompanying a physical or chemical process that is of importance. ΔU is a measurable quantity. Internal energy of a system is an extensive property, as its value depends upon the amount of the substance or system present.

If U_A and U_B be the internal energy of the system in the initial state (A) and final state (B), respectively then change in internal energy (ΔU) is given by,

$$\Delta U = U_B - U_A$$

Internal energy (U) is related to enthalpy (H) according to the relation,

$$H = U + PV$$

where P and V are the pressure and volume, respectively.

From kinetic molecular theory, the internal energy of a given mass of an ideal gas at constant temperature is independent of value, i.e., $\left(\frac{\partial U}{\partial V}\right)_T = 0$

If such a gas is expanded isothermally, i.e., T is constant then $dT = 0$. Substituting these values in above equation, we get

$$dU = 0.$$

So, the *change in internal energy when an ideal gas is expanded isothermally is zero.*

• 1.5. ENTHALPY (H)

Suppose the change in the state of a system is carried out at constant pressure. In such a case, there will be a change in volume. Let the volume changes from V_A to V_B , at constant pressure P . The work done (W) by the system will be given by,

$$W = P(V_B - V_A) \quad \dots(1)$$

From first law of thermodynamics,

$$\Delta U = Q - W \quad \dots(2)$$

So, combining equations (1) and (2) we get,

$$\Delta U = Q - P(V_B - V_A)$$

or $U_B - U_A = Q - P(V_B - V_A)$

or $Q = (U_B + PV_B) - (U_A + PV_A) \quad \dots(3)$

The quantity $U + PV$ is known as **enthalpy** of the system. It is represented by H and shows the *total energy contained in the system*. Therefore,

$$H = U + PV$$

As, U , P and V are definite properties depending upon the state of the system, it follows that H is also a definite property depending upon the state of a system. From equation (3), therefore,

$$Q = H_B - H_A = \Delta H \quad \dots(4)$$

ΔH represents the increase in enthalpy of a system when it changes from state **A** to state **B**. Like ΔU , ΔH depends on the initial and final states of a system and it is a definite quantity. According to equation (4), the *change in enthalpy is equal to the heat absorbed when the change is carried out at constant pressure.*

From equations (1), (2) and (4), we get,

$$\Delta U = (H_B - H_A) - P(V_B - V_A)$$

or

$$\Delta U = \Delta H - P \Delta V$$

or

$$\Delta H = \Delta U + P \Delta V$$

... (5)

• 1.6. FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics, also known as law of conservation of energy states that *energy can neither be created nor destroyed, although it can be converted from one form to another.* In other words, it can also be stated as '*the total energy of an isolated system always remains constant, although there may be change from one form to another.*' Thus, whenever energy in one form disappears, an equal amount of energy in some other form appears. This law was based on the failure to construct a perpetual motion machine, i.e., a machine which could produce energy without expenditure of energy.

It is now known that energy can be produced by the destruction of mass according to Einstein's expression, $U = mc^2$, where U is the energy produced by the destruction of mass m and c is the velocity of light. In the light of this fact, the modified first law can be defined as, *the total mass and energy of an isolated system remains constant.*

Mathematical statement of first law of thermodynamics : Let U_1 and U_2 be the energy of the system in state **A** and state **B**, respectively. Suppose a system while undergoing change from state **A** to state **B** absorbs heat Q from its surroundings and also performs some work W , either mechanical or electrical. On checking the amount of heat supplied and work done we find that Q is not equal to W .

According to first law of thermodynamics, the total energy must remain constant. In order to balance, we say that energy equivalent to $(Q - W)$ is stored in the system. It means that :

$$Q - W = \text{Energy of the system in its final state} \\ - \text{Energy of the system in its initial state}$$

or

$$\Delta U = Q - W$$

... (1)

When small changes are involved, equation (1) may be written as,

$$dU = dQ - dW$$

... (2)

Equations (1) and (2) are the *mathematical statements* of first law of thermodynamics.

• 1.7. HEAT CAPACITY

The *heat capacity* or more accurately the *mean heat capacity* of a system is defined as the *quantity of heat required to raise the temperature of the system from a lower to higher temperature divided by the temperature difference.* The heat capacity of a system between temperatures T_1 and T_2 is given by,

$$C(T_2, T_1) = \frac{Q}{T_2 - T_1} \quad \dots (1)$$

As heat capacity varies with temperature, the true heat capacity is represented by the differential equation,

$$C = \frac{dQ}{dT}$$

For one mole of the gas, the heat capacity is called molar heat capacity and is denoted by the symbol, C.

Molar heat capacity of gases have two values, one at **constant volume** (C_V) and the other at **constant pressure** (C_P). At constant volume, no external work ($P \Delta V$) is done either by the system or on the system, as there is no change in volume. So, from first law of thermodynamics ($\Delta U = Q - W$),

$$Q = \Delta U$$

$$C_V (T_2, T_1) = \left(\frac{\Delta U}{T_2 - T_1} \right)_V \quad (\text{From equation 1}).$$

or

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad \dots(2)$$

So, molar heat capacity of a system at constant volume is defined as the increase in internal energy of the system per degree rise in temperature.

At constant pressure P , the heat supplied is used in raising the internal energy of the system and also in doing work by expansion. Let the volume increases by ΔV . So, the value of C_P is always greater than the value of C_V . So, from first law of thermodynamics,

$$Q = \Delta U + W = \Delta U + P \Delta V$$

$$C_P (T_2, T_1) = \left(\frac{Q}{T_2 - T_1} \right)_P = \left(\frac{\Delta U + P \Delta V}{\Delta T} \right)_P = \left(\frac{\Delta H}{\Delta T} \right)_P$$

or

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad \dots(3)$$

So, molar heat capacity of a system at constant pressure is defined as the increase in enthalpy of the system per degree rise in temperature.

Derivation of $C_P - C_V = R$

We know that,

$$C_P = \frac{dH}{dT} \quad \text{and} \quad C_V = \frac{dU}{dT}$$

$$C_P - C_V = \frac{dH}{dT} - \frac{dU}{dT} = \frac{d(U + PV)}{dT} - \frac{dU}{dT} = \frac{dU}{dT} + \frac{d(PV)}{dT} - \frac{dU}{dT}$$

or

$$C_P - C_V = \frac{d(PV)}{dT} \quad \dots(4)$$

For an ideal gas, $PV = RT$. Differentiating this equation with respect to T , we get

$$\frac{d(PV)}{dT} = R$$

So, equation (4) becomes,

$$C_P - C_V = R.$$

• 1.8. WORK DONE IN AN ISOTHERMAL REVERSIBLE AND IRREVERSIBLE EXPANSION OF A GAS

A process is said to be reversible if the properties of the system at every instant remain uniform during the process. In a reversible process, the change from one equilibrium state to another is brought about in infinitesimal steps so that the properties of each step change infinitesimally from those of the next step. A reversible process is extremely slow and requires infinite time to complete. Reversible process is an ideal process which is difficult to be realised in actual practice. However, the reversible processes are very helpful in studying thermodynamics. From a reversible process maximum amount of work can be obtained from a given net process. This is explained as follows:

Consider a gas enclosed in a cylinder fitted with a weightless and frictionless

piston. The pressure, volume and temperature of the gas be P_1 , V_1 and T_1 , respectively. Suppose the volume is expanded from V_1 to V_2 isothermally and reversibly. Let the final pressure be P_2 . The work done (W_{rev}) in a reversible process is given by,

$$W_{\text{rev}} = nRT \log \frac{V_2}{V_1} = nRT \log \frac{P_1}{P_2} = nRT \log \left(1 + \frac{P_1 - P_2}{P_2} \right)$$

Expanding the logarithmic term and neglecting the higher powers of $(P_1 - P_2)/P_2$, as this quantity is small, we get

$$W_{\text{rev}} = nRT \frac{P_1 - P_2}{P_2} \quad [\because \log(1+x) = x] \dots (1)$$

When the work done by the same volume expansion from V_1 to V_2 is considered in an Irreversible way by suddenly reducing the pressure from P_1 to P_2 , the work done (W_{irr}) is given by,

$$\begin{aligned} W_{\text{irr}} &= \text{External pressure } (P_2) \times \text{Volume change} \\ &= P_2 (V_2 - V_1) = P_2 \left[\frac{nRT}{P_2} - \frac{nRT}{P_1} \right] = nRT \left(1 - \frac{P_2}{P_1} \right) \end{aligned} \dots (2)$$

Subtracting equation (2) from (1), we get

$$\begin{aligned} W_{\text{rev}} - W_{\text{irr}} &= nRT \left[\frac{P_1 - P_2}{P_2} - \left(1 - \frac{P_2}{P_1} \right) \right] = nRT \left[\frac{P_1 - P_2}{P_2} - \frac{P_1 - P_2}{P_1} \right] \\ &= nRT (P_1 - P_2) \left[\frac{1}{P_2} - \frac{1}{P_1} \right] \\ &= \text{Positive quantity} \quad (\because P_1 > P_2) \end{aligned}$$

Thus, work done in a reversible isothermal process is definitely greater than the work done in an irreversible process. No other process will give greater amount of work than this. So, it proves that the work done in reversible expansion process is maximum.

Consider n moles of an ideal gas enclosed in a cylinder fitted with a weightless and frictionless piston. Let its pressure be P which in equilibrium state is equal to the external pressure on the piston. Keeping the temperature constant at T , the pressure is decreased by an infinitesimal amount dP , so that there is an infinitesimal increase in volume, dV . The very small amount of work done (dW) during this isothermal reversible expansion is,

$$\begin{aligned} dW &= (P - dP) dV = P dV - dP \cdot dV \\ \text{or} \quad dW &= P dV \quad (\text{Neglecting } dP \cdot dV) \end{aligned}$$

Since the step is reversible, the value dW corresponds to the maximum work. The maximum work, W_{max} for the isothermal expansion of the gas from volume V_1 to V_2 or pressure P_1 to P_2 will be :

$$W_{\text{max}} = \int_{V_1}^{V_2} dW_{\text{max}} = \int_{V_1}^{V_2} P dV \dots (3)$$

For n moles of an ideal gas, $PV = nRT$, i.e., $P = nRT/V$

$$W_{\text{max}} = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1} = 2.303 nRT \log \frac{V_2}{V_1} \dots (4)$$

From Boyle's law, $P_1/P_2 = V_2/V_1$, therefore

$$W_{\text{max}} = nRT \ln \frac{P_1}{P_2} = 2.303 nRT \log \frac{P_1}{P_2} \dots (5)$$

For 1 mole of an ideal gas, equations (4) and (5) become

$$W_{\text{max}} = RT \ln \frac{V_2}{V_1} = 2.303 RT \log \frac{V_2}{V_1} \dots (6)$$

$$W_{\max} = RT \ln \frac{P_1}{P_2} = 2.303 RT \log \frac{P_1}{P_2} \quad \dots(7)$$

For n moles of an ideal gas, we can write equations (4) and (5) as,

$$W_{\max} = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2} \quad \dots(8)$$

$$= 2.303 nRT \log \frac{V_2}{V_1} = 2.303 nRT \log \frac{P_1}{P_2} \quad \dots(9)$$

• 1.9. WORK DONE IN ADIABATIC REVERSIBLE EXPANSION OF A GAS OR DEDUCTION OF $PV^\gamma = \text{constant}$

In adiabatic expansion, no heat is absorbed or evolved in the system, i.e., $Q = 0$. So, from first law of thermodynamics,

$$\Delta U = -W$$

In adiabatic expansion, work is done by the system on the surroundings, so W must be positive. So, ΔU is negative, i.e., there is a decrease in internal energy of the system. Thus, the temperature of the system falls.

Let P be the external pressure and ΔV be the increase in volume. The external work done by the system is equal to $P \Delta V$.

$$\therefore \Delta U = -W = -P \Delta V$$

If ΔT be the fall in temperature, then we know that,

$$\Delta U = C_V \Delta T \quad \left(\because C_V = \frac{\Delta E}{\Delta T} \right)$$

or $C_V \Delta T = -P \Delta V = -W$

or $W = P \Delta V = -C_V \Delta T$
 $= -C_V (T_2 - T_1) \quad \dots(1)$

Equation (1) gives the maximum work involved.

For infinitesimally small quantities, equation (1) becomes

$$C_V dT = -P dV = -RT \frac{dV}{V}$$

or $C_V \cdot \frac{dT}{T} = -R \frac{dV}{V}$

or $\int_{T_1}^{T_2} C_V \frac{dT}{T} = - \int_{T_1}^{T_2} R \frac{dV}{V}$

or $C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} = R \ln \frac{V_1}{V_2} \quad \dots(2)$

Knowing $C_P - C_V = R$ and $C_P / C_V = \gamma$, equation (2) becomes

$$\ln \frac{T_2}{T_1} = \frac{R}{C_V} \ln \frac{V_1}{V_2} = \left(\frac{C_P - C_V}{C_V} \right) \ln \frac{V_1}{V_2} = \left(\frac{C_P}{C_V} - 1 \right) \ln \frac{V_1}{V_2}$$

or $\ln \frac{T_2}{T_1} = (\gamma - 1) \ln \frac{V_1}{V_2} = \ln \left(\frac{V_1}{V_2} \right)^{\gamma - 1}$

or $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma - 1} \quad \dots(3)$

As $P_1 V_1 = RT_1$ and $P_2 V_2 = RT_2$, it follows from equation (3)

$$\frac{P_2 V_2 / R}{P_1 V_1 / R} = \left(\frac{V_1}{V_2} \right)^{\gamma - 1}$$

or $\frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^{\gamma}$

or $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$... (4)

or $PV^{\gamma} = \text{constant.}$

Also, $P_1^{1-\gamma} \cdot T_1^{\gamma} = P_2^{1-\gamma} \cdot T_2^{\gamma}$

(From equations 3 or 4)

$$\left(\frac{T_1}{T_2} \right)^{\gamma} = \left(\frac{P_2}{P_1} \right)^{1-\gamma}$$

... (5)

Ex. 1. Calculate Q , W , ΔU and ΔH for the isothermal reversible expansion of one mole of an ideal gas from an initial pressure of 1 atm to a final pressure of 0.1 atm at a constant temperature of 273 K.

Solution. Here $P_1 = 1$; $P_2 = 0.1$, $n = 1$, $R = 2$, $T = 273$.

$$W = 2.303 nRT \log \frac{P_1}{P_2} = 2.303 \times 1 \times 2 \times 273 \log \frac{1.0}{0.1}$$

$$= 1257.43 \text{ calories}$$

For an ideal gas expansion at constant temperature,

$$\Delta U = C_V dT = 0$$

From first law of thermodynamics,

$$\Delta U = Q - W = 0 \text{ or } Q = W$$

$$Q = 1257.43 \text{ calories}$$

When temperature is constant, $PV = \text{constant}$, i.e.,

$$\Delta PV = 0.$$

$$\Delta H = \Delta U + \Delta PV = 0.$$

Ex. 2. Calculate the work done when 1.0 mole of water at 100°C vaporises against an atmospheric pressure of 1.0 atm (assuming ideal gas behaviour).

Solution. Work done, $W = P \times \Delta V = P(V_g - V_l)$

$$P = h \cdot dg = 76 \times 13.6 \times 981 / \text{dyne cm}^{-2}$$

$$V_l = 18 \text{ ml}$$

($\because V = m/d$)

$$V_2 = \text{Volume of steam at } 100^\circ\text{C} = \frac{22400 \times 373}{273} = 30600 \text{ ml} \quad (\because \frac{V_1}{T_1} = \frac{V_2}{T_2})$$

$$W = 76 \times 13.6 \times 981 (30600 - 18) \text{ erg}$$

$$= \frac{76 \times 13.6 \times 981 \times 30582}{4.184 \times 10^7} \text{ cal}$$

$$= 741.4 \text{ cal}$$

($\because 4.184 \times 10^7 \text{ erg} = 1 \text{ cal}$)

Ex. 3. Calculate the work that must be done at 25°C on two moles of CO_2 to compress them from a volume of 20 litres to a volume of 1 litre. (Assume ideal gas behaviour for CO_2).

Solution. Here $V_1 = 20$, $V_2 = 1$, $n = 2$, $T = 298$, $R = 2$.

$$W = 2.303 nRT \log \frac{V_2}{V_1}$$

$$= 2.303 \times 2 \times 2 \times 298 \log \frac{1}{20}$$

$$= -3571.47 \text{ calories.}$$

Ex. 4. Calculate the work done during isothermal expansion of one mole of an ideal gas from 10 atm to 1 atm at 300 K.

Solution. Here $n = 1, P_1 = 10, P_2 = 1, T = 300, R = 2$.

$$\begin{aligned} W &= 2.303 nRT \log P_1 / P_2 \\ &= 2.303 \times 1 \times 2 \times 300 \log \frac{10}{1} \\ &= 1381.8 \text{ calories.} \end{aligned}$$

Ex. 5. Calculate ΔU and ΔH when 10 litres of an ideal gas at STP is heated to 100°C in a closed container. (Given $C_V = \frac{3}{2} R$)

Solution. We know that

$$C_V (T_2, T_1) = \left(\frac{\Delta U}{T_2 - T_1} \right)$$

$$\begin{aligned} \text{or } \Delta U &= C_V (T_2 - T_1) = \frac{3}{2} R \times (373 - 273) \\ &= \frac{3}{2} \times 2 \times 100 = 300 \text{ calories.} \end{aligned}$$

We know that, $\Delta H = \Delta U + P \Delta V$

$$\begin{aligned} \text{or } \Delta H &= \Delta U + R\Delta T \quad \left\{ \begin{array}{l} PV_1 = RT_1, PV_2 = RT_2 \\ P(V_2 - V_1) = R(T_2 - T_1) \end{array} \right\} \\ &= 300 + 2(373 - 273) = 500 \text{ calories.} \end{aligned}$$

Ex. 6. To what pressure must a given volume of nitrogen originally at 100°C and 1 atm. pressure be adiabatically compressed in order to raise its temperature to 400°C ? (C_P / C_V for nitrogen = 1.4).

Solution. For adiabatic expansion :

$$P_1^{1-\gamma} T_1^\gamma = P_2^{1-\gamma} T_2^\gamma \quad \text{or} \quad \left(\frac{P_2}{P_1} \right)^{1-\gamma} = \left(\frac{T_1}{T_2} \right)^\gamma$$

$$\text{or } (1-\gamma)(\log P_2 - \log P_1) = \gamma(\log T_1 - \log T_2)$$

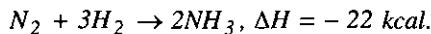
Here $P_1 = 1, T_1 = 373, T_2 = 673, \gamma = 1.4, P_2 = ?$

$$\therefore (1-1.4)(\log P_2 - \log 1) = 1.4(\log 373 - \log 673)$$

$$\begin{aligned} \text{or } \log P_2 &= \frac{1.4}{0.4} (\log 673 - \log 373) = 3.5(2.8280 - 2.5717) \\ &= 0.89705. \end{aligned}$$

$$\therefore P_2 = \text{antilog } 0.89705 = 7.889 \text{ atmospheres}$$

Ex. 7. What is the enthalpy of NH_3 if,



Solution. $\Delta H = 2H_{\text{NH}_3} - (H_{\text{N}_2} + 3H_{\text{H}_2}) = 2H_{\text{NH}_3} - (0 + 0)$

$$\text{or } -22 = 2H_{\text{NH}_3} \text{ or } H_{\text{NH}_3} = -11 \text{ kcal.}$$

• 1.10. SECOND LAW OF THERMODYNAMICS

We know that first law of thermodynamics tells us about the relation between heat and work and their equivalence. It also tells us about the conservation of energy during all processes, physical and chemical. It does not, however, give us any idea about the extent of convertibility of one form of energy into another. It also does not give us an idea about the spontaneity of a reaction, i.e., whether a given change is possible under given conditions of pressure and temperature or not.

If we study the relationship between work and heat, we see that whereas different forms of energy can be readily and completely converted into heat, it is not possible to

completely reconvert heat into work. In order to represent the limitations on the convertibility of heat into work and to predict the direction of change of all naturally occurring processes, Kelvin, Clausius, etc. put forward a law, known as *second law of thermodynamics*. This law tells us the direction of change under given conditions of temperature and pressure.

Second law of thermodynamics states that, "whenever a spontaneous process occurs, it is accompanied by an increase in the total energy of the universe."

Second law of thermodynamics can also be stated in a number of ways as follows :

(1) **Planck's definition** : *It is impossible to construct a machine working in cycles which can convert heat completely into an equivalent amount of work without producing any changes elsewhere.*

(2) **Kelvin's definition** : *It is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of heat to a cooler reservoir.*

(3) **Clausius' definition** : *It is impossible for a cyclic process to transmit heat from a body at a lower temperature to one at a higher temperature, without at the same time converting some work into heat.*

Second law of thermodynamics gives us an idea about free energy, entropy etc. which tell us about the spontaneity or feasibility of a process.

• 1.11. ENTROPY

Clausius (1850) introduced a new thermodynamic state function and termed it **entropy**. From **Carnot's cycle**, we can show that

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \quad \dots(1)$$

where q_2 is the heat absorbed at a higher temperature T_2 and q_1 is the heat evolved at a lower temperature T_1 . From equation (1),

$$1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

or $\frac{q_1}{q_2} = \frac{T_1}{T_2}$ or $\frac{q_1}{T_1} = \frac{q_2}{T_2}$... (2)

Giving proper signs, i.e., positive to heat absorbed and negative to heat evolved, we can write equation (2) as

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

or $\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$... (3)

Equation (3) shows that in a Carnot cycle, the summation of all q/T terms is zero. Any reversible cycle, say ABA, may be taken to be made up of a larger number of small Carnot cycles as shown in figure (1) (horizontals are adiabatics and verticals are isothermals). For each Carnot cycle, the sum of two q/T terms involved is zero vide equation (3).

For the complete reversible cycle ABA, we can write

$$\sum \frac{q}{T} = 0 \quad \dots(4)$$

For an infinitesimal change, equation (4) can be written as ,

$$\int \frac{dq}{T} = 0 \quad \dots(5)$$

The cycle ABA can be performed in two steps, viz, from A to B along path I and then from B to A along path II. We can thus write from equation (5),

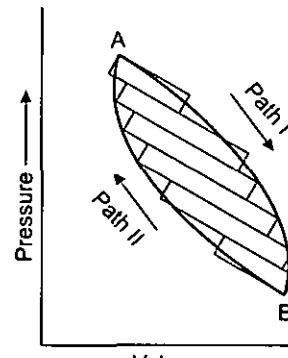


Fig. 1. Concept of entropy

$$\int \frac{dq}{T} = \int_A^B \frac{dq}{T} \text{ (Path I)} + \int_B^A \frac{dq}{T} \text{ (Path II)} = 0$$

or $\int_A^B \frac{dq}{T} \text{ (Path I)} = -\int_B^A \frac{dq}{T} \text{ (Path II)}$

or $\int_A^B \frac{dq}{T} \text{ (Path I)} = \int_A^B \frac{dq}{T} \text{ (Path II).}$

This shows that $\int_A^B \frac{dq}{T}$ is the same and independent of the path taken from A to B.

Its value depends only on the initial and final states, i.e., A and B of the system. This quantity, like ΔU or ΔH , is dependent only on the states of the system. This function is called **entropy** and is denoted by S.

If S_A and S_B be the entropy of the system in the initial and final states, then change in entropy (ΔS) is given by

$$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T} \quad \dots(6)$$

For a finite change, equation (6) can also be written as,

$$\Delta S = \frac{q}{T} \quad \dots(7)$$

For an infinitesimally small change,

$$dS = \frac{dq}{T} \quad \dots(8)$$

[I] Physical Significance of Entropy

Entropy of a substance is a real physical quantity and like pressure, temperature, internal energy, it is a definite function of the state of the body.

Entropy is also defined as the degree of disorder of a system.* Greater the disorder or randomness of a system, greater will be the entropy of the system.

Entropy is related to thermodynamic probability according to Boltzmann's equation,

$$S = k \log W + K$$

where k = Boltzmann's constant, K = another constant and W = thermodynamic probability. Planck (1912) showed that $K = 0$ and so

$$S = k \log W$$

This equation is known as **Boltzmann's-Planck equation**. It is not possible to evaluate the absolute value of entropy. It is only the entropy change which can be measured and is of great value as it provides valuable information regarding the spontaneity or feasibility of a process.

[II] Unit of Entropy

As entropy change (ΔS) is given by $\Delta S = q/T$, the unit of entropy will be *calorie per degree per mole* (in C.G.S. unit) or *joule per degree Kelvin per mole* (in S.I. unit). This unit is generally referred to as entropy unit (e.u.).

[III] Entropy Change During Isothermal Expansion

Suppose one mole of an ideal gas is allowed to expand reversibly and isothermally from volume V_1 to volume V_2 at a constant temperature T .

The amount of work done when 1 mole of an ideal gas is allowed to expand isothermally from volume V_1 to volume V_2 is given by

$$w = 2303 RT \log_{10} \frac{V_2}{V_1}$$

*Second law of thermodynamics tells us that all the internal energy of any substance cannot be converted into useful work. The portion of this total energy which is used for doing useful work is called *available energy* and the remaining part which cannot be converted into useful work is called *unavailable energy*. Entropy is thus a measure of this unavailable energy. Entropy is thus the unavailable energy per unit temperature, i.e.,

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{Temperature}}$$

In an isothermal process, $\Delta U = 0$ and so according to first law of thermodynamics ($\Delta U = q - w$), we have

$$0 = q - w$$

or $q = w = 2.303 RT \log_{10} \frac{V_2}{V_1}$... (1)

We know that change in entropy (ΔS) is given by

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{2.303 RT \log_{10} \frac{V_2}{V_1}}{T}$$

or $\Delta S = 2.303 R \log_{10} \frac{V_2}{V_1} = 2.303 R \log_{10} \frac{P_1}{P_2}$... (2)

($\because P_1 V_1 = P_1 V_2$, at constant temperature)

For n moles of an ideal gas, equation (2) can be written as

$$\Delta S = 2.303 nR \log_{10} \frac{V_2}{V_1} = 2.303 nR \log_{10} \frac{P_1}{P_2}$$
 ... (3)

[IV] Standard Entropy of a Gas

If the entropy of the gas at 1 atmospheric pressure and 298 K is expressed in terms of an ideal gas at the same pressure, then this value is referred to as the **standard entropy** of the gas.

• 1.12. ENTROPY CHANGES FOR DIFFERENT PROCESSES

[I] Entropy Change Accompanying Change from Solid to Liquid Phase

A solid changes into liquid state at its fusion point. The process requires absorption of heat (i.e., latent heat of fusion).

Consider melting of 1 mole of a substance reversibly at fusion point T_f at constant pressure. Let ΔH be the molar heat of fusion. The entropy change (ΔS_f) will then be given by,

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$
 ... (1)

[II] Entropy Change Accompanying Change from Liquid to Vapour Phase

Suppose 1 mole of a substance changes from the liquid to vapour state reversibly at its boiling point, T_b under constant pressure. If ΔH_v be the molar heat of vaporisation, then the entropy change (ΔS_v) is given by,

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$
 ... (2)

[As ΔH_f and ΔH_v are positive, hence processes of fusion and vaporisation are both accompanied by increase of entropy.]

(III) Entropy Changes in Reversible and Irreversible Processes

Suppose a system undergoes a change of state by a reversible process at constant temperature, T . The heat that it absorbs from the surroundings may be represented by q_{rev} . The increase in entropy of the system ΔS_{system} will be given by the equation,

$$\Delta S_{\text{system}} = \frac{q_{\text{rev}}}{T}$$
 ... (3)

Since the surroundings have lost heat equal to q_{rev} reversibly at the same temperature T , the entropy change of surroundings, ΔS_{surr} will be given by the equation,

$$\Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T}$$
 ... (4)

As heat is lost by the surroundings, it is given a negative sign. The sum total of the entropy of the system and its surroundings during a reversible process is zero, i.e.,

$$\Delta S_{\text{universe}} = S_{\text{system}} + \Delta S_{\text{surr}} \\ = \frac{q_{\text{rev}}}{T} - \frac{q_{\text{rev}}}{T} = 0. \quad \dots(5)$$

Therefore, the **net entropy change of the universe is constant in a reversible process.**

Suppose the same system undergoes the same change of state by irreversible or spontaneous process at constant temperature, T . The work done by the system will now be less and so the heat absorbed q_{irr} will be less than q_{rev} . Since entropy is a function of the state of the system, the increase in entropy of the system will be the same irrespective of the fact whether the change has been brought about reversibly or irreversibly. Hence, ΔS_{system} will remain the same as before, i.e., equal to q_{rev}/T as given by equation (3). But as the work done by the system during irreversible process is less, the heat absorbed by the system will also be less, say equal to q_{irr} . It follows that the heat lost by the surroundings will be less than q_{rev} .

However, the loss of heat by the surroundings can be considered to take place infinitesimally slowly, i.e., reversibly in view of an infinitely large size of the surroundings. So, the entropy change of the surroundings is given by,

$$\Delta S_{\text{surr}} = -\frac{q_{\text{irr}}}{T} \quad \dots(6)$$

The sum total of entropy change of the system and its surroundings during an irreversible process is given by,

$$\Delta S_{\text{system}} + \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T} - \frac{q_{\text{irr}}}{T}$$

Since

$$\frac{q_{\text{rev}}}{T} > \frac{q_{\text{irr}}}{T}$$

$$\therefore \frac{q_{\text{rev}}}{T} - \frac{q_{\text{irr}}}{T} > 0$$

$$\therefore \Delta S_{\text{system}} + \Delta S_{\text{surr}} > 0 \quad \dots(7)$$

Thus, we can conclude that entropy of the system and its surroundings taken together increases in a thermodynamically irreversible or spontaneous process at constant temperature, but it remains constant in a thermodynamically reversible process.

Combining equations (5) and (7), we get

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} \geq 0$$

An equal sign refers to a reversible process, while the greater sign refers to an irreversible process.

As most of the processes going on in nature are spontaneous and irreversible, it can be said that the "entropy of the universe always tends towards a maximum". So, ΔS also helps us in predicting whether a reaction is feasible or not. In case, ΔS is positive, the process is feasible or spontaneous.

Ex. 1. Calculate the entropy increase in the evaporation of a mole of water at 100°C . Latent heat of evaporation of water is 540 calorie per gram.

Solution. We know that

$$\Delta S = \frac{q}{T} = \frac{mL_e}{T_b}$$

where m = molecular weight, L_e = latent heat of evaporation per gram,

T_b = boiling point

$$\therefore \Delta S = \frac{18 \times 540}{373} = 29.058 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

Ex. 2. Calculate the entropy change during the formation of water from 1 gram mole of ice at 0°C . The latent heat of fusion of ice is 80 calorie per gram.

$$\text{Solution.} \quad \Delta S = \frac{q}{T} = \frac{mL_f}{T_f}$$

where L_f = Latent heat of fusion per gram, T_f = freezing point and m = molecular weight.

$$\Delta S = \frac{18 \times 80}{273} = 5.274 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

Ex. 3. Calculate the entropy change involved in the isothermal expansion of 5 moles of an ideal gas from a volume of 10 litres to a volume of 100 litres at 300 K in SI units.

Solution. In an isothermal expansion,

$$\begin{aligned}\Delta S &= 2.303 nR \log_{10} \frac{V_2}{V_1} \\ &= 2.303 \times 5 \times 8.314 \times \log_{10} \frac{100}{10} \\ &= 2.303 \times 5 \times 8.314 \times 1 \quad \left(\because \log \frac{100}{10} = \log 10 = 1 \right) \\ &= 95.735 \text{ JK}^{-1} \text{ mole}^{-1}\end{aligned}$$

Ex. 4. 10 moles of H_2 gas having ideal behaviour at 300 K is expanded under isothermal and reversible conditions from 15 litres to 150 litres. Calculate W and ΔG ($R = 2 \text{ cal}$)

$$\text{Solution. } W = 2.303 nRT \log_{10} \frac{V_2}{V_1}$$

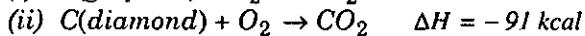
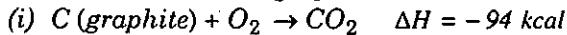
$$= 2.303 \times 10 \times 2 \times 300 \log \frac{150}{15}$$

$$= 2.303 \times 10 \times 2 \times 300 = 13818 \text{ cal.}$$

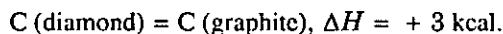
$$\Delta G = 2.303 nRT \log_{10} \frac{V_1}{V_2}$$

$$= 2.303 \times 10 \times 2 \times 300 \log \frac{15}{150} = -13818 \text{ cal.}$$

Ex. 5. From the following values, calculate entropy change when 1.2 kg of diamond is converted into graphite at 300 K.



Solution. Subtracting equation (i) from (ii), i.e.,



Heat change when 12 g diamond is converted into graphite = 3 kcal

So, heat change when 1200 g diamond is converted into graphite = 300 kcal.

$$\begin{aligned}\Delta S &= \frac{q}{T} = \frac{\Delta H}{T} = \frac{300 \times 1000 \text{ cal}}{300 \text{ K}} \\ &= 1000 \text{ cal K}^{-1}\end{aligned}$$

Ex. 6. Calculate the entropy change in 400 kg of water at 55°C when 75 J heat flows out of it into the surroundings at 20°C.

Solution. $\Delta S = \text{Loss in entropy of hot water} + \text{Gain in entropy of surroundings.}$

$$\begin{aligned}\text{Loss in entropy of hot water} &= \frac{-q}{T} = \frac{-75}{328} \\ &= -0.2286 \text{ JK}^{-1}\end{aligned}$$

$$\text{Gain in entropy of surroundings} = +q/T$$

$$= +\frac{75}{293} = +0.2559 \text{ JK}^{-1}$$

$$\begin{aligned}\Delta S &= -0.2286 \text{ JK}^{-1} + 0.2559 \text{ JK}^{-1} \\ &= 0.0273 \text{ JK}^{-1}\end{aligned}$$

• 1.13. CRITERIA OF SPONTANEITY (IRREVERSIBILITY) OF A REACTION

The following are the thermodynamic conditions of spontaneity and equilibrium :

(i) Spontaneous change is uni-directional or irreversible. Now work has to be

done for spontaneous change. It occurs by itself. On the other hand, reversible change is bi-directional. For a reversible change to occur, work has to be done.

(2) There is no time factor for spontaneous change; it may occur rapidly or very slowly.

(3) Conditions in terms of entropy change

$$dS \geq \frac{dq}{T} \quad (\text{Second law of thermodynamics})$$

$$dq = dU + P dV \quad (\text{First law of thermodynamics})$$

$$TdS \geq dU + P dV \quad \dots(1)$$

If, U = constant, then $dU = 0$

If, V = constant, then $dV = 0$ $\dots(2)$

So, from equations (1) and (2), we get

$$T(\partial S)_{E, V} \geq 0 \quad \text{or} \quad (\partial S)_{U, V} \geq 0 \quad \dots(3)$$

From equation (3), we conclude that

(a) If $(\partial S)_{U, V} = 0$, i.e., S is **maximum**, then process is reversible, i.e., this is the condition of equilibrium.

(b) If $(\partial S)_{U, V} > 0$ or positive, then the process is spontaneous.

(4) Conditions in terms of internal energy change.

$$dS \geq \frac{dq}{T}$$

$$\text{or} \quad dS \geq \frac{dU + PdV}{T}$$

$$\text{or} \quad TdS \geq dU + PdV$$

$$\text{or} \quad dU + PdV - TdS \leq 0 \quad \dots(4)$$

If S = constant, then $dS = 0$

$$V = \text{constant}, \text{then } dV = 0 \quad \dots(5)$$

From equations (4) and (5), we get

$$T(dU)_{S, V} \leq 0$$

$$\text{or} \quad (\partial U)_{S, V} \leq 0 \quad \dots(6)$$

Therefore, from equation (6), we can conclude that :

(a) If $(\partial U)_{S, V} = 0$, the process will be reversible. This is the condition of reversibility (equilibrium). When equilibrium state is reached, the internal energy becomes minimum.

(b) If $(\partial U)_{S, V} < 0$, then the process will be spontaneous. This is the condition of spontaneity.

(5) Conditions in terms of enthalpy change.

$$H = U + PV$$

$$\therefore dH = dU + PdV + VdP$$

$$\text{or} \quad dH - VdP = dU + PdV \quad \dots(7)$$

$$\text{We know that} \quad TdS \geq dE + PdV \quad \dots(8)$$

From equations (7) and (8), we get

$$TdS \geq dH - VdP$$

$$\text{or} \quad dH - VdP - TdS \leq 0 \quad \dots(9)$$

If S = constant, then $dS = 0$

$$P = \text{constant}, \text{then } dP = 0 \quad \dots(10)$$

From equations (9) and (10), we get

$$(dH)_{S, P} \leq 0$$

$$\text{or} \quad (\partial H)_{S, P} \leq 0 \quad \dots(11)$$

That is, in a real process $dH < 0$ or H diminishes. When equilibrium is reached, H is minimum. We can say,

(a) For spontaneity (irreversibility), $(\partial H)_{S, P} < 0$

(b) For equilibrium, $(\partial H)_{S, P} = 0$

(6) Conditions in terms of work function (A) change.

We know that, $A = U - TS$ or $dA = dU - TdS - SdT$

$$\text{or } dA + SdT = dU - TdS$$

$$\text{But } TdS \geq dU + PdV \quad \dots(12)$$

$$\text{or } -PdV \geq dU - TdS \quad \dots(13)$$

From equations (12) and (13), we get

$$-PdV \geq dA + SdT$$

$$\text{or } dA + SdT + PdV \leq 0$$

$$\text{If, } T = \text{constant, then } dT = 0 \quad \dots(14)$$

$$\text{If, } V = \text{constant, then } dV = 0 \quad \dots(15)$$

Hence, from equations (14) and (15), we get

$$(dA)_{T,V} \leq 0$$

$$\text{or } (\partial A)_{T,V} \leq 0 \quad \dots(16)$$

$$\therefore \text{(a) For spontaneity (irreversibility). } (\partial A)_{T,V} < 0$$

$$\text{(b) For equilibrium (reversibility). } (\partial A)_{T,V} = 0$$

(7) Conditions in terms of Gibbs free energy (G) change.

$$\text{We know that, } G = H - TS$$

$$dG = dH - TdS - SdT$$

$$= d(E + PV) - TdS - SdT$$

$$\text{or } dG = dU + PdV + VdP - TdS - SdT \quad \dots(17)$$

$$\text{or } dG - VdP + SdT = dU + PdV - TdS$$

$$\text{Also } TdS \geq dU + PdV$$

$$\text{or } 0 \geq dU + PdV - TdS \quad \dots(18)$$

From equations (17) and (18), we get

$$dG - VdP + SdT \leq 0 \quad \dots(19)$$

$$\text{If } P = \text{constant, then } dP = 0$$

$$T = \text{constant, then } dT = 0 \quad \dots(20)$$

From equations (19) and (20), we get

$$(dG)_{P,T} \leq 0 \quad \text{or} \quad (\partial G)_{P,T} \leq 0 \quad \dots(21)$$

$$\text{(a) For spontaneity } (\partial G)_{P,T} < 0$$

$$\text{(b) For equilibrium, } (\partial G)_{P,T} = 0$$

The criteria for spontaneity of a process can be summarised as follows :

S.No.	Spontaneity (Irreversibility)	Equilibrium (Reversibility)
1.	$(\partial S)_{U,V} > 0$	$(\partial S)_{U,V} = 0$
2.	$(\partial U)_{S,V} < 0$	$(\partial U)_{S,V} = 0$
3.	$(\partial H)_{S,P} < 0$	$(\partial H)_{S,P} = 0$
4.	$(\partial A)_{T,V} < 0$	$(\partial A)_{T,V} = 0$
5.	$(\partial G)_{P,T} < 0$	$(\partial G)_{P,T} = 0$

Usually, the physical or chemical changes occur at constant temperature and pressure. The direction of such changes can be predicted with the help of free energy change. We know that at constant pressure and constant temperature,

$$(\partial G)_{P,T} \leq 0 \quad \dots(22)$$

From equation (22), it is clear that,

(a) When $(\partial G)_{P,T} = 0$, then process is reversible, i.e., state of equilibrium exists.

(b) When $(\partial G)_{P,T} < 0$, i.e., free energy change is negative, the process is non-spontaneous.

(c) When $(\partial G)_{P,T} > 0$, i.e., free energy change is positive, the process is spontaneous.

The above conclusions can be used to predict whether a given process is possible or not, provided free energy change (ΔG or dG) is known. The value of ΔG can be calculated from the equation $G = H - TS$.

\therefore At constant temperature, we can write

$$\Delta G = \Delta H - T\Delta S$$

...(23)

The equation (23) can be used to predict the possibility of chemical reactions. The following cases may arise :

Case 1. When $\Delta H = \text{positive}$ and $\Delta S = \text{positive}$.

Under such conditions, if $T\Delta S > \Delta H$, then only ΔG will be negative and so the process will occur spontaneously otherwise not.

Case 2. When $\Delta H = \text{negative}$ and $\Delta S = \text{negative}$.

Under such conditions, if $\Delta H > T\Delta S$, then only ΔG will be negative and so the process will occur spontaneously.

Case 3. When $\Delta H = \text{positive}$ and $\Delta S = \text{negative}$.

Under such conditions, ΔG will be positive and so the process or reaction can never take place.

Case 4. When $\Delta H = \text{negative}$ and $\Delta S = \text{positive}$.

Under such conditions, ΔG will be negative and so the process will take place spontaneously.

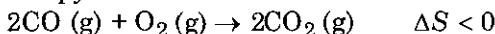
• 1.14. MOLECULAR AND STATISTICAL INTERPRETATION OF ENTROPY

(I) Molecular interpretation of Entropy : As discussed above that total entropy of the universe increases. But there are many processes in which system's entropy, increases $\Delta S > 0$ e.g.

- Increasing the volume that a gas can occupy will increase the disorder of a gas.
- Dissolving a solute into a solvent will increase the entropy of the solute.
- Phase changes from solid to liquid, liquid to gas, lead to an increase in the entropy of the system etc.

On the other hand there are some processes in which system's entropy decreases, $\Delta S < 0$ e.g.

- Dissolution of a gas in a liquid.
- Phase changes from liquid to solid, gas to liquid.
- A chemical reaction between gas molecules that results in a net decrease in the overall number of gas molecules will decrease the disorder of the system and decrease in the entropy.



Evidently in the product new C—O bonds are formed in the molecule. Thus molecular degree of freedom decreases.

(II) Statistical Definition of Entropy : The microscopic description of the entropy of a system C , composed of parts A and B should be given by

$$S_C = S_A + S_B$$

The average of the function over all the microstates is defined by

$$S = \langle f \rangle = \sum_i p_i f(p_i)$$

where the function $f(p_i)$ is to be found. Let system A has n microstates and system B has m microstates. Thus the entropies of systems A , B and C are defined by

$$S_A = \sum_{i=1}^n p_i f(p_i)$$

$$S_B = \sum_{j=1}^m p_j f(p_j)$$

$$S_C = \sum_{i=1}^n \sum_{j=1}^m p_{ij} f(p_{ij}) = \sum_{i=1}^n p_i f(p_i) \sum_{j=1}^m p_j f(p_j)$$

$$S_C = \sum_{i=1}^n p_i f(p_i) + \sum_{j=1}^m p_j f(p_j) = S_A + S_B.$$

If $f() = \ln()$, the above equation may be written as :

$$S_C = \sum_{i=1}^n \sum_{j=1}^m p_i p_j \ln(p_i) + \sum_{i=1}^n \sum_{j=1}^m p_i p_j \ln(p_j).$$

Since

$$\sum_{i=1}^n p_i = \sum_{j=1}^m p_j = 1$$

We can write,

$$S_C = \sum_{i=1}^n p_i \ln(p_i) + \sum_{j=1}^m p_j \ln(p_j)$$

Reynold and Perkins show that the most general $f(p_i)$ is $f = C \ln(p_i)$, where C is an arbitrary constant. Because the values of p_i are less than unity, the value of C is chosen to be negative to make the entropy positive. Based on the above a statistical definition of entropy can be given as :

$$S = -k \sum_i p_i \ln(p_i).$$

where k is the Boltzmann constant. It may be given as R/N . Its value is $1.38 \times 10^{-23} \text{ JK}^{-1}$

[R = Universal gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$) and N_A = Avogadro number ($6.023 \times 10^{23} \text{ mol}^{-1}$)].

• 1.15. THERMODYNAMIC OR KELVIN SCALE OF TEMPERATURE

It follows from Carnot's theorem that the efficiency of a reversible engine is solely a function of the two temperatures between which it works and does not depend in any way on the nature and properties of the working substance.

This led William Thomson who later became Lord Kelvin to show that it is possible to define temperature in terms of energy with the aid of Carnot theorem. The scale he obtained in 1894 is independent of the nature and properties of any substance. This scale of temperature is known as absolute scale of temperature, in the sense that it is different from conventional temperature scale (which depends on the nature and properties of the substance). This Kelvin's scale of temperature is also known as thermodynamic scale of temperature or work scale of temperature. This scale serves as the standard scale in terms of which all temperature measurements must ultimately be expressed. To define this scale of temperature, we proceed as follows :

Let us consider a reversible engine working between two temperatures θ_1 and θ_2 on any scale. If η be its efficiency, then

$$\eta = \frac{Q_1 - Q_2}{Q_1}$$

$= f(\theta_1, \theta_2)$ according to Carnot's theorem.

Hence, it follows that,

$$1 - \frac{Q_2}{Q_1} = f(\theta_1, \theta_2)$$

where, f denotes some function of θ_1 and θ_2 .

Clearly $\frac{Q_2}{Q_1}$ and, therefore, $\frac{Q_1}{Q_2}$ must be a function of these two temperatures θ_1 and θ_2 . Therefore,

$$\frac{Q_1}{Q_2} = F(\theta_1, \theta_2) \quad \dots(1)$$

where, F is some other function of θ_1 and θ_2 .

If the reversible engine works between θ_2 and θ_3 ($\theta_2 > \theta_3$), then we have,

$$\frac{Q_2}{Q_3} = F(\theta_2, \theta_3) \quad \dots(2)$$

Multiplying equations (1) and (2), we get

$$\frac{Q_1}{Q_2} \times \frac{Q_2}{Q_3} = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3)$$

or

$$\frac{Q_1}{Q_3} = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3)$$

But $\frac{Q_1}{Q_3}$ can be represented by $F(\theta_1, \theta_3)$ for we may employ the reversible engine to work between the temperatures θ_1 and θ_3 .

$$\text{Therefore, } F(\theta_1, \theta_3) = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3) \quad \dots(3)$$

Equation (3) is known '**functional equation**'.

As there is no θ_2 on the left hand side, it enables us to choose the form of the function F such that θ_2 may disappear from the right hand side when substitution is made of this new form for F in equation (3).

Choosing the form for $F(\theta_1, \theta_2)$ to be $\frac{\psi(\theta_1)}{\psi(\theta_2)}$, where ψ is another function which solely depends upon temperature, we have

$$F(\theta_1, \theta_2) = \frac{\psi(\theta_1)}{\psi(\theta_2)},$$

and

$$F(\theta_2, \theta_3) = \frac{\psi(\theta_2)}{\psi(\theta_3)}.$$

Hence,

$$F(\theta_1, \theta_2) \times F(\theta_2, \theta_3) = \frac{\psi(\theta_1)}{\psi(\theta_2)} \times \frac{\psi(\theta_2)}{\psi(\theta_3)} = \frac{\psi(\theta_1)}{\psi(\theta_3)}$$

Thus, by choosing $F(\theta_1, \theta_2)$ as $\frac{\psi(\theta_1)}{\psi(\theta_2)}$, we can eliminate θ_2 from the right side of equation (3). The fact that $F(\theta_1, \theta_2)$ can be expressed as $\frac{\psi(\theta_1)}{\psi(\theta_2)}$, carries an important consequence, for it involves the simple relation,

$$F(\theta_1, \theta_2) = \frac{Q_1}{Q_2} = \frac{\psi(\theta_1)}{\psi(\theta_2)}$$

Since temperature can be measured in terms of any property which depends upon it, we can make use of the temperature dependent function ' ψ ' for measuring temperature. Assuming that $\psi(\theta)$ represents temperature Γ on a scale called the absolute scale of temperature, we have

$$\frac{Q_1}{Q_2} = \frac{\Gamma_1}{\Gamma_2} \quad \dots(4)$$

Equation (4) defines the absolute scale of temperature mathematically. This new scale of temperature is such that, "*any two temperatures on this scale bear to each other the same ratio as the quantities of heat taken in and rejected by a reversible heat engine working between these two temperatures.*"

In terms of this scale, the efficiency of the reversible engine is given by

$$\begin{aligned} \eta &= \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{\Gamma_2}{\Gamma_1} \\ &= \frac{\Gamma_1 - \Gamma_2}{\Gamma_1} \end{aligned}$$

where Γ_1 and Γ_2 are the two temperatures on the absolute scale between which the engine works.

Suppose $Q_2 = 0$, then $\eta = 1$ or in other words, the whole quantity of heat Q_1 absorbed at the higher temperature is converted into external work.

Also $\eta = 1$, when $\Gamma_2 = 0$. So, *this temperature of the sink, when the efficiency of the engine is unity corresponds to the zero of the absolute scale of temperature*. This zero temperature really forms the limit of the lowest temperature that we can think of because if Γ_2 is less than zero i.e., negative, then it will mean that more heat is being converted into work than what is absorbed at a higher temperature, which is contrary to the second law of thermodynamics.

It has been seen that the absolute scale of temperature is identical with the perfect gas scale. Hence, it is in this indirect way that this absolute scale can be realized practically. In order to make the two scales exactly identical it is only necessary to make the size of a degree the same on both the scales, viz., ice point and the steam point on the thermodynamics scale differ by 100 degrees.

$$\frac{Q_{steam}}{Q_{ice}} = \frac{\Gamma_{steam}}{\Gamma_{ice}} = \frac{\Gamma_{ice} + 100}{\Gamma_{ice}}$$

• 1.16. NERNST HEAT THEOREM

Nernst heat theorem gives the variation of enthalpy change (ΔH) and free energy change (ΔG) of a system with decrease of temperature. According to Gibbs-Helmholtz equation,

$$\Delta G = \Delta H + T \left(\frac{\partial (\Delta G)}{\partial T} \right)_P$$

From this equation, it is evident that at absolute zero, i.e., when $T = 0$, $\Delta G = \Delta H$. However, Nernst observed that as the temperature is lowered towards absolute zero, the value of $\partial(\Delta G)/\partial T$ decreases and then approaches zero asymptotically. This means that ΔG and ΔH are not only equal to the absolute zero but the values approach each other asymptotically in the vicinity of this temperature. This result is known as *Nernst heat theorem*. Mathematically, it may be expressed as:

$$\lim_{T \rightarrow 0} \frac{d(\Delta G)}{dT} = \lim_{T \rightarrow 0} \frac{d(\Delta H)}{dT} = 0 \quad \dots(1)$$

Graphically, the result may be represented by fig. (2). In fig. (2), ΔG has been shown to be greater than ΔH at temperature away from absolute zero. However, the reverse is also possible because $\partial(\Delta G)/\partial T$ can be both positive or negative.

Since gases do not exist at absolute zero, this means that the heat theorem is not applicable to gases. Similarly, it has been found to be inapplicable to liquids also. Nernst heat theorem is applicable to solids only.

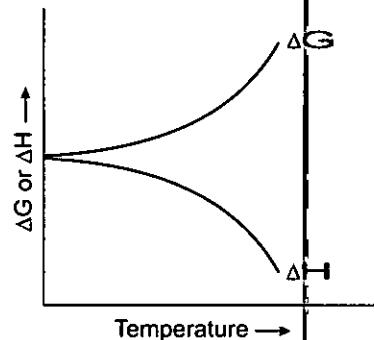


Fig. 2. Nernst heat theorem

• 1.17. THIRD LAW OF THERMODYNAMICS

[I] Third Law of Thermodynamics

According to third law of thermodynamics, *The entropy of all perfectly crystalline solids may be taken as zero at the absolute zero temperature.*

This law is also stated as follows :

Every substance has finite positive entropy but at the absolute zero of temperature, the entropy may become zero and in fact it does become zero in case of perfectly crystalline solids.

[II] Importance of Third Law of Thermodynamics

Calculation of absolute entropies from heat capacity data : It helps us in the calculation of the absolute entropies of chemical compounds at any desired temperature. This is shown as under:

The infinitesimal entropy change is given by

$$dS = \frac{dq}{T} \quad \dots(1)$$

But $C_P = \frac{dq}{dT}$ so that $dq = C_P dT$

Substituting this value in equation (1), we have

$$dS = \frac{C_P dT}{T}$$

Hence, the entropy change of a substance when its temperature changes from absolute zero to temperature (T) can be obtained from the equation,

$$\int_{S=S_0}^{S=S} dS = \int_{T=0}^{T=T} C_P \frac{dT}{T}$$

or $S - S_0 = \int_0^T C_P \frac{dT}{T} \quad \dots(2)$

where S_0 is the entropy of the substance at absolute zero and S is the entropy of the substance at temperature T .

According to third law of thermodynamics, $S_0 = 0$.

$$\therefore S = \int_0^T C_P \frac{dT}{T} \\ = \int_0^T C_P d \ln T \quad \dots(3)$$

Thus, the entropy (S) of the substance at temperature T can be calculated from the measurements of heat capacities (C_P) at a number of temperatures between 0 K to T K. The integral in equation (3) can be evaluated by plotting C_P vs $\ln T$, or $2.303 \log T$ and then measuring the area under the curve between $T = 0$ to $T = T$ as shown in fig. (3).

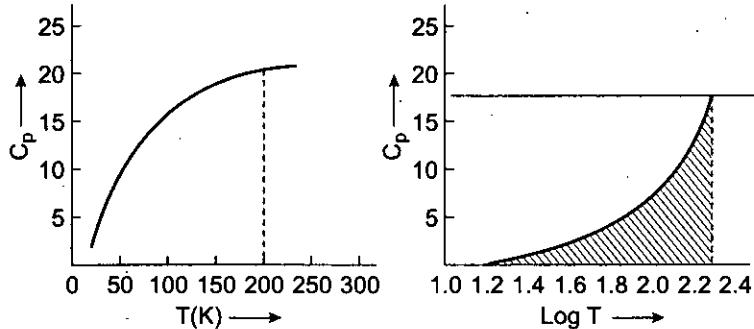


Fig. 3. Plot of heat capacities (C_P) vs T in the first case and vs $\log T$ in the second case.

If C_P is supposed to remain almost constant in the temperature range 0 to T K, equation (3) can be simplified to :

$$S = C_P \ln T = 2.303 C_P \log T$$

This equation helps to calculate the value of S directly from the values of C_P and T .

For liquid and gaseous substances : The total absolute entropy of the substance at the given temperature will be the sum of all the entropy changes which the substance has to undergo in order to reach that particular state starting from the crystalline solid at absolute zero. Thus, if a substance is gaseous at 1 atm pressure and 25°C, the entropy of the gas at 25°C will be the sum of the following entropies involved at different stages :

- (1) The entropy of heating the crystalline solid from $T = 0$ to $T = T_m$, the melting point;
- (2) The entropy of melting, $\frac{\Delta H_m}{T_m}$ is latent heat of melting;
- (3) The entropy of heating the liquid from T_m to T_b , the boiling point;
- (4) The entropy of vaporization, $\frac{\Delta H_v}{T_b}$, where ΔH_v is latent heat of vaporisation;
- (5) The entropy of heating the gas from T_b to 25°C (i.e., 298 K).

Thus, the complete expression for the calculation of entropy at temperature T may be written as :

$$S = \underbrace{\int_0^{T_m} C_{P(s)} d \ln T}_{1} + \underbrace{\frac{\Delta H_m}{T_m}}_{2} + \underbrace{\int_{T_m}^{T_b} C_{P(l)} d \ln T}_{3} + \underbrace{\frac{\Delta H_v}{T_b}}_{4} + \underbrace{\int_{T_b}^T C_{P(g)} d \ln T}_{5}$$

• 1.18. CONCEPT OF RESIDUAL ENTROPY

Certain chemical reactions between crystals do not give $\Delta S = 0$ at 0K, which seems to show that exceptions to this law exist. Nearly all these exceptional reactions involve either ice, carbon monoxide, nitrous oxide or hydrogen. In the crystalline state, these four substances appear to retain a finite entropy at 0K. Thus, any reaction in which one mole of ice is a product gives $\Delta S = 3.3 \text{ JK}^{-1}$, at 0K and any reaction in which 1 mole of ice is a reactant gives $\Delta S = -3.3 \text{ JK}^{-1}$ at 0K. This shows that if entropies of zero

are assigned to the other substances involved, then ice at 0K appears to have a residual entropy of 3.3 JK^{-1} . Similarly at 0K, CO has a residual entropy of 5.8 JK^{-1} , N₂O has a residual entropy of 5.8 JK^{-1} and hydrogen has a residual entropy of 6.2 JK^{-1} . This leads to the suggestion that the molecules in the crystals of the substances are not in true thermodynamic equilibrium at 0K. The molecular origin of residual entropy is well understood with the help of statistical thermodynamics.

A number of liquids are readily supercooled below their thermodynamic freezing points and can exist in this state even at 0K. For such substance the entropy change of the reaction, Crystal \rightarrow Liquid, at 0K can be determined and it has been found that liquid has a greater entropy than the crystal. Thus, the third law is also not applicable to supercooled liquids e.g., glass etc.

• 1.19. APPLICATIONS OF THIRD LAW OF THERMODYNAMICS

Third law of thermodynamics has been useful in calculating (i) the absolute entropies of solids, liquids and gases at different temperatures, and (ii) the entropy changes of chemical reactions and other processes.

(1) Determination of absolute entropy of solids : The variation of entropy with temperature at constant pressure is given by,

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_p}{T} \quad \dots (1)$$

For a pure crystalline substance,

$$\lim_{T \rightarrow 0} S = 0$$

From equation (1),

$$\int_0^{S_T} dS = \int_0^T C_p \cdot \frac{dT}{T}$$

or

$$S_T = \int_0^T C_p \cdot \frac{dT}{T} = \int_0^T C_p \cdot d \log T \quad \dots (2)$$

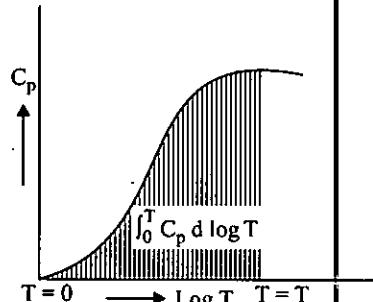


Fig. 4

In order to calculate the absolute entropy (S_T) at temperature T , we must know the values of C_p from $T = 0$ to $T = T$. The value of the integral of equation (2) can be calculated by plotting a curve between C_p and $\log T$. The area under the curve between $T = 0$ to $T = T$ gives the value of the integral as shown in fig. (4). It is not always possible to calculate the value of C_p at 0K, hence heat capacities are measured upto as low a temperature as possible, say upto 25K. The value of C_p at 0K can then be calculated from extrapolation. A curve between C_p and $\log T$ is plotted and extrapolated to 0K. The area under the curve directly gives the value of S_T as given in equation (2).

(2) Determination of absolute entropy of gases and liquids : The third law is also used to calculate the value of absolute entropies of gases and liquids at any temperature. In every case, we start with crystalline solid state at 0K, when its absolute entropy is taken to be zero. The total absolute entropy of the substance is then taken to be the sum of all the entropy changes that the substance has to undergo in order to have the given state.

Suppose we want to find the absolute entropy of a gas at $T^\circ \text{C}$ under atmospheric pressure. This is done as follows :

(i) The crystalline solid is heated from absolute zero to its fusion point. i.e., from $T = 0$ to $T = T_f$, where T_f is the fusion point. The entropy of this process is given by,

$$\Delta S_1 = \int_0^{T_f} (C_p)_s \cdot \frac{dT}{T}$$

where, $(C_p)_s$ = heat capacity of the solid. The value of ΔS_1 can be evaluated graphically as discussed above.

(ii) The entropy in changing solid into the liquid state at the fusion temperature T_f is given by,

$$\Delta S_2 = \frac{\Delta H_f}{T_f}$$

where, ΔH_f = molar latent heat of fusion.

(iii) The liquid is heated from its fusion point (T_f) to its boiling point (T_b). The entropy in this process is given by,

$$\Delta S_3 = \int_{T_f}^{T_b} (C_p)_l \cdot \frac{dT}{T}$$

where, $(C_p)_l$ = heat capacity of the substance in the liquid state.

(iv) The entropy in changing the liquid into the gaseous state at the boiling point (T_b) is given by,

$$\Delta S_4 = \frac{\Delta H_v}{T_b}$$

where, ΔH_v = molar latent heat of vaporisation.

(v) The entropy involved in heating the gas from temperature T_b to the given temperature T is given by,

$$\Delta S_5 = \int_{T_b}^T (C_p)_g \cdot \frac{dT}{T}$$

where, $(C_p)_g$ = heat capacity of the substance in the gaseous state.

The absolute entropy (S_T) of the gas at temperature T is given by,

$$S_T = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$$

$$S_T = \int_0^{T_f} (C_p)_s \cdot \frac{dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^T (C_p)_l \cdot \frac{dT}{T} + \frac{\Delta H_v}{T_b} + \int_{T_b}^T (C_p)_g \cdot \frac{dT}{T}$$

The absolute entropy (S_T) of a liquid at a temperature T is given by,

$$S_T = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$= \int_0^{T_f} (C_p)_s \cdot \frac{dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^T (C_p)_l \cdot \frac{dT}{T}$$

The absolute entropy (S_T) of a solid at temperature T is given by,

$$S_T = \int_0^T (C_p)_s \cdot \frac{dT}{T}$$

Absolute entropies of some of the elements and compounds in their standard states at 25°C, calculated from the third law of thermodynamics, are given in table 1.

Table - 1. Standard absolute entropies (S°) of elements and compounds at 298K

Substance	Absolute entropy (JK ⁻¹ mol ⁻¹)	Substance	Absolute entropy (JK ⁻¹ mol ⁻¹)
Hydrogen (g)	130.60	Mercury (l)	77.40
Nitrogen (g)	191.62	Mercury (g)	174.83
Oxygen (g)	205.01	Mercuric chloride (s)	144.76
Hydrogen chloride (g)	186.22	Mercurous chloride (s)	98.32
Hydrogen bromide (g)	199.15	Cuprous iodide (s)	6.65
Hydrogen iodide (g)	206.27	Lead bromide (s)	161.50
Carbon (diamond)	2.43	Silver bromide (s)	96.11
Carbon (graphite)	5.69	Silver chloride (s)	107.15
Water (l)	70.29	Silver iodide (s)	115.57
Water (g)	188.74	Silver oxide (s)	121.75
Ammonia (g)	192.46	Ferric oxide (s)	89.95
Carbon monoxide (g)	197.90	Cupric oxide (s)	43.55
Carbon dioxide (g)	213.80	Magnesium oxide (s)	27.00
Nitric oxide (g)	210.45	Mercuric oxide (s)	71.46
Sulphur dioxide (g)	247.86	Sodium chloride (s)	72.38
Sodium (s)	51.04	Potassium chloride (s)	82.62
Magnesium (s)	32.51	Potassium bromide (s)	93.72
Sulphur (rhombic)	31.88	Methane (g)	186.14
Sulphur (monoclinic)	32.55	Ethane (g)	229.49
Chlorine (g)	222.96	Ethylene (g)	185.35
Bromine (g)	245.34	Acetylene (g)	201.10
Bromine (l)	153.97	Methanol (l)	126.69
Aluminium (s)	28.32	Ethanol (l)	160.66
Iron (s)	27.15	Benzene (l)	172.79
Copper (s)	83.34	Phenol (l)	142.24
Silver (s)	42.67	Acetone (l)	200.03
Iodine (s)	116.73	Acetic acid (l)	159.82
Iodine (g)	260.62	Methyl chloride (g)	234.05
Zinc (s)	41.00	Methyl chloride (l)	245.22
Lead (s)	64.85	Ether (l)	85.27

Ex. 1. C_V for uranium metal is $3.04 \text{ JK}^{-1} \text{ mol}^{-1}$ at 20K . Calculate the absolute entropy of the metal in $\text{JK}^{-1} \text{ mol}^{-1}$ at 20K .

Solution : At low temperature, ($0 < T < 20\text{K}$), $C_P = C_V = aT^3$

[Debye's $-T^3$ law]

$$a = C_V / T^3 = 3.04 \text{ JK}^{-1} \text{ mol}^{-1} / (20\text{K})^3 = 38.03 \times 10^{-5} \text{ JK}^{-4} \text{ mol}^{-1}$$

$$\text{Hence, } C_P = aT^3 = (38.03 \times 10^{-5} \text{ J mol}^{-1} \text{ K}^{-4})T^3$$

$$\text{We know that, } dS = C_P \frac{dT}{T} = 38.03 \times 10^{-5} \text{ J mol}^{-1} \text{ K}^{-4} T^2 dT$$

$$\text{or } S_{20} - S_0 = 38.03 \times 10^{-5} \text{ JK}^{-4} \text{ mol}^{-1} (20\text{K})^3 / 3$$

$$\text{or } S_{20} = 1.01 \text{ JK}^{-1} \text{ mol}^{-1} \quad [\because S_0 = 0]$$

Ex. 2. Show that the entropy of any substance at very low temperatures ($0 < T < 20\text{K}$), where Debye's relation for heat capacities of crystals is valid, is one-third of the molar heat capacity.

Solution : At low temperature ($0 < T < 20\text{K}$),

$$C_P = aT^3$$

[The Debye- T^3 law]

$$\text{We know that, } dS = C_P \frac{dT}{T}$$

$$\therefore \int_0^T dS = \int_0^T \frac{C_P}{T} \cdot dT$$

$$\text{or } S_T - S_0 = \int_0^T \frac{dT^3}{T} dT$$

$$= a \int_0^T T^2 dT = \frac{a}{3} T^3$$

$$\text{or } S_T = aT^3 / 3$$

$$\text{Evidently, } S_T = C_P / 3$$

[$\because S_0 = 0$]

Ex. 3. The heat capacity, C_P (in $\text{JK}^{-1} \text{ mol}^{-1}$) of a substance is given by the following equations :

$$C_P(s) = 16.74 \times 10^{-5} T^3 \quad (0 < T < 50\text{K})$$

$$C_P(s) = 20.92 \quad (50 < T < 150 \text{ K})$$

$$C_P(l) = 25.10 \quad (150 < T < 400 \text{ K})$$

At the melting point (150K), $\Delta H_f = 1255.2 \text{ J mol}^{-1}$. Calculate the absolute entropy of the substance in the liquid state at 300 K .

$$\text{Solution : } \Delta S_1 = \int_0^{50} \frac{C_P(s)}{T} dT = \int_0^{50} \frac{16.74 \times 10^{-5} T^3}{T} dT \quad (\text{Debye's } T^3 \text{ law})$$

$$= \left[\frac{16.74 \times 10^{-5} T^3}{3} \right]_0^{50}$$

$$= 5.58 \times 10^{-5} \times (50)^3 = 6.97 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta S_2 = \int_{50}^{150} \frac{C_P(s)}{T} dT = 20.92 \text{ JK}^{-1} \text{ mol}^{-1} \ln \left(\frac{150}{50} \right)$$

$$= 20.92 \text{ JK}^{-1} \text{ mol}^{-1} \times 1.09861 = 22.98 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta S_3 = \Delta S_f = \frac{1255.2 \text{ J mol}^{-1}}{150\text{K}} = 8.37 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta S_4 = \int_{150}^{300} \frac{C_P(l)}{T} dT = 25.10 \text{ JK}^{-1} \text{ mol}^{-1} \ln \left(\frac{300}{150} \right)$$

$$= 25.10 \text{ JK}^{-1} \text{ mol}^{-1} \times 0.6931 = 17.40 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\text{Hence, } \Delta S = S_T - S_0 = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$$

$$\therefore S_T = 6.97 + 22.98 + 8.37 + 17.40 = 55.73 \text{ JK}^{-1} \text{ mol}^{-1} \quad (\because S_0 = 0)$$

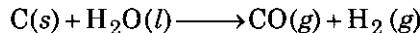
(3) Determination of entropy changes accompanying chemical reactions:

The values of absolute entropies can be utilised in calculating the entropy changes accompanying chemical reactions.

Ex. 1. For the reaction, $Pb(s) + Br_2(l) = PbBr_2(s)$, the values of absolute entropies of Pb , Br_2 and $PbBr_2$ are 15.5, 36.8 and 38.6 e.u./mole, respectively. Calculate the increase in entropy.

Solution : We know that, $\Delta S^\circ = \Delta S^\circ_{PbBr_2} - S^\circ_{Pb} - S^\circ_{Br_2}$
 $= 38.6 - 15.5 - 36.8 = - 13.7$ e.u./mole.

Ex. 2. Calculate the standard entropy change of the reaction,



Solution : From table-1, the total standard entropy of products

$$\begin{aligned} &= 197.90 \text{ JK}^{-1} \text{ mol}^{-1} \text{ for CO} + 130.60 \text{ JK}^{-1} \text{ mol}^{-1} \text{ for H}_2 \\ &= 328.50 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

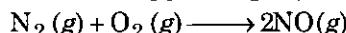
From the same table, the total standard entropy of reactants

$$\begin{aligned} &= 5.69 \text{ JK}^{-1} \text{ mol}^{-1} \text{ for C(s)} + 70.29 \text{ JK}^{-1} \text{ mol}^{-1} \text{ for H}_2O(l) \\ &= 75.98 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

The standard entropy change (ΔS°) of the reaction is given by

$$\begin{aligned} \Delta S^\circ_T &= \Sigma S^\circ_{Products} - \Sigma S^\circ_{Reactants} \\ &= 328.50 - 75.98 = 252.52 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

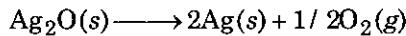
Ex. 3. Calculate the standard entropy change of the reaction,



Solution : The standard entropy change (ΔS°) for the reaction is given by

$$\begin{aligned} \Delta S^\circ &= S^\circ_{Products} - S^\circ_{Reactants} \\ &= (2 \text{ mol} \times 210.45 \text{ JK}^{-1} \text{ mol}^{-1}) - (1 \text{ mol} \times 191.62 \text{ JK}^{-1} \text{ mol}^{-1}) \\ &\quad + 1 \text{ mol} \times 205.01 \text{ JK}^{-1} \text{ mol}^{-1} \\ &= 24.27 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

Ex. 4. Calculate the standard entropy change of the reaction,



Solution : The standard entropy change (ΔS°) of the reaction is given by

$$\begin{aligned} \Delta S^\circ &= \Sigma S^\circ_{Products} - \Sigma S^\circ_{Reactants} \\ &= (2 \text{ mol} \times 42.67 \text{ mol}^{-1} \text{ JK}^{-1}) + 1/2 \text{ mol} \times 205.01 \text{ JK}^{-1} \text{ mol}^{-1} \\ &\quad - (1 \text{ mol} \times 121.75 \text{ JK}^{-1} \text{ mol}^{-1}) \\ &= 66.09 \text{ JK}^{-1} \text{ mol}^{-1}. \end{aligned}$$

Ex. 5. Calculate the standard entropy change in the formation of sodium chloride from its elements at 25°C.

Solution : The reaction is : $Na(s) + \frac{1}{2} Cl_2(g) = NaCl(s)$

$$\begin{aligned} \Delta S^\circ &= S^\circ [NaCl(s)] - \{S^\circ [Na(s)] + \frac{1}{2} S^\circ [Cl_2(g)]\} \\ &= 72.38 - [51.04 + 1/2 (222.96)] = 72.38 - (51.04 + 111.48) \\ &= - 90.14 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

(4) Calculation of free energy change : Once the entropy change for a certain reaction is known, the free energy can also be calculated by means of the relation,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where, ΔH° = heat of reaction at constant pressure.

• SUMMARY

- System is a specified portion of matter which is separated from the rest of the universe with a bounding surface.

- **Surroundings :** The rest of the universe which might be in a position to exchange matter and energy with the system is called surroundings.
- **Extensive variables :** The variable of a system which depends upon the amount of the substance(s) present in the system is known as extensive variable, e.g. mass, volume, energy etc.
- **Intensive variables :** The variable of a system which is independent of the amount of the substance present in the system is known as intensive variable, e.g. pressure, temperature, viscosity, refractive index etc.
- If a process is carried out infinitesimally slowly so that the driving force is only infinitesimally greater than the opposing force, it is called a reversible process.
- If the temperature of the system remains constant during each step of a process, it is called an isothermal process.
- If the heat neither enters nor leaves the system during any step of the process, it is called an adiabatic process.
- **Zeroth Law of thermodynamics** states that, if body A is in equilibrium with body C and body B is also in equilibrium with body C, then bodies A and B are in equilibrium with each other.
- **First law of thermodynamics :** The total energy and mass of an isolated system remains constant, though one form of energy can be converted into another form. Mathematically,

$$dU = dQ - dW$$

- The relation between ΔH and ΔU is $\Delta H = \Delta U + P\Delta V$.
- In an isothermal expansion of an ideal gas, the work done is given by

$$W_m = 2303 nRT \log \frac{V_2}{V_1} = 2303 nRT \log \frac{P_1}{P_2}$$

- When a system after completing a series of changes returns to its original state, it is called a cyclic process.
- The degree of disorder of a system is called its entropy.
- The net entropy change of the universe is constant in a reversible process.
- The entropy of the universe always tends to a maximum.
- **Third law of thermodynamics :** Every substance has a finite entropy but at the absolute zero of temperature, the entropy may become zero and in fact it does become zero in case of perfectly crystalline solids.

• STUDENT ACTIVITY

1. State and explain first law of thermodynamics.

2. Define isothermal and adiabatic processes.

3. Define extensive and intensive variables.

4. What do you know about entropy ?

5. Explain thermodynamic scale of temperature.

6. State and explain third law of thermodynamics.

7. What is residual entropy ?

• TEST YOURSELF

Answer the following questions :

1. Define thermodynamics. State its main objectives and limitations.
2. Differentiate between the terms 'isolated system' and 'closed system' as used in thermodynamics.
3. Explain the term 'isolated system'.
4. Distinguish clearly between extensive and intensive properties.
5. Write short note on the criteria for reversible and irreversible processes.
6. Explain what is a reversible process according to thermodynamics ?
7. Write if the following processes are reversible or not ?
 - (i) Mixing of gases by diffusion,
 - (ii) Dissolution of a solute in pure solvent.
 - (iii) Expansion of a gas in vacuum.
 - (iv) Melting of ice without rise in temperature
8. What are isothermal and adiabatic changes or differentiate clearly between isothermal and adiabatic processes ?
9. What is meant by an adiabatic change ?
10. Explain the difference between isobaric and isochoric processes.
11. Define a cyclic process.
12. Explain the terms :
 - (i) Thermodynamic system
 - (ii) Types of thermodynamic system.
13. Discuss the nature of work and heat.
14. State and explain first law of thermodynamics. Give its mathematical statement also.
15. Write a short note on first law of thermodynamics.
16. Write an explanatory note on the following :
 - (i) Internal energy
 - (ii) Enthalpy
 - (iii) Heat capacity
17. Derive the relation $\Delta H = \Delta U + P\Delta V$.
18. Derive the relation $C_P - C_V = R$.
19. Derive an expression for maximum work done during an isothermal reversible expansion of n moles of an ideal gas.
20. Derive the expression $PV^\gamma = \text{constant}$.

21. Derive the expression for the maximum work done in an adiabatic reversible expansion of an ideal gas.

22. Discuss thermodynamic scale of temperature.

23. Describe zeroth law of thermodynamics.

24. State and explain second law of thermodynamics.

25. What do you mean by residual entropy ?

26. State and explain entropy from the point of view of second law of thermodynamics.

27. Write a short note on entropy.

28. Discuss and derive the various entropy changes for the following processes :

 - Change from solid to liquid phase
 - Change from liquid to vapour phase.
 - Change for reversible and irreversible processes.

29. Discuss the criteria of spontaneity or irreversibility and conditions of equilibrium.

30. Describe briefly the applications of third law of thermodynamics.

31. Describe Nernst heat theorem.

32. State and explain third law of thermodynamics.

33. Find the work done when 2 moles of an ideal gas expand isothermally from 2 litres to 5 litres against a constant pressure of 1 atm at 298 K.

34. Calculate the entropy change involved in isothermal expansion of 2 moles of the gas from a volume of 5 litres to a volume of 50 litres at 30°C.

35. Calculate the entropy increase in the evaporation of a mole of water at 100°C (Heat of vaporisation = 540 cal g⁻¹).

36. Thermodynamics is applicable to which system :

 - Microscopic systems only
 - Macroscopic systems only
 - Homogeneous systems only
 - Heterogeneous systems only

37. A thermos flask is an example of :

 - Isolated system
 - Closed system
 - Open system
 - Heterogeneous system

38. The dimensions of entropy is :

 - $\text{work} \times \text{temperature}$
 - energy
 - $\text{energy} \times \text{temperature}$
 - work

39. The entropy change at constant pressure is given by :

 - $C_p \log \frac{T_2}{T_1}$
 - $C_V \log \frac{T_2}{T_1}$
 - $nRT \log \frac{V_2}{V_1}$
 - $nRT \log \frac{V_1}{V_2}$

40. Which of the following is not an intensive property ?

 - Pressure
 - Concentration
 - Density
 - Volume

41. Which of the following condition holds good for an adiabatic process ?

 - $dQ < 0$
 - $dQ > 0$
 - $dQ = 0$
 - $dQ = 1$

42. The enthalpy change of a reaction is independent of :

 - State of the reactants and products
 - Nature of the reactants and products
 - Initial and final enthalpy change of the reaction
 - Different intermediate reactions

43. When the total energy change in an isothermal cycle is zero, it represents :

 - A reversible cycle
 - An adiabatic change
 - A thermodynamic equilibrium
 - An irreversible cycle

44. The work done when 1 mole of a gas expands reversibly and isothermally from 5 atm to 1 atm at 300 K is :

 - 4015 J
 - + 4015 J
 - Zero
 - 150 J

45. The first law of thermodynamics may be given as :

 - $U = q - w$
 - $U = q + w$
 - $\Delta U = q + w$
 - $\Delta U = q - w$

46. When water is cooled to ice, its entropy :

 - Increases
 - Decreases
 - Remains the same
 - Becomes zero

47. For a spontaneous process :
 (i) $\Delta G > 0$ (ii) $\Delta G < 0$ (iii) $\Delta G = 0$ (iv) None of these
48. The entropy change of a spontaneous process is :
 (i) positive (ii) negative (iii) zero (iv) none of these
49. The entropy of a solid at 0K is :
 (i) positive (ii) zero (iii) negative (iv) none of these
50. Which is the correct unit for entropy ?
 (i) kJ mol^{-1} (ii) $\text{JK}^{-1} \text{mol}$ (iii) $\text{JK}^{-1} \text{mol}$ (iv) kJ mol^{-1}
51. C_p , C_V and R are related as :
 (i) $C_p + C_V = R$ (ii) $C_p - C_V = R$
 (iii) $C_p \times C_V = R$ (iv) $\frac{C_p}{C_V} = R$
52. Fill in the blanks :
 (i) In a process $\Delta H = 100 \text{ kJ}$ and $\Delta S = 100 \text{ JK}^{-1}$ at 400 K. The value of ΔG will be
 (ii) A spontaneous process occurs with a in free energy.
 (iii) The change in free energy is a measure of net
 (iv) For solid, liquid and gas, the entropy of the system increases in the order
 (v) The entropy of a pure crystal is zero at absolute zero. This is a statement of law of thermodynamics.
 (vi) Entropy is a measure of of the molecules of the system.
 (vii) A spontaneous change is accompanied by of internal energy or enthalpy.
 (viii) In an adiabatic process can flow into or out of the system.
 (ix) In an adiabatic process must change.
 (x) For the reaction $\text{H}_2 + \text{I}_2 = 2\text{HI}$, ΔH is equal to

ANSWERS

33. 1085 cal 34. 38.29 JK^{-1} 35. $26.06 \text{ cal K}^{-1} \text{ mol}^{-1}$ 36. (ii) 37. (i) 38. (iii)
 39. (i) 40. (iv) 41. (ii) 42. (iv) 43. (i) 44. (i) 45. (iv) 46. (ii) 47. (ii) 48. (i)
 49. (ii) 50. (iii) 51. (ii) 52. (i) 60 kJ (ii) decrease (iii) work done (iv) solid < liquid < gas (v) third (vi) randomness or disorder (vii) decrease (viii) no heat
 (ix) temperature (x) ΔU



2

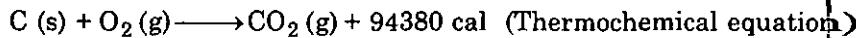
THERMOCHEMISTRY

LEARNING OBJECTIVES

- Heat of Reaction (Enthalpy of Reaction)
- Heat of Formation (Enthalpy of Formation)
- Heat of Combustion (Enthalpy of Combustion)
- Bond-, Dissociation- and Resonance Energy
- Kirchoff's Equation
- Flame and Explosion Temperature
 - Summary
 - Student Activity
 - Test Yourself

It is a well known fact that chemical reactions are usually accompanied by energy change. These changes occur, ordinarily in the form of evolution or absorption of heat. 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 study of the conversion of chemical energy into heat energy or vice-versa is known as thermochemistry.

An equation which shows the amount of heat change (evolved or absorbed) in the chemical reaction is called a *thermochemical equation*.



A thermochemical equation must essentially (i) be balanced (ii) mention the physical state of the reactants and products. The physical states are represented by the symbols (s), (l), (g) and (aq.) for solid, liquid, gas and aqueous states respectively. (iii) gives the values of ΔH or ΔE corresponding to the quantities of substances given by the equation. Such an equation can be multiplied, added or subtracted just like simple algebraic equation.

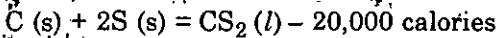
• 2.1. HEAT OF REACTION (ENTHALPY OF REACTION*)

Heat of reaction is defined as the, "the amount of heat evolved or absorbed in a reaction when the number of moles of reactants as represented by the balanced equation have completely reacted."

For example, $C(s) + O_2(g) = CO_2(g) + 94380 \text{ calories}$

According to the equation, when 12 g of carbon reacts with 32 g of oxygen to form 44 g of carbon dioxide, 94,380 calories of heat is evolved. Thus, the heat of reaction is 94,380 calories.

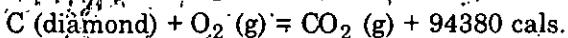
Similarly, in the equation :



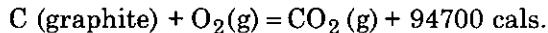
When 12 g of carbon reacts with 64 g of sulphur to form 76 g of carbon disulphide, 20,000 calories of heat is absorbed. Thus, the heat of reaction is -20,000 cal.

Heat of reaction depends on the following factors :

(i) Physical state of substances : Heat of reaction is different for different physical state of substances, e.g.,



• Enthalpy of reaction : It is defined as the enthalpy change when the number of gram moles of the substances as specified by the chemical reaction have completely reacted.



(ii) **Temperature** : The heat of reaction varies with temperature due to variation in its specific heat and is related by Kirchoff's equation, i.e.,

$$\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$$

where, ΔH_1 and ΔH_2 are the heats of reaction at temperatures T_1 and T_2 respectively. ΔC_P is difference in the heat capacities of products and reactants.

(iii) The heat of reaction depends on the fact whether the reaction is carried out at constant pressure (ΔH) or at constant volume (ΔE). The two are related by the expression :

$$\Delta H = \Delta E + \Delta nRT$$

where, Δn = Difference in the number of moles of gaseous products and gaseous reactants.

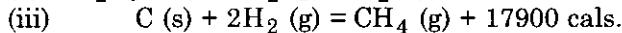
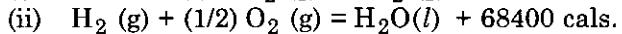
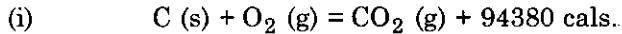
T = Absolute temperature.

The standard state of a substance is taken as its natural state at 25°C , at one atmospheric pressure. It is represented by ΔH° .

• 2.2. HEAT OF FORMATION (ENTHALPY OF FORMATION)

Heat of formation is defined as, "the amount of heat evolved or absorbed (or enthalpy change) when one mole of a compound is formed from its constituent elements."

For example :



The heats of formation of $CO_2(g)$, $H_2O(l)$ and $CH_4(g)$ are 94380 cals, 68400 cals and 17900 cals, respectively.

In the equation :



The heat of formation of HCl is not 44000 cals., but $44000/2$, i.e., 22,000 cals, as one mole of HCl is formed by the evolution of 22,000 cals, of heat.

If ion is formed during the reaction in place of molecule then it is called enthalpy of formation of ion.

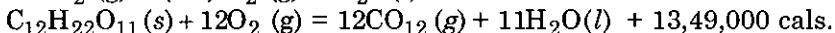
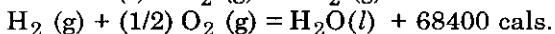
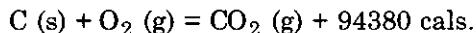
Standard heat of formation or standard enthalpy of formation. The standard enthalpy of formation of compound is the enthalpy change when one mole of a compound is formed from its elements, all substances being in their standard states. It is represented by ΔH_f° . The standard state of any substance is taken as its natural state at 298 K and under one atmospheric pressure.

By convention, the standard heat of formation of all elements is taken as zero.

• 2.3. HEAT OF COMBUSTION (ENTHALPY OF COMBUSTION)

Heat of combustion is defined as the, "amount of heat evolved (or enthalpy change) when 1 mole of a compound is burnt completely in excess of air or oxygen at a given temperature and under normal pressure."

For example :



The heats of combustion of carbon, hydrogen and cane sugar are 94380 cals., 68400 cals. and 1349000 cals. respectively.

[I] Determination of Heat of Combustion

The calorimeter used to carry out the determination of heat of combustion is called a **bomb calorimeter** (fig. 1). The inner vessel or the bomb is a strong walled tight fitting air tight vessel coated inside with gold or platinum or some other non-oxidisable material. The cover can be fitted tightly to the vessel by means of a metal lid screwed down on a lead washer. A weighed quantity of the substance is taken in a platinum cup C which is supported on a rod R. This bomb is placed inside a double

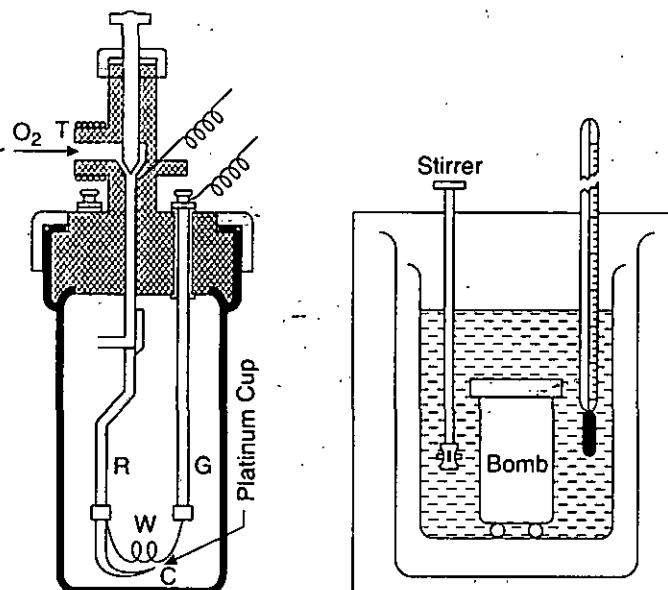


Fig. 1. Bomb calorimeter

jacketed polished and metallic calorimeter and the substance is burnt electrically by passing a current through a copper wire W from which heat is conducted to the substance through a platinum loop touching it. A mechanical stirrer is also provided as shown.

When the current is passed, the temperature of water starts rising. The rise in temperature of water in the calorimeter is noted by means of an accurate thermometer, upto an accuracy of $\pm 0.01^\circ$. The difference between the final and initial temperatures gives the rise of temperature. The heat capacity of the calorimeter system is obtained by taking and burning a known weight of a substance, whose heat of combustion is known. Generally, we take benzoic acid of very high purity, whose heat of combustion is taken to be 771.2 kcal.

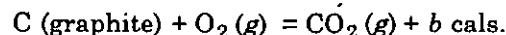
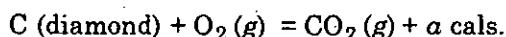
If the heat capacity of the calorimeter system is Z and ΔT is the rise in temperature produced by burning w g of the given substance of molecular weight M , then

$$\text{Heat of combustion} = Z \times \Delta T \times \frac{M}{w} \text{ calories}$$

[III] Applications of Heat of Combustion

(i) **Calculation of heat of formation :** The heats of combustion of organic compounds can be determined very easily, so these values are used to calculate their heats of formation. The direct determination of these is often impossible.

(ii) **Calculation of heat of transition :** Suppose we want to calculate the heat of transition of diamond into graphite. It is done as follows :



On subtracting the two equations, we get,



\therefore Heat of transition = $(a - b)$ cals.

(iii) **Determination of calorific values of foods and fuels :** The heat of combustion helps us in calculating the calorific values* of foods and fuels.

(iv) **In deciding constitution :** Heat of combustion of organic compounds is to a large extent an additive property and so has proved very valuable in deciding their

* The amount of heat produced in calories (or joule) when 1 g of a substance is completely burnt. It is expressed in cal g^{-1} , kcal g^{-1} or kJ g^{-1} .

chemical constitution.

• 2.4. BOND ENERGY, DISSOCIATION ENERGY AND RESONANCE ENERGY

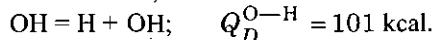
The amount of energy required to separate an atom by breaking a bond is the dissociation energy of that bond. The dissociation energy (Q_D) is dependent on the nature of the atoms united by a bond as well as the nature of the molecule. For example, the dissociation energy of a C—H bond in methane and of the same in benzene will be different because the residual portions of the two molecules are different.

[I] Bond Energy (ΔH_D)

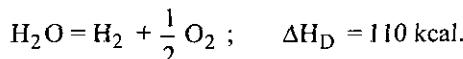
Bond energy is defined as *the average amount of energy required to dissociate bonds of that type present in one molecule of the compound or it is simply the average value of the dissociation energies of a given bond in a series of different dissociating species*. Bond energy is also known as the enthalpy of formation of the bond and the enthalpy of formation of a bond of a particular type is largely an additive property. For example, in water the dissociation energy of separating a H-atom is 120.0 kcal., i.e.,



But when second H-atom is separated from the residual OH group, a similar O—H bond is broken as before, but the dissociation energy is different.



But the enthalpy of dissociation of water into hydrogen and oxygen is 100 kcal., i.e.,



If we take the average of dissociation energies of the two bonds of O—H in water, we have

$$\frac{Q_D + Q_D'}{2} = \frac{120 + 101}{2} = 110.5 \text{ kcal.},$$

which is practically equal to the bond energy (ΔH_D).

Bond energies are very useful in the calculation of thermal changes in chemical processes. Some of the values of bond energies are given in the table-1.

Table-1. Bond energies (ΔH_D) in kcals.

Bond	ΔH_D	Bond	ΔH_D
C—C	83.1	H—H	103.2
C = C	140.0	O—O	33.0
C ≡ C	198.0	O = O	118.0
C—O	84.0	Cl—H	103.0
C = O	173.0	N ≡ N	225.0
C—H	99.0	O—H	110.5
C—N	69.5	Cl—Cl	57.8
C—Cl	78.5	Br—Br	46.0

[II] Heat of Atomisation

The standard state of an element is the state in which the element occurs at 25°C and one atmospheric pressure. The enthalpy of atomisation of an element is defined as *the amount of heat required to produce one mole of atoms in the standard state*. Some values are given in table-2.

Table-2. Enthalpies of atomisation (ΔH) in kcals.

Elements	Atomisation	ΔH
Carbon	C (s) → C (g)	170.8
Hydrogen	$\frac{1}{2}\text{H}_2$ (g) → H (g)	52.1

Oxygen	$\frac{1}{2} \text{O}_2 (\text{g}) \rightarrow \text{O} (\text{g})$	59.5
Nitrogen	$\frac{1}{2} \text{N}_2 (\text{g}) \rightarrow \text{N} (\text{g})$	113.1

[III] Calculation of Bond Energies

- (i) C—H bond energy : The heat of formation of methane is -17.9 kcal .
 (a) $\text{C} (\text{s}) + 2\text{H}_2 (\text{g}) = \text{CH}_4 (\text{g})$; $\Delta H_f = -17.9$
 also (b) $\text{C} (\text{s}) = \text{C} (\text{g})$; $\Delta H = 170.8$
 (c) $2\text{H}_2 (\text{g}) = 4\text{H} (\text{g})$; $\Delta H = 4 \times 52.1$

On rearranging and subtracting, we get

$$\text{C} (\text{g}) + 4\text{H} (\text{g}) = \text{CH}_4 (\text{g}); Q = 17.9 + 170.8 + 208.4 = 397.1 \text{ kcal.}$$

Here Q is the total net heat evolved and conversely, in breaking the four C—H bonds, the energy required is 397.1 kcal .

$$\text{C—H bond energy} = \frac{Q}{4} = \frac{397.1}{4} = 99.3 \text{ kcal.}$$

- (ii) C = C bond energy : The heat of formation of ethylene is $+12.5 \text{ kcal}$. Therefore,

- (a) $2\text{C} (\text{s}) + 4\text{H} (\text{g}) = \text{C}_2\text{H}_4 (\text{g})$; $\Delta H_f = -12.5$
- (b) $2\text{C} (\text{s}) = 2\text{C} (\text{g})$; $\Delta H = 2 \times 170.8$
- (c) $2\text{H}_2 (\text{g}) = 4\text{H} (\text{g})$; $\Delta H = 4 \times 52.1$

On rearranging and subtracting, we get

$$2\text{C} (\text{g}) + 4\text{H} (\text{g}) = \text{C}_2\text{H}_4 (\text{g})$$

$$Q = -12.5 + 2 \times 170.8 + 4 \times 52.1 = 537.5 \text{ kcal.}$$

Hence the necessary energy to break one C=C bond and four C—H bonds is 537.5 kcal .

The bond energy of 4 C—H bonds $= 4 \times 99.3 = 397.2 \text{ kcal}$.

∴ The C = C bond energy $= 537.5 - 397.2 = 140.3 \text{ kcal}$.

[IV] Resonance Energy

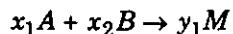
By the use of bond energies given in the above table, it is possible to calculate the heats of formation and reaction in many cases, provided the substances involved do not contain certain double bonded compounds. Whenever wave mechanical resonance is possible, the energy required to dissociate the molecule, as calculated from the above results, is too small. It is, however, necessary in such cases to make allowance for the resonance energy. Although its value varies from one compound to another, its values for different groups are given in the following table.

Groups	C_6H_6	C_{10}H_8	COOH	CO_2	COOEt
Res. energy (kcal.)	38	75	28	33	24

• 2.5. KIRCHOFF'S EQUATION

Heat of reaction, in general, varies with temperature and its variation with temperature can be deduced as follows :

Let x_1 moles of a substance A react with x_2 moles of B to form y_1 moles of M, at a constant temperature; each substance being in a certain specific state. Thus,



The enthalpy of the reactants (H_1) is given by,

$$H_1 = x_1 H_A + x_2 H_B$$

The enthalpy of the products (H_2) is given by,

$$H_2 = y_1 H_M$$

The increase in enthalpy (ΔH) for the change at constant pressure is,

$$\Delta H = H_2 - H_1 = y_1 H_M - x_1 H_A - x_2 H_B$$

Similarly, the increase in internal energy (ΔE) at constant volume is,

...(1)

$$\Delta E = E_2 - E_1 = y_1 E_M - x_1 E_A - x_2 E_B \quad \dots(2)$$

where, E terms represent the respective internal energy.

Differentiating equation (1) with respect to temperature, at constant pressure, and differentiating equation (2) with respect to temperature at constant volume, we get,

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_P = y_1 \left(\frac{\partial H_M}{\partial T} \right)_P - x_1 \left(\frac{\partial H_A}{\partial T} \right)_P - x_2 \left(\frac{\partial H_B}{\partial T} \right)_P \quad \dots(3)$$

$$\left[\frac{\partial(\Delta E)}{\partial T} \right]_V = y_1 \left(\frac{\partial E_M}{\partial T} \right)_V - x_1 \left(\frac{\partial E_A}{\partial T} \right)_V - x_2 \left(\frac{\partial E_B}{\partial T} \right)_V \quad \dots(4)$$

We know that,

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \text{ and } C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

Therefore, equations (3) and (4) reduce to,

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_P = y_1 (C_P)_M - x_1 (C_P)_A - x_2 (C_P)_B = \Delta C_P \quad \dots(5)$$

$$\left[\frac{\partial(\Delta E)}{\partial T} \right]_V = y_1 (C_V)_M - x_1 (C_V)_A - x_2 (C_V)_B = \Delta C_V \quad \dots(6)$$

where, ΔC_P and ΔC_V refer to overall changes in heat capacities in the reaction, i.e., to their algebraic sum. Expressions (5) and (6) are **mathematical forms of Kirchoff's equation** and represent the variation of heat content and internal energy of the reactants and products with temperature.

Integrating equations (5) and (6) between proper limits, we have

$$\int_{H_1}^{H_2} d(\Delta H) = \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_P \cdot dT$$

Assuming ΔC_P to be independent of temperature, we get

$$\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1) \quad \dots(7)$$

where, ΔH_1 and ΔH_2 are the heats of reaction at constant pressure at temperatures T_1 and T_2 , respectively.

Integrating equation (6) between proper limits, we get

$$\int_{E_1}^{E_2} (d\Delta E) = \int_{T_1}^{T_2} \Delta C_V \cdot dT$$

or

$$\Delta E = \Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_V \cdot dT$$

Assuming ΔC_V to be independent of temperature, we get

$$\Delta E_2 - \Delta E_1 = \Delta C_V (T_2 - T_1) \quad \dots(8)$$

where, ΔE_1 and ΔE_2 are the heats of reaction at constant volume, at temperatures T_1 and T_2 , respectively.

Kirchoff's law is valid for physical and chemical changes and is independent of nature and complexity of the systems. For an extended range of temperature, it is necessary to take into account the variation of heat capacities with temperature. The above expressions (5) and (6) may be used quite accurately over a range of temperature for which mean heat capacities remain constant.

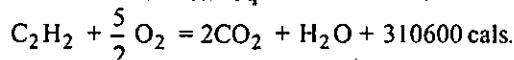
Since, $\Delta H = \Delta E + \Delta nRT$ as the value of Δn (Difference in the number of moles of gaseous products and gaseous reactants) changes the value of ΔH changes. Δn is related with pressure therefore ΔH depends upon pressure.

• 2.6. ADIABATIC FLAME TEMPERATURE

If a spontaneous process takes place at once and the heat produced during the chemical change does not have a chance of going to the surroundings, then obviously the heat evolved will increase the temperature of the resultant system. This process can be taken to be equivalent to an adiabatic change. Such condition gives rise to the production of flames. The gas or gases undergoing combustion produce an enormous

quantity of heat which is utilised to heating up the flame zone containing the gases produced after combustion. We can easily calculate to what temperature these gases can be raised by the heat of combustion in the flame, provided we know the values of heats of reaction and combustion and heat capacities of the resultant gases. We can then easily know the maximum flame temperature.

As an illustration, we can cite the example of acetylene, whose heat of combustion is -310600 cals. The thermochemical equation is thus



In the flame zone, the gases present after combustion are carbon dioxide, water vapour and unreacted nitrogen of the air. Since 5/2 moles of oxygen are used in combustion, therefore, the nitrogen present would be nearly 10 moles. The composition of the gases after combustion would, therefore, be 2 moles of carbon dioxide, 1 mole of water vapour and 10 moles of nitrogen. The approximate heat capacities of these gases are :

$$2 \times (C_P)_{CO_2} = 2(6.4 + 10.1 \times 10^{-3} T) = 12.8 + 20.2 \times 10^{-3} T$$

$$(C_P)_{H_2O} = 7.22 + 2.4 \times 10^{-3} T$$

$$10 \times (C_P)_{N_2} = 10(6.45 \times 1.4 \times 10^{-3} T) = 64.5 + 14 \times 10^{-3} T$$

$$\text{Thus, } \Sigma n C_P = 84.52 + 36.6 \times 10^{-3} T.$$

The gases have been heated from room temperature, say 25°C (298°K) to a higher temperature (T) by the heat of combustion.

$$\begin{aligned} Q &= \int_{298}^T \Sigma n C_P dT = \int_{298}^T (84.52 + 36.6 \times 10^{-3} T) dT \\ &= \left[84.52T + 18.3 \times 10^{-3} T^2 \right]_{298}^T \end{aligned}$$

$$\text{or } 84.52(T - 298) + 18.3 \times 10^{-3} (T^2 - 298^2) = 310600$$

$$\text{or } 84.52 T + 18.3 \times 10^{-3} T^2 = 337415$$

This is a quadratic equation and if we solve it, we will find that $T = 2450$ K. Thus, the maximum attainable temperature during the combustion of acetylene is 2450 K. But the actual flame temperature is somewhat less than 2450 K, because of heat radiation as well as dissociation of water vapour and carbon dioxide at high temperatures.

• 2.7. EXPLOSION TEMPERATURE

As discussed above the flame temperature is considered at constant pressure, on the other hand if the combustion is carried out under adiabatic conditions at *constant volume*, the maximum temperature attained is called **explosion temperature**.

At constant pressure i.e. isobaric adiabatic process the flame temperature may be given as :

$$\frac{d(\Delta H)}{dT} = \Delta C_P$$

$$\text{or } d(\Delta H) = \Delta C_P \cdot dT \quad \dots (1)$$

On integration within the limits, T_i (initial temperature) and T_f (final temperature),

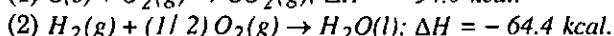
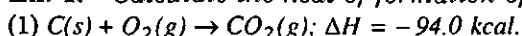
$$\int d(\Delta H) = \Delta C_P \int_{T_i}^{T_f} dT$$

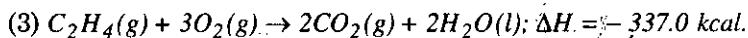
$$\text{or } \Delta H = \Delta C_P (T_f - T_i) \quad \dots (2)$$

At constant volume, ΔH is replaced by ΔU . The pressure required for the reacting system at the explosion temperature is called the explosion pressure.

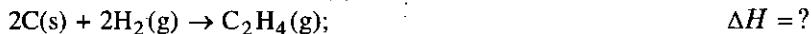
NUMERICAL PROBLEMS

Ex. 1. Calculate the heat of formation of ethylene from the following data :

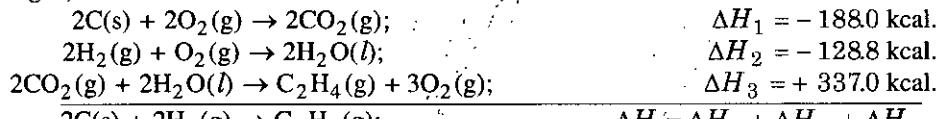




Solution. We should aim at :



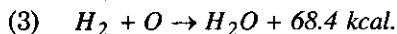
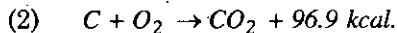
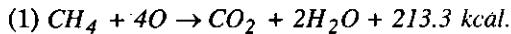
Multiplying equation (1) by 2, equation (2) by 2 and reversing equation (3) and adding, we get,



$$\begin{aligned} \text{or } \Delta H &= (-188.0 - 128.8 + 337.0) \text{ kcal.} \\ &= +20.2 \text{ kcal.} \end{aligned}$$

∴ Heat of formation of ethylene, $\Delta H = 20.2 \text{ kcal.}$

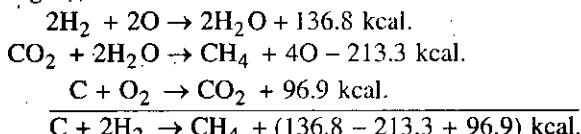
Ex. 2. Calculate the heat of formation of methane from the following data :



Solution. We should aim at :



Multiplying equation (3) by 2, reversing equation (1) and adding both with equation (2), we get,

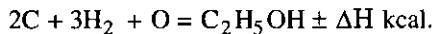


$$\text{or } C + 2H_2 \rightarrow CH_4 + 20.4 \text{ kcal.}$$

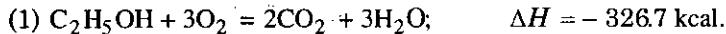
∴ Heat of formation of methane = 20.4 kcal.

Ex. 3. Calculate the heat of formation of ethyl alcohol, given that ΔH for combustion of ethyl alcohol, ΔH for formation of carbon dioxide and water are -326.7, -94.05 and -68.3 kcal. respectively.

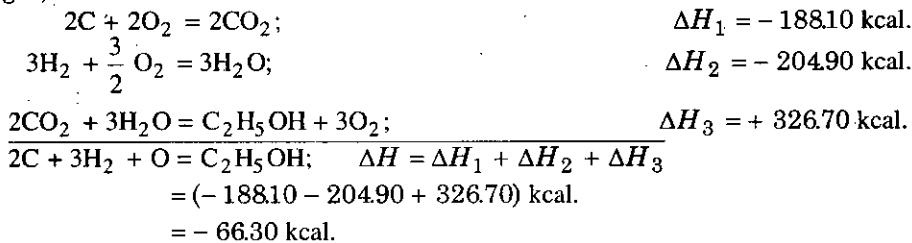
Solution. We should aim at :



Given :



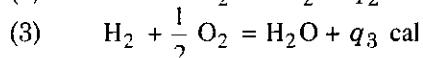
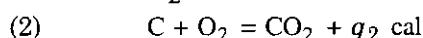
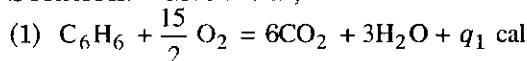
Multiplying equation (2) by 2, equation (3) by 3, reversing equation (1) and adding, we get,



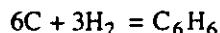
∴ Heat of formation of ethyl alcohol, $\Delta H = -66.3 \text{ kcal.}$

Ex. 4. If the heats of combustion of benzene, carbon and hydrogen are q_1 , q_2 and q_3 cal. respectively, what will be the heat of formation of benzene?

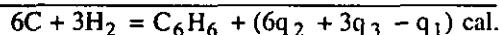
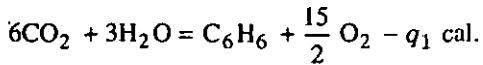
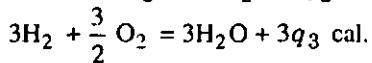
Solution. Given that,



We should aim at :



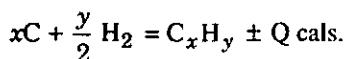
Multiplying equation (2) by 6, (3) by 3, reversing equation (1) and then adding, we get,



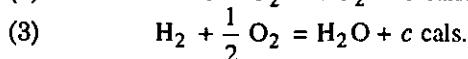
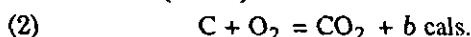
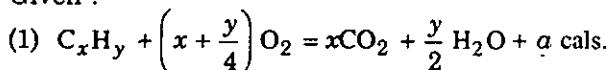
\therefore Heat of formation of benzene = $(6q_2 + 3q_3 - q_1)$ cal.

Ex. 5. Calculate the heat of formation of hydrocarbon C_xH_y , if its heat of combustion is a cals and the heats of formation of CO_2 and H_2O are b and c cals, respectively.

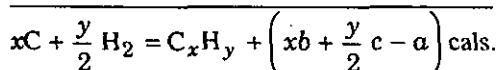
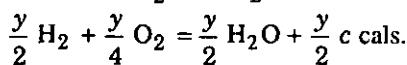
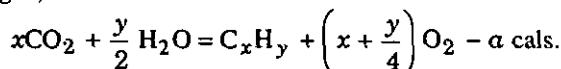
Solution. We should aim at :



Given :

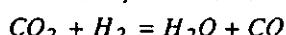


Multiplying equation (2) by x , equation (3) by $y/2$, reversing equation (1) and adding we get,



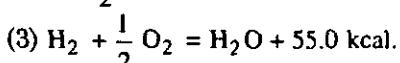
\therefore Heat of formation of $C_xH_y = \left(xb + \frac{y}{2} c - a\right)$ cals.

Ex. 6. Calculate the heat of reaction :

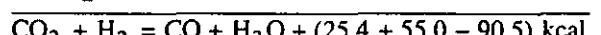
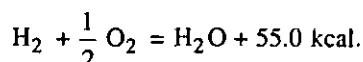
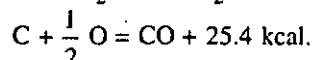


The heats of formation of CO , CO_2 , and H_2O are 25.4, 90.5 and 55.0 cal., respectively.

Solution. Given :



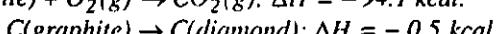
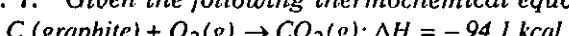
Reversing equation (2) and adding it with equations (1) and (3), we get,



or $CO_2 + H_2 = CO + H_2O - 10.1 \text{ kcal.}$

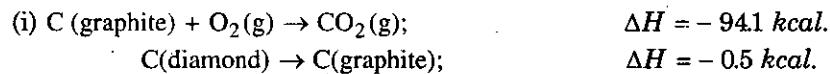
Heat of reaction = - 10.01 kcal.

Ex. 7. Given the following thermochemical equations :



- (i) Calculate ΔH for burning of diamond to CO_2 .
(ii) Calculate the quantity of graphite that must be burned to evolve 1000 kcals. of heat.

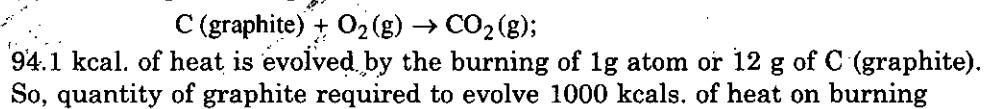
Solution.



Adding the above equations,



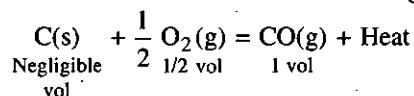
(ii) According to the equation,



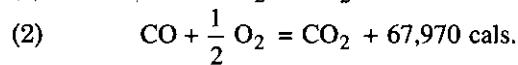
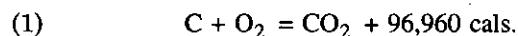
$$\begin{aligned} &= \frac{12 \times 1000}{941} \text{ g} \\ &= 127.52 \text{ g} \end{aligned}$$

Ex. 8. At $17^\circ C$, the heat of combustion at constant pressure of amorphous carbon into CO_2 is 96,960 cals and that of CO into CO_2 is 67,970 cals. Determine the heat of formation of CO at constant volume.

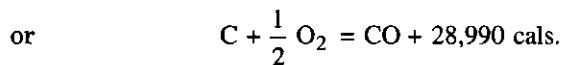
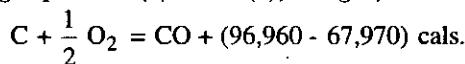
Solution. The heat of formation of CO is given by :



Given (At constant pressure) :



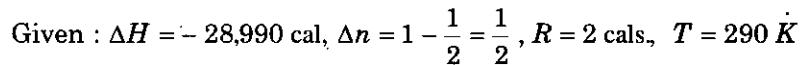
Subtracting equation (2) from (1), we get,



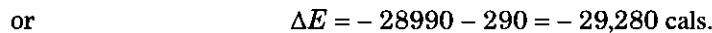
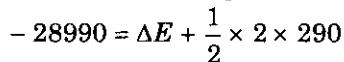
\therefore Heat of formation of CO at constant pressure = 28,990 cals.



We know that, $\Delta H = \Delta E + \Delta nRT$... (1)



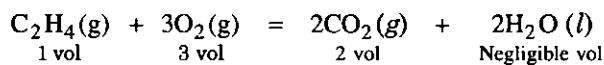
Putting the above values in equation (1), we get



\therefore Heat of formation of CO at constant volume = 29,280 cals.

Ex. 9. At $27^\circ C$ and constant volume, the heat of combustion of ethylene is -335.8 kcal. Calculate the heat of combustion at constant pressure at the same temperature. ($R = 2 \text{ cal deg}^{-1} \text{ mole}^{-1}$)

Solution. The heat of combustion of ethylene is represented as :



Given : $\Delta E = 335.8 \text{ kcal. } \Delta n = 2 - 4 = -2, T = 300 K, R = -0.002 \text{ kcal., } \Delta H = ?$

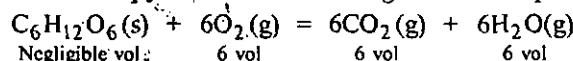
We know that, $\Delta H = \Delta E + \Delta nRT$

$$\therefore \Delta H = -335.8 + (-2) \times 0.002 \times 300 = -335.8 - 1.2 = -337.0$$

Heat of combustion at constant pressure (ΔH) = -337 kcal.

Ex. 10. Enthalpy of combustion of glucose at constant pressure and at 17°C was found to be $-6,51,000$ cals. Calculate the enthalpy of combustion of glucose at constant volume considering water to be in gaseous state.

Solution. The enthalpy of combustion of glucose is represented as :



Given : $\Delta H = -6,51,000$ cal. $\Delta n = 12 - 6 = 6$.

$$T = 17 + 273 = 290 \text{ K}, R = 2 \text{ cal deg}^{-1} \text{ mole}^{-1}, \Delta E = ?$$

We know that,

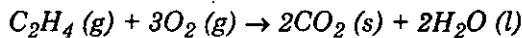
$$\Delta H = \Delta E + \Delta nRT$$

$$\text{or} \quad -6,51,000 = \Delta E + (6) \times 2 \times 290$$

$$\begin{aligned} \text{or} \quad \Delta E &= -6,51,000 - (6) \times 2 \times 290 \\ &= -6,51,000 - 3,480 \\ &= -6,54,480. \end{aligned}$$

\therefore Enthalpy of combustion at constant volume = $-6,54,480$ cals.

Ex. 11. Enthalpy of formation of $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$ and $\text{C}_2\text{H}_4(\text{g})$ are -94 , -68 and -36 kcal, respectively at constant pressure and 300 K . Calculate the enthalpy of following reaction at constant volume and at 300 K .



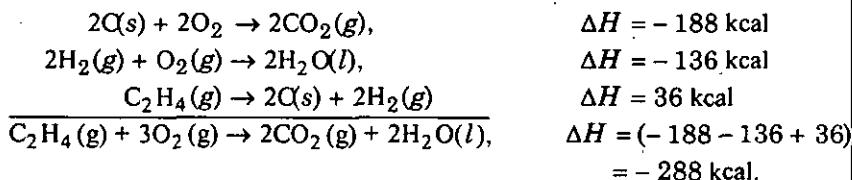
Solution. Given

$$(1) \quad \text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{s}), \quad \Delta H = -94 \text{ kcal}$$

$$(2) \quad \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}, \quad \Delta H = -68 \text{ kcal}$$

$$(3) \quad 2\text{C(s)} + 2\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g}), \quad \Delta H = -36 \text{ kcal}$$

Multiplying equations (1) and (2) by 2, reversing equation (3) and then adding, we get,



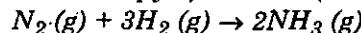
Now

$$\Delta H = \Delta E + \Delta nRT$$

$$-288 = \Delta E + (2 - 4)(0.002)(300)$$

$$\text{or} \quad \Delta E = -288 + 1 \cdot 2 = -286.8 \text{ kcal.}$$

Ex. 12. At 27°C the enthalpy of reaction (ΔH) for



is -21.974 kcal. Calculate the enthalpy of reaction at 50°C . The molar heat capacities at constant pressure and between the given temperature range for $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$ and $\text{NH}_3(\text{g})$ are 8.86 , 6.77 and 8.86 cal deg^{-1} , respectively.

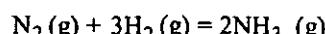
Solution. From Kirchoff's equation, we have

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p = \Sigma C_p (\text{products}) - \Sigma C_p (\text{reactants}) \quad \dots(1)$$

Given : $\Delta H_1 = -21.974$ kcal., $\Delta H_2 = ?$

$$T_1 = 300 \text{ K}, T_2 = 323 \text{ K}$$

The given reaction is :



$$\begin{aligned} \Delta C_p &= \Sigma \text{Heat capacity of products} - \Sigma \text{Heat capacities of reactants} \\ &= (2 \times 8.86) - [6.86 + (3 \times 6.77)] \\ &= 17.72 - (6.86 + 20.31) = -9.45 \text{ cal.} \\ &= -0.00945 \text{ kcal.} \end{aligned}$$

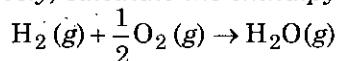
Substituting the given values in equation (1) we get,

$$\frac{\Delta H_2 - (-21.974)}{(323 - 300)} = 0.00945$$

$$\text{or } \Delta H_2 = 23 \times (-0.00945) - 21.974 \\ = -0.21735 - 21.974 = 0 - 22.19135 \text{ kcal}$$

\therefore Enthalpy of reaction of $50^\circ\text{C} = -22.191 \text{ kcal}$.

Ex. 13. If the bond energies for $H-H$, $O=O$ and $O-H$ bonds are 104, 118 and 111 kcal mol^{-1} , respectively, calculate the enthalpy of the reaction,

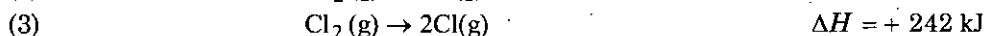
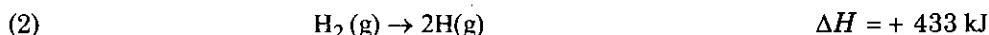
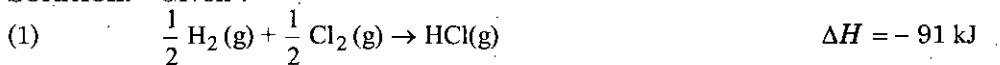


Solution. In this reaction, two $O-H$ bonds are formed and one $H-H$ bond is broken. So we can write for ΔH ,

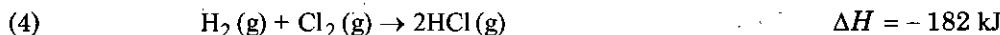
$$\begin{aligned} \Delta H &= -2\Delta H(\text{O}-\text{H}) + \Delta H(\text{H}-\text{H}) + \frac{1}{2}\Delta H(\text{O}=O) \\ &= (-2 \times 111) + 104 + \left(\frac{1}{2} \times 118\right) \\ &= -222 + 104 + 59 = -59 \text{ kcal. mol}^{-1} \end{aligned}$$

Ex. 14. Calculate the bond energy of HCl , if the $H-H$ bond energy is 433 kJ mol^{-1} , $\text{Cl}-\text{Cl}$ bond energy is 242 kJ mol^{-1} and H_f for HCl is -91 kJ mol^{-1} .

Solution. Given :



Multiplying equation (1) by 2, we get,



Adding equations (2) and (3) we get,



Subtracting equation (4) from (5), we get



Dividing the last equation by 2, we get



\therefore Bond energy of $\text{H}-\text{Cl}$ bond is 428.5 kJ

Ex. 15. Calculate the dissociation energy and resonance energy for energy (C_6H_6) (Kekulé structure). Given that $\Delta H_{\text{C}-\text{C}} = 347.3$, $\Delta H_{\text{C}=\text{C}} = 615.0$ and $\Delta H_{\text{C}-\text{H}} = 416.2 \text{ (kJ mol}^{-1}\text{)}$. The experimental value is $5535.1 \text{ kJ mol}^{-1}$.

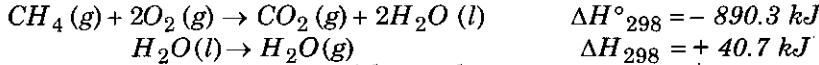
Solution. According to Kekulé structure of benzene there are $3\text{C}-\text{C}$, $3\text{C}=\text{C}$ and $6\text{C}-\text{H}$ bonds in benzene.

$$\begin{aligned} \therefore \Delta H_d &= 3(\Delta H_{\text{C}-\text{C}}) + 3(\Delta H_{\text{C}=\text{C}}) + 6(\Delta H_{\text{C}-\text{H}}) \\ &= 3(347.3) + 3(615.0) + 6(416.2) \\ &= 5384.1 \text{ kJ mol}^{-1} \end{aligned}$$

But the experimental value is $5535.1 \text{ kJ mol}^{-1}$.

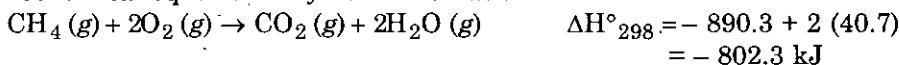
\therefore Resonance energy of benzene is $5535.1 - 5384.1 = 151 \text{ kJ mol}^{-1}$.

Ex. 16. In a Bunsen burner, methane gas (CH_4) is premixed with excess air (20% O_2 , 80% N_2) to allow complete combustion. At flame temperature water is converted into steam. Using the following thermochemical equations. Calculate the flame temperature.



Assume that $\Sigma C_p = 41.8 \text{ JK}^{-1} \text{ mol}^{-1}$ and initial temperature = 25°C

Solution. Since at flame temperature water is converted into steam hence thermochemical equation may be written as :



ΔC_p of the gaseous products (CO_2 , H_2O and N_2) = $41.8 \text{ JK}^{-1} \text{ mol}^{-1}$

The total number of moles of gaseous products = $1 + 2 + (4 \times 2) = 11$
(Since the ratio of O_2 and N_2 is $1 : 4$ in air).

According to Kirchoff's equation

$$n \cdot \Sigma C_p (T_f - T_i) = \Delta H$$

$$(11 \text{ mol}) (41.8 \text{ JK}^{-1} \text{ mol}^{-1}) (T_f - 298 \text{ K}) = 802.3 \text{ kJ}$$

or

$$(T_f - 298 \text{ K}) = \frac{802.3 \text{ kJ}}{(11)(41.8 \text{ JK}^{-1})}$$

$$= \frac{802.3 \times 1000 \text{ J}}{11 \times 41.8 \text{ JK}^{-1}}$$

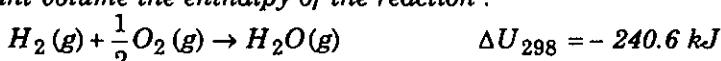
$$= 1746 \text{ K}$$

$$T_f = (1746 + 298) \text{ K}$$

$$= 2043 \text{ K}$$

Thus flame temperature = 2043 K

Ex. 17. In a closed vessel H_2 gas is mixed with air at 25°C at 1 atm pressure and exploded. At constant volume the enthalpy of the reaction :



The C_p s for $H_2O(g)$ and N_2 in the temperature range 298 K and 3200 K are 39.1 and 26.4 ($\text{JK}^{-1} \text{ mol}^{-1}$) respectively. Calculate the explosion temperature under adiabatic conditions.

Solution. Since at constant volume for a process

$$\Delta U = \Delta U_{\text{heating}} + \Delta U_{298} = 0$$

$$\text{Hence } \Delta U_{\text{heating}} = -\Delta U_{298} = -\int_{298}^{T_f} \sum n C_V \cdot dT \quad \dots \text{(i)}$$

$$= -240.6 \text{ kJ}$$

Since $\frac{1}{2} O_2$ mole is associated with 2 N_2 moles, hence

$$\sum n C_V = C_V(H_2O, g) + 2C_V(N_2, g)$$

$$= (39.1 + 2 \times 26.4) \text{ JK}^{-1} = 91.9 \text{ JK}^{-1}$$

On integration eq. (i), we get

$$91.9 \text{ JK}^{-1} (T_f - 298) = 240.6 \text{ kJ}$$

or

$$(T_f - 298) = \frac{240.6 \times 1000 \text{ J}}{91.9 \text{ JK}^{-1}}$$

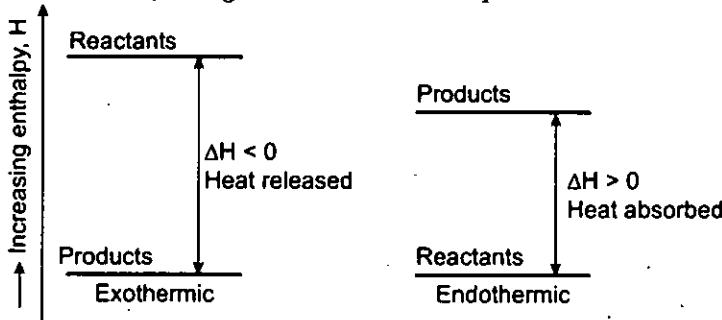
$$= 2618 \text{ K}$$

or

$$T_f = 2618 \text{ K} + 298 \text{ K} = 2916 \text{ K}$$

• SUMMARY

- Thermochemistry is that branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.
- In an exothermic reaction heat is evolved and the internal energy of reactants is greater than the internal energy of the products.
- In an endothermic reaction, heat is absorbed and the internal energy of reactants is less than the internal energy of the products.
- The change in internal energy (ΔE) is the heat change accompanying a chemical reaction at constant volume because no external work is performed.
- While the heat change in a process is equal to its change in internal energy (ΔE) at constant volume, it gives at constant pressure the enthalpy change



(ΔH) , i.e., ΔE = Heat change in a reaction at constant volume, ΔH = Heat change in a reaction at constant pressure.

- Heat of reaction may be defined as the amount of heat evolved or absorbed in a reaction when the number of moles of reactants as represented by the balanced chemical equation change completely into products.
- Kirchoff's equation may be represented as

$$(i) \frac{d(\Delta E)}{dT} = (C_V)_2 - (C_V)_1 = \Delta C_V$$

i.e., change in heat of reaction at constant volume per degree change in temperature is equal to the difference in heat capacities at constant volume of products and reactants.

$$(ii) \frac{d(\Delta H)}{dT} = (C_P)_2 - (C_P)_1 = \Delta C_P$$

i.e., change in heat of reaction at constant pressure per degree change in temperature is equal to the difference in heat capacities at constant pressure of products and reactants.

- Heat of formation is defined as the change in enthalpy that takes place when one mole of the compound is formed from its elements.
- Heat of combustion is defined as the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.
- Heat of combustion of a substance (ΔH_C) is always negative
- Flame temperature is considered at constant pressure while explosion temperature is considered at constant volume.
- Bond energy is defined as the average amount of energy required to break all bonds of a particular type in one mole of the substance.

• STUDENT ACTIVITY

- Describe the factors on which heat of reaction depends.

- State and explain heat of combustion.

- State and explain bond energy?

- What do you mean by flame temperature?

- ### 5. Define heat of formation.

6. Describe briefly the determination of heat of combustion.

7. Write Kirchoff's equation.

- TEST YOURSELF

Answer the following questions :

- (ii) Flame temperature is considered at constant
- (iii) The fuel efficiency of methane (mol. mass = 16) is that of ethane (mol. mass = 30).
- (iv) In an exothermic reaction, the heat energy is while in an endothermic reaction it is
- (v) For exothermic reaction, ΔH is, while for endothermic reaction it is
- (vi) The calorific value is defined as the amount of heat produced in calories when of a substance is completely burnt.

ANSWERS

- 9. 18.70 k cal
- 10. (i) 11. (iv)
- 12. (ii) 13. (i)
- 14. (iv) 15. (i) higher (ii) pressure
(iii) greater (iv) released, absorbed (v) negative, positive (vi) one gram



3

CHEMICAL EQUILIBRIUM

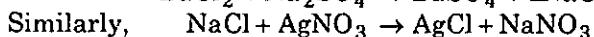
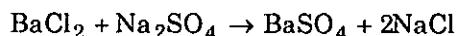
LEARNING OBJECTIVES

- Chemical Equilibrium
- Free Energy
- Law of Mass Action
- Thermodynamic Derivation of Law of Mass Action
- Le Chatelier's Principle
 - Summary
 - Student Activity
 - Test Yourself

• 3.1. CHEMICAL EQUILIBRIUM

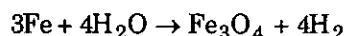
[I] Reversible and Irreversible Reactions

It was observed that when BaCl_2 and Na_2SO_4 are mixed in molecular proportions the reactants are completely converted into products. Such reactions proceed in one direction only and can be represented as :

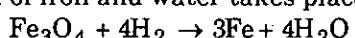


Hence, the reactions which proceed only in one direction, and it is not easily possible to convert the products into reactants, are known as **irreversible reactions**.

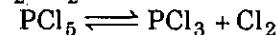
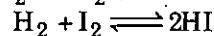
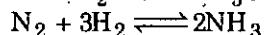
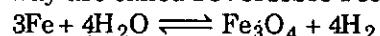
But certain reactions can proceed in both directions. For example, when we pass steam over red hot iron, the formation of iron oxide takes place with an evolution of hydrogen.



On the other hand, when we pass a current of dry hydrogen over red hot oxide of iron, the formation of iron and water takes place.



Thus, those reactions which proceed in both the directions and do not reach completion in any way are called **reversible reactions** and can be represented as,



[II] Chemical Equilibrium

If we study a reversible reaction in a closed vessel, then we clearly observe the conversion of reactants into products and vice-versa. But after sometime, a state is reached when the concentrations of reactants and products become constant. This state is known as equilibrium state. Therefore,

"The state of reversible reaction in which the concentrations of the reactants and products do not change is called **chemical equilibrium**".

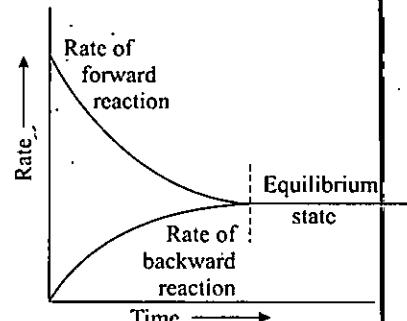


Fig. 1.

[III] Characteristics of Chemical Equilibrium

- (i) Chemical equilibrium, at a given temperature, is characterised by constancy of certain observable properties such as pressure, concentration, density or colour.
- (ii) Chemical equilibrium can be attained from either direction.
- (iii) Chemical equilibrium is dynamic in nature.
- (iv) A catalyst can hasten or delay the approach of equilibrium, but does not change the state of equilibrium. In other words, the relative concentrations of the reactants and products remain the same irrespective of the presence or absence of a catalyst.

• 3.2. FREE ENERGY

We know that neither only entropy nor only enthalpy decides the feasibility of the reaction. For this Gibb proposed a new function which is known as **Gibbs free energy function** or only **Free energy**. It is represented by G . It may be defined as :

$$G = H - TS \quad \dots (1)$$

where, H = Enthalpy, T = Temperature in Kelvin and S = Entropy.

If at constant temperature T , the thermodynamic functions at initial state are G_1 , H_1 and S_1 and at final state are G_2 , H_2 and S_2 then

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

or $\Delta G = \Delta H - T \cdot \Delta S \quad \dots (2)$

But at constant pressure,

$$\Delta H = \Delta E + P \cdot \Delta V$$

$$\Delta G = \Delta E + P \cdot \Delta V - T \Delta S$$

or $\Delta G = \Delta A + P \cdot \Delta V \quad \dots (3)$

where ΔA is change in work function,

and $\Delta A = \Delta E - T \cdot \Delta S$

But $\Delta A = -w$

$$\therefore \Delta G = -w + P \cdot \Delta V$$

or $-\Delta G = w - P \cdot \Delta V \quad \dots (4)$

In eq.(4) w and $P \cdot \Delta V$ represent maximum work and work done in expansion of gas respectively. Difference of these two terms is called **net work**. Therefore,

$$-\Delta G = \text{net work} = w - P \cdot \Delta V$$

Evidently, $-\Delta G$ represents maximum work of the system at a definite temperature and pressure. Since this term is used by Gibbs, hence it is known as **Gibbs free energy**. Generally it is known as only **Free energy**.

Change of free energy with temperature and pressure

We know that, $G = H - TS$

and $H = E + PV$

Thus $G = E + PV - TS \quad \dots (5)$

On differentiation of eq. (5)

$$dG = dE + P \cdot dV + VdP - TdS - SdT \quad \dots (6)$$

But according to first law of thermodynamics,

$$q = E + w$$

For small change, $dq = dE + dw$

If work done, dw , is only expansion, then

$$dq = dE + P \cdot dV$$

For reversible process, $dS = \frac{dq}{T}$

$$\text{or } dq = T \cdot dS = dE + P \cdot dV \quad \dots (7)$$

$$\text{or } dE + P \cdot dV - T \cdot dS = 0 \quad \dots (8)$$

On substituting the value of $dE + PdV - dq$ from eq. (8) in eq. (6)

We get, $dG = VdP - SdT \quad \dots (9)$

Eq.(9) represents the change in free energy for the small change of pressure and temperature.

At constant pressure $dP = 0$. Thus according to eq. (9)

$$dG = -SdT$$

$$= \frac{(x_{m_1} P)^{m_1} \times (x_{m_2} P)^{m_2}}{(x_{n_1} P)^{n_1} \times (x_{n_2} P)^{n_2}}$$

$$= \left(\frac{x_{m_1} x_{m_2}}{x_{n_1} x_{n_2}} \right) P^{(m_1 + m_2) - (n_1 + n_2)}$$

$$K_P = K_x(P)^{\Delta h}$$

where $(m_1 + m_2) - (n_1 + n_2) = \Delta n$

From eq. (4) and (5)

$$K_P = K_C(RT)^{\Delta n} = K_x(P)^{\Delta n}$$

If $\Delta n = 0$ i.e. $m_1 + m_2 = n_1 + n_2$ (i.e. the number of moles of products equals to the number of moles of reactants) then

$$K_P = K_C = K_x$$

• 3.4. THERMODYNAMIC DERIVATION OF LAW OF MASS ACTION

The law of mass action can be derived from two concepts, viz., chemical potential concept and equilibrium box concept.

[I] Chemical Potential Concept

The chemical potential (μ) of i^{th} component in a mixture is defined as,

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P, T, n_1, n_2, \dots} \quad (1)$$

where n_1, n_2, \dots etc. represent the number of moles of constituent components of the mixture.

Consider the following reversible reaction :



Suppose all the reactants and products are in the gaseous states and behave as ideal gases. The Gibbs potential, i.e., Gibbs free energy of reactants is given by

$$G_{\text{reactants}} = n_1 \mu_A + n_2 \mu_B \quad (2)$$

where μ_A and μ_B are the chemical potentials of the constituents A and B , respectively. Similarly, the Gibbs potential of the products is given by

$$G_{\text{products}} = m_1 \mu_C + m_2 \mu_D \quad (3)$$

The pressure and temperature remain constant in each case. We know that the energy of the reaction is equal to the difference between the free energy of the products and that of reactants, i.e.,

$$\begin{aligned} \Delta G_{\text{reaction}} &= G_{\text{products}} - G_{\text{reactants}} \\ &= (m_1 \mu_C + m_2 \mu_D) - (n_1 \mu_A + n_2 \mu_B) \end{aligned} \quad (4)$$

When the reaction attains equilibrium, $\Delta G_{\text{reaction}} = 0$, so from equation (4),

$$(m_1 \mu_C + m_2 \mu_D) - (n_1 \mu_A + n_2 \mu_B) = 0 \quad (5)$$

The chemical potential of the i^{th} component in the gaseous reaction is given by

$$\mu_i = \mu_i^{\circ} + RT \ln p_i \quad (6)$$

where μ_i° is the standard chemical potential and p_i is the partial pressure of i^{th} component.

From equations (5) and (6), we get

$$[m_1 (\mu_C^{\circ} + RT \ln p_C) + m_2 (\mu_D^{\circ} + RT \ln p_D)] - [n_1 (\mu_A^{\circ} + RT \ln p_A) + n_2 (\mu_B^{\circ} + RT \ln p_B)] = 0$$

$$\begin{aligned} \text{or } RT \ln \left(\frac{p_C^{m_1} \cdot p_D^{m_2}}{p_A^{n_1} \cdot p_B^{n_2}} \right) &= - [(m_1 \mu_C^{\circ} + m_2 \mu_D^{\circ}) - (n_1 \mu_A^{\circ} + n_2 \mu_B^{\circ})] \\ &= - [G_{\text{products}}^{\circ} - G_{\text{reactants}}^{\circ}] = - \Delta G_{\text{reaction}}^{\circ} \end{aligned} \quad (7)$$

$$\begin{aligned} \text{or } \frac{p_C^{m_1} \cdot p_D^{m_2}}{p_A^{n_1} \cdot p_B^{n_2}} &= e^{- \Delta G_{\text{reaction}}^{\circ} / RT} \end{aligned} \quad (8)$$

The right hand side of equation (8) is constant, because $\Delta G_{\text{reaction}}$ depends only on temperature and R is a constant. Therefore,

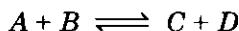
$$\frac{p_C^{m_1} \cdot p_D^{m_2}}{p_A^{n_1} \cdot p_B^{n_2}} = \text{constant} = K_p \quad \dots (9)$$

Since partial pressures are proportional to molar concentration of the components, so from equation (9), we have

$$\frac{[C]^{m_1} \cdot [D]^{m_2}}{[A]^{n_1} \cdot [B]^{n_2}} = K_C \quad \dots (10)$$

Equations (9) and (10) represent the expressions for equilibrium constant as obtained from law of mass action and chemical equilibrium.

(2) From equilibrium box*: Consider the gaseous reaction



Suppose there are two large vessels at the same temperature, in each of which the four substances A, B, C and D are always in equilibrium. Suppose each of the four walls of the vessels is permeable to only one of the substances.

Let p_A, p_B, p_C and p_D be the partial pressures of A, B, C, D in the first vessel, whereas p'_A, p'_B, p'_C and p'_D that of A, B, C, D in the second vessel. The vessels are supposed to be so large that the transfer of relatively small quantities of the material from one vessel to the other results in no appreciable change in the concentrations or partial pressures of the substances. It is also assumed that all substances are ideal gases.

First a reversible and isothermal process is carried out. Suppose 1 mole of A is transferred isothermally and reversibly from the first vessel to the second. This is done by means of the wall permeable to A . If p_A and p'_A represent the initial and final pressures, respectively, then the change in free energy (ΔG) is given by,

$$\Delta G = \int_{p_1}^{p_2} V dP$$

So, increase of free energy of the substance A is given by,

$$\begin{aligned} \Delta G_A &= \int_{p_A}^{p'_A} V dP = \int_{p_A}^{p'_A} \frac{RT}{P} dP = RT \int_{p_A}^{p'_A} \frac{dP}{P} \\ &= RT \log \frac{p'_A}{p_A} \end{aligned}$$

Similarly, for the transfer of 1 mole of B from p_B to p'_B in the same direction, the change in free energy is given by,

$$\Delta G_B = RT \log \frac{p'_B}{p_B}$$

During the time A and B are transferred in one direction, 1 mole of C and 1 mole of D are transferred isothermally and reversibly in the opposite direction.

Thus, the free energy change for the transfer of 1 mole of C from p'_C to p_C is given by,

$$\Delta G_C = RT \log \frac{p_C}{p'_C}$$

For the transfer of 1 mole of D , we have

$$\Delta G_D = RT \log \frac{p_D}{p'_D}$$

The total change of free energy is given by,

$$\begin{aligned} \Delta G &= \Delta G_A + \Delta G_B + \Delta G_C + \Delta G_D \\ &= RT \log \frac{p'_A}{p_A} + RT \log \frac{p'_B}{p_B} + RT \log \frac{p_C}{p'_C} + RT \log \frac{p_D}{p'_D} \quad \dots (11) \end{aligned}$$

*An equilibrium box is a very large vessel and it is assumed that if small amounts of substances are withdrawn or introduced in them, no change in concentrations or partial pressures of the substances contained therein occur.

As the vessels are large and the system is in equilibrium at constant temperature T , the total change of free energy of constant temperature is zero, i.e., $\Delta G = 0$.

$$\therefore \log \frac{p'_A}{p_A} + \log \frac{p'_B}{p_B} + \log \frac{p'_C}{p'_C} + \log \frac{p'_D}{p'_D} = 0 \quad [\text{From equation (12)}]$$

$$\text{or } \log \frac{p'_A}{p_A} + \log \frac{p'_B}{p_B} = \log \frac{p'_C}{p_C} + \log \frac{p'_D}{p_D}$$

$$\text{or } \log \frac{p'_A p'_B}{p_A p_B} = \log \frac{p'_C p'_D}{p_C p_D}$$

$$\text{or } \frac{p'_A p'_B}{p_A p_B} = \frac{p'_C p'_D}{p_C p_D}$$

$$\text{or } \frac{p_C p_D}{p_A p_B} = \frac{p'_C p'_D}{p'_A p'_B} = \text{Constant} (K_P) \quad \dots (12)$$

As the partial pressure is proportional to the molar concentration, equation (12) becomes,

$$\frac{C_C \cdot C_D}{C_A \cdot C_B} = \frac{[C][D]}{[A][B]} = K_c \quad \dots (13)$$

The equations (12) and (13) are different forms of law of mass action which have been deduced thermodynamically.

• 3.5. Le CHATELIER'S PRINCIPLE

[I] Definition

A system attains the state of equilibrium under a given set of temperature, pressure and concentration of the components. If any change is made in either of the above condition or variable, the equilibrium is disturbed. In other words, the reaction will occur and helps to attain the equilibrium again, though the new state of equilibrium is different from the earlier one. In order to predict the effect of changes of pressure, temperature and concentration on the course of two opposing processes at equilibrium, Henry Louis Le Chatelier (French chemist) and Braun (1888) put a generalisation. The principle is known Le Chatelier's principle, Le Chatelier-Braun's principle or law of mobile equilibrium. This can be stated as follows :

(i) When a stress (or constraint) is applied on a system at equilibrium, the system behaves in such a way so as to counteract the stress.

(ii) If a system at equilibrium is subjected to a change which displaces it from the equilibrium, a net reaction will occur in a direction that opposes the change.

Le Chatelier's principle is of a general nature and can be applied to any physical or chemical system at equilibrium. To a chemical system at equilibrium, the constraint can be applied by changing the temperature of the system by changing the pressure of the system or by changing the concentration of reactants or products. Therefore, for a chemical system at equilibrium, Le Chatelier's principle can also be stated as follows :

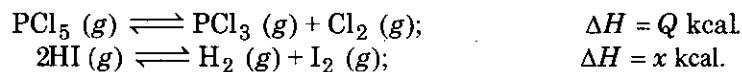
'If a system is in equilibrium and one of the factors involved in the equilibrium is altered, i.e., pressure, temperature or concentration, the equilibrium will shift so as to tend to annul the effect of the change.'

Examples of Le Chatelier's principle are :

(a) Heat added or temperature increase	The equilibrium will shift in the endothermic direction, i.e., it is shifted to high enthalpy side.
(b) Pressure increase	Reaction will shift in a direction where the number of gaseous molecules is reduced, thus lowering the pressure.
(c) One of the components of the system is added	Reaction proceeds in a direction so as to reduce the amount of this component.

[II] Effect of Temperature Change on the Position of Equilibrium

In reactions which proceed entirely in the gas phase, phosphorous pentachloride dissociates to phosphorous trichloride and chlorine or hydrogen iodide dissociates to hydrogen and iodine in a reversible reaction as follows :



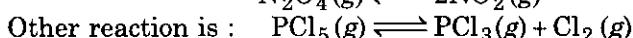
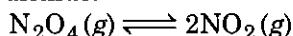
In the above, forward reaction (dissociation of PCl_5 or HI) is accompanied by the absorption of heat. If the temperature is increased, the equilibrium will be disturbed. Le-Chatelier's principle requires the reaction to respond to oppose this change, that is to lower the temperature. This can be achieved if the forward reaction which is endothermic, is allowed to predominate over the backward reaction, which is exothermic. In such a case, the position of balance of the reaction is disturbed and we say that the position of equilibrium has been shifted from left to right. In other words, the dissociation of PCl_5 or HI increases.

We may summarise the effect of temperature on a chemical equilibrium as follows :

Forward reaction (left to right)	Change in temperature	Effect on position of equilibrium
Exothermic	Increase	New equilibrium has more of substances on left (reactants in forward reaction).
	Decrease	New equilibrium has more of substances on right (products in forward reaction).
Endothermic	Increase	New equilibrium has more of substances on right (products in forward reaction).
	Decrease	New equilibrium has more of substances on left (reactants in forward reaction).

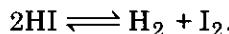
[III] Effect of Pressure Change on the Position of Equilibrium

Consider the gas phase reaction involving the decomposition of dinitrogen tetra-oxide into nitrogen dioxide.



At equilibrium, the mixture will contain the two compounds in a definite proportion. If the pressure is increased, Le Chatelier's principle demands that the equilibrium position of the reaction should change in order to restore the balance and this can occur by a decrease in volume (since the total capacity of the reaction vessel is fixed, a decrease in volume of the gases is equivalent to a decrease in pressure). An increase of pressure will thus shift the equilibrium to the left, i.e., dissociation of N_2O_4 or PCl_5 is decreased.

However, pressure will have no effect on those reactions in which there is no change in the number of molecules as a result of the reaction, i.e., in the reaction

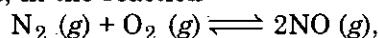


The effect of pressure on an equilibrium system may be summarised as follows:

Type of reaction	Effect of increase in pressure	Effect of decrease in pressure
1. Increase in number of molecules, left to right, e.g., $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$.	Position of equilibrium moves to the left, i.e., less dissociation of PCl_5 .	Position of equilibrium moves to the right, i.e., more dissociation of PCl_5 .
2. Decrease in number of molecules left to right, e.g., $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$	Position of equilibrium moves to the right, i.e., more NH_3 will be formed.	Position of equilibrium moves to the right, i.e., more NH_3 will be formed.
3. No change in number of molecules, left to right, e.g., $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$	No effect Position of equilibrium maintained.	No effect. Position of equilibrium maintained.

[IV] Effect of Concentration Change on the Position of Equilibrium

If the concentration of one of the substances present in an equilibrium reaction is changed without change in any of the other conditions, then by Le-Chatelier's principle, the position of equilibrium will move to decrease the concentration of the added substance. Thus, in the reaction



at a given temperature, adding N_2 or O_2 would shift the equilibrium from left to right, i.e., more nitric oxide will be formed.

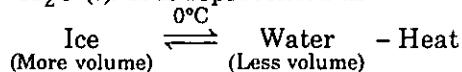
The effect of changes in concentration of substances on the position of equilibrium in a chemical reaction may be summarised as follows :

Change in concentration of substance	Effect on equilibrium position of reaction $A + B \rightleftharpoons C + D$
Increase in concentration of A or B	Proportion of C and D increased, i.e., equilibrium shifts to right
Decrease in concentration of A or B	Proportion of C and D decreased, i.e., equilibrium shifts to left
Increase in concentration of C or D	Proportion of A and B increased, i.e., equilibrium shifts to left
Decrease in concentration of C or D	Proportion of A and B decreased, i.e., equilibrium shifts to right.

[V] Applications of Le Chatelier's Principle

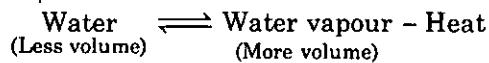
(1) Physical Equilibria

(a) Melting point of ice : Ice melts with decrease in volume as well as absorption of heat, e.g., $H_2O(s) \rightleftharpoons H_2O(l)$. It is represented as :



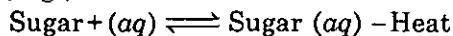
Increase of pressure or temperature will shift the equilibrium from left to right. In other words, *melting point of ice is lowered by an increase of pressure or temperature*.

(b) Vaporisation of water : The equilibrium between water and steam is represented as :



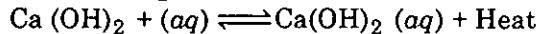
On increasing the temperature, the equilibrium will shift in that direction in which heat is absorbed, i.e., forward reaction. So, more steam will be produced. Similarly, on increasing the pressure, the equilibrium will shift in that direction in which volume is decreased, i.e., backward reaction. So, steam will condense into liquid. In other words, *formation of steam will be favoured by increase of temperature and decrease of pressure*.

(c) Solubility of substances : Certain substances like sugar, NaCl etc. dissolve with an absorption of heat, e.g.,



So, increase of temperature will shift the equilibrium to the right. So, the *solubility of such substances increase on increasing the temperature*.

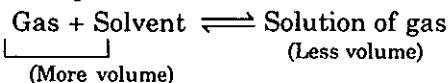
Certain substances like $\text{Ca}(\text{OH})_2$ etc. dissolve with an evolution of heat, e.g.,



So, increase of temperature will shift the equilibrium to the left, i.e., direction in which heat is absorbed. So, the *solubility of such substances decrease on increasing the temperature*.

(d) Solubility of gases in liquids : Consider the solution of a gas in equilibrium with the gas.

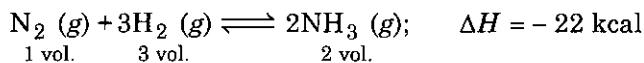
The equilibrium can be represented as :



If pressure is increased, volume will be reduced without affecting the pressure and some of the gas will dissolve in the solvent. Thus, the *solubility of the gas increases on increasing the pressure*.

(2) Chemical Equilibria

(a) Synthesis of ammonia by Haber's process : Haber's process involves the reaction



(i) *Effect of temperature* : If the temperature of the reaction is lowered, the equilibrium must shift so as to tend to raise the temperature again (Le-Chatelier's principle). That is, heat must be liberated by the production of ammonia. That is, low temperature favours the formation of ammonia. But lowering of temperature reduces the rate of reaction, so it is necessary to use a catalyst which will give a sufficient reaction rate inspite of a relatively low temperature.

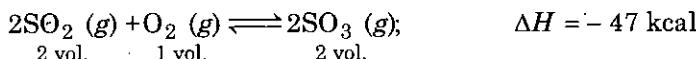
(ii) *Effect of pressure*. Ammonia is produced from its elements with reduction of volume. Therefore, if the system is in equilibrium and the pressure is then raised, the equilibrium must shift so as to tend to lower the pressure (Le-Chatelier's principle). To do this, the volume must be reduced by the production of more ammonia. That is, *high pressure favours the formation of ammonia*.

(iii) *Effect of concentration*. If the system is in equilibrium and more N_2 is added to increase its concentration, then according to Le-Chatelier's principle, the equilibrium will shift so as to tend to reduce the N_2 concentration. That is, more ammonia will be produced to use up N_2 . This increases the yield of ammonia relative to H_2 , and vice versa if the H_2 concentration is increased.

The formation of ammonia is favoured by :

- (i) Low temperature
- (ii) High pressure, and
- (iii) High concentration of the reactants.

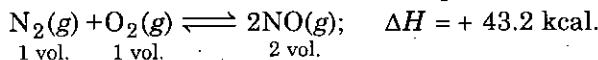
(b) **Formation of sulphuric acid by the contact process** : The first step in the production of sulphuric acid is the conversion of sulphur dioxide into sulphur trioxide according to the reaction



This reaction is just similar to the synthesis of ammonia described above. So, the effect of pressure, temperature and concentration will be the same as mentioned in the synthesis of ammonia. *Low temperature, high pressure and increased concentrations of SO_2 and O_2 will favour the formation of sulphur trioxide*.

The SO_3 is removed from the equilibrium mixture by dissolving it in fairly concentrated sulphuric acid, forming **oleum** which is then diluted to get the acid of the required concentration.

(c) **Formation of nitric oxide** : The reaction is represented as



(i) *Effect of pressure* : As no change of volume occurs during the formation of nitric oxide, there will be *no effect of pressure* on the equilibrium.

(ii) *Effect of temperature* : If the temperature is increased then the equilibrium will shift in that direction in which heat is absorbed, i.e., in the forward direction. So, high temperature favours the formation of nitric oxide.

(iii) *Effect of concentration* : If to the system in equilibrium N_2 is added, the equilibrium will shift in that direction so as to reduce the concentration of N_2 . So, more nitric oxide will be formed. Similar is the effect of adding oxygen.

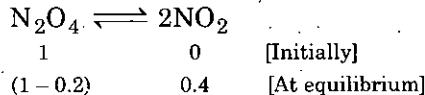
So, the formation of nitric oxide is favoured by

- (i) high temperature and
- (ii) high concentrations of N_2 or O_2 .

NUMERICAL PROBLEMS

Ex. 1. At 300 K and 1 atmosphere pressure N_2O_4 is 20% dissociated to NO_2 . Calculate the standard free energy change for the reaction.

Solution.



$$\text{Total number of moles} = 1 - 0.2 + 0.4 = 1.2$$

$$p_{\text{N}_2\text{O}_4} = \frac{0.8}{1.2} \times p = \frac{0.8}{1.2} \times 1 = \frac{2}{3}$$

and $p_{\text{NO}_2} = \frac{0.4}{1.2} \times 1 = \frac{1}{3}$

On applying the law of mass action,

$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}} = \frac{1/9}{2/3} = \frac{1}{6}$$

Standard free energy change (ΔG°) is given by,

$$\begin{aligned}\Delta G^\circ &= -RT \log_e K_p = -2.303 RT \log_{10} K_p \\ &= -2.303 \times 1.98 \times 300 \log \frac{1}{6} = 1075.22 \text{ cals.}\end{aligned}$$

Ex. 2. At 1000 K water vapour at 1 atmosphere pressure has been found to be dissociated into hydrogen and oxygen to the extent of $3 \times 10^{-5}\%$. Calculate the free energy decrease of the system in this reaction. ($R = 1.98 \text{ cal/mole/degree}$).

Solution. The partial pressures in the equilibrium mixture are thus given as,

$$p_{\text{eH}_2\text{O}} = 1; \quad p_{\text{eH}_2} = 3 \times 10^{-7}; \quad p_{\text{eO}_2} = \frac{3}{2} \times 10^{-7}$$

as one molecule of water yields one molecule of hydrogen and half a molecule of oxygen.

For the reaction $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$

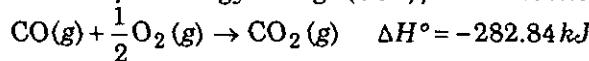
We have $K_p = \frac{p_{\text{eH}_2\text{O}}^2}{p_{\text{eH}_2}^2 \times p_{\text{eO}_2}} = \frac{1}{9 \times 10^{-14} \times 1.5 \times 10^{-7}} = \frac{1}{1.35 \times 10^{-20}}$

The change in free energy is given by,

$$\begin{aligned}\Delta G &= -RT \log_e K_p = -2.303 \times RT \log_{10} K_p \\ &= -2.303 \times 1.98 \times 1000 \log \frac{1}{1.35 \times 10^{-20}} \\ &= -2.303 \times 1.98 \times 1000 (\log 10^{20} - \log 1.35) \\ &= -2.303 \times 1.98 \times 1000 \times 19.8697 \\ &= -90,610 \text{ cals.}\end{aligned}$$

Decrease in free energy of the system is 90,610 cals.

Ex. 3. Calculate the standard free energy change (ΔG°) for the reaction :



Given that,

$$S_{\text{CO}}^\circ = 197.9, S_{\text{O}_2}^\circ = 205.0 \text{ and } S_{\text{CO}_2}^\circ = 213.8 \text{ (JK}^{-1})$$

Is the reaction feasible at 25°C ?

Solution. Since, $\Delta S^\circ = S_{\text{prod.}}^\circ - S_{\text{react.}}^\circ$

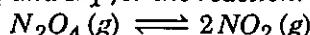
$$\begin{aligned}&= S_{\text{CO}_2}^\circ - \left[S_{\text{CO}}^\circ + \frac{1}{2}S_{\text{O}_2}^\circ \right] \\ &= 213.8 - \left(197.9 + \frac{205.0}{2} \right) = -86.6 \text{ JK}^{-1}\end{aligned}$$

Now,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -282840 \text{ J} - (298 \text{ K})(-86.6 \text{ JK}^{-1}) \\ &= -257033 \text{ J} = -257.033 \text{ kJ}\end{aligned}$$

Since ΔG° has a negative value hence the reaction is **feasible** at 25°C .

Ex. 4. Calculate K_c and K_p for the reaction.



At 27°C and 1 atm. pressure $K_p = 0.157 \text{ atm}$

Solution. $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$

Here,

$$\Delta n = 2 - 1 = 1$$

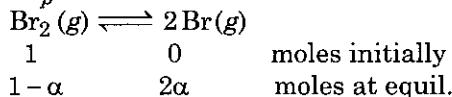
Since,

$$K_p = K_c (RT)^{\Delta n}$$

or

$$\begin{aligned}
 K_c &= \frac{K_p}{(RT)^{\Delta n}} = K_p (RT)^{-\Delta T} \\
 &= (0.157 \text{ atm}) (0.082 \text{ dm}^3 \text{ atm} K^{-1} \text{ mol}^{-1} 300 \text{ K})^{-1} \\
 K_c &= 6.38 \times 10^{-3} \text{ mol dm}^{-3} \\
 \text{Since, } K_p &= K_x (P)^{\Delta n} \\
 \text{or } K_x &= K_p (P)^{\Delta n} \\
 &= (0.157 \text{ atm}) (1 \text{ atm})^{-1} \\
 K_x &= 0.157.
 \end{aligned}$$

Ex. 5. Calculate the degree of dissociation of $\text{Br}_2(g)$ into Br atoms at 1600K and 0.5 atm . pressure. Given that $K_p = 0.255 \text{ atm}$.

Solution.

$$\text{Total no. of moles} = 1 - \alpha + 2\alpha = 1 + \alpha$$

$$\begin{aligned}
 p_{\text{Br}_2} &= \frac{1 - \alpha}{1 + \alpha} P \quad \text{and} \quad p_{\text{Br}} = \frac{2\alpha}{1 + \alpha} P \\
 K_p &= \frac{(p_{\text{Br}})^2}{p_{\text{Br}_2}} = \frac{\left[\frac{2\alpha}{1 + \alpha} P \right]^2}{\frac{1 - \alpha}{1 + \alpha} P} \\
 &= \frac{4\alpha^2}{(1 - \alpha^2)} P
 \end{aligned}$$

On substituting the values

$$0.255 \text{ atm} = \frac{4\alpha^2}{(1 - \alpha^2)} (0.1)$$

$$\text{or } \frac{\alpha^2}{1 - \alpha^2} = \frac{0.255}{0.4} = 0.64$$

$$\text{or } \alpha = 0.62$$

Thus, the degree of dissociation is **0.62** or **62%**.

• SUMMARY

- The state of reversible reaction in which the concentrations of the reactants and products do not change is called chemical equilibrium.
 - Gibbs free energy function (Free energy) is represented by G . It may be defined as : $G = H - TS$.
 - Change in free energy may be given as :
- $$\Delta G = \Delta H - T\Delta S = n RT \log_e \frac{P_2}{P_1} = n RT \log_e \frac{V_1}{V_2}$$
- K_p, K_c and K_x are related as :
- $$K_p = K_c (RT)^{\Delta n} = K_x (P)^{\Delta n}$$
- According to Le Chatelier's principle, if a system is in equilibrium and one of the factors involved in the equilibrium is altered (temp. press. or conc.) the equilibrium will shift so as to tend to annul the effect of the change.

• STUDENT ACTIVITY

- What do you understand by chemical equilibrium ?

2. Explain the term free energy.

3. Derive the relationship between K_p , K_c and K_x .

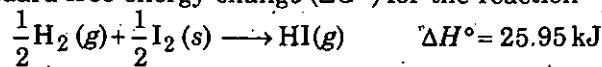
4. Discuss Le Chatelier's principle and its applications.

5. Differentiate between ΔG and ΔG° .

• TEST YOURSELF

Answer the following questions

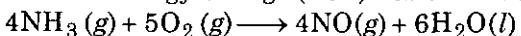
1. What is reversible reaction? What do you understand by equilibrium constant of reversible reaction? What are the factors affecting it? Describe in detail.
2. What is Gibb's free energy function? How it is changed with temperature and pressure.
3. Derive Law of mass action thermodynamically.
4. What is Le-Chatelier's principle? Discuss its use for any two physical and chemical equilibria.
5. What is the equilibrium constant of reversible reaction? Which factors affect it?
6. Explain free energy of a reaction.
7. Define Le-Cheteliers principle.
8. Explain the application of Le-Cheteliers principle on the following equilibrium :
 - (i) Melting of ice
 - (ii) Vaporisation of water
 - (iii) Synthesis of ammonia
 - (iv) Dissociation of phosphorus pentachloride
 - (v) Formation of nitric oxide
9. The equilibrium constant is the of the velocity constant of forward and backward reactions.
10. The equilibrium constant for the formation of ammonia from its element is of the equilibrium constant for the dissociation of ammonia.
11. The solubility of a solute with the rise of temperature when heat is evolved during dissolution of the solute.
12. The decomposition of nitric oxide :
$$2\text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g) \quad \Delta H = -21.5 \text{ kcal}$$
is favoured by of temperature.
13. The equilibrium constant with temperature.
14. In the formation of ammonia by Haber's process pressure is favourable.
15. At high pressure, the melting of ice
16. Calculate the standard free energy change (ΔG°) for the reaction



Whether it is feasible at standard state or not.

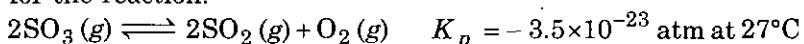
Given that, $S_{\text{HI}(g)}^\circ = 206.27$, $S_{\text{H}(g)}^\circ = 130.6$, $S_{\text{I}_2(s)}^\circ = 116.72(\text{JK}^{-1})$

17. Calculate the standard free energy change (ΔG°) for the reaction :



The standard free energies of formation of $\text{NH}_3(\text{g})$, $\text{NO}(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -16.65 , 86.61 and $-237.2 \text{ kJ mol}^{-1}$ respectively.

18. Calculate K_c for the reaction.



19. Calculate the degree of dissociation of N_2O_4 if the $K_p = 0.12 \text{ atm}$ at 298 K and a total pressure of 2 atm .

20. At one atm pressure PCl_5 dissociates upto 20% . Calculate the pressure at which PCl_5 half dissociated at the same temperature.

21. In a chemical reaction equilibrium is said to have been established when the :

- (a) operating reactions ceases
- (b) concentrations of reactants and products are equal.
- (c) velocities of opposing reactions become equal.
- (d) temperatures of opposing reactions are equal.

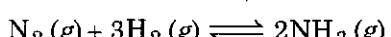
22. The equilibrium constant of a reversible reaction at a given temperature :

- (a) Depends on initial concentration of the reactants.
- (b) Depends on the concentration of the products at equilibrium.
- (c) Does not depend on the initial concentration.
- (d) It is not a characteristic of the reaction.

23. For a reaction in equilibrium.

- (a) There is no volume change
- (b) The reaction has stopped completely.
- (c) The rate of forward reaction equal to the rate of backward reaction.
- (d) The forward reaction is faster than reverse reaction.

24. In the reaction :



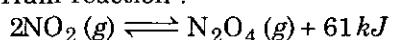
The value of the equilibrium constant depends on :

- (a) Volume of the reaction vessel
- (b) Total pressure of the system
- (c) The initial concentration of nitrogen and hydrogen.
- (d) The temperature.

25. In a reversible reaction : $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ If the concentration of H_2 and I_2 increases, the value of K_{eq} .

- (a) decreases
- (b) increases
- (c) remains the same
- (d) changes exponentially

26. For the equilibrium reaction :



Increase of temperature would :

- (a) favour the decomposition of N_2O_4
- (b) favour the formation of N_2O_4
- (c) no effect on equilibrium
- (d) stop the reaction

27. The expression for equilibrium constant K , of the reaction :



- (a) $\frac{[\text{HCl}][\text{Br}]}{[2\text{HBr}][2\text{Cl}]}$
- (b) $\frac{[\text{HCl}]^2 [\text{Br}_2]}{[\text{Cl}_2][\text{HBr}]^2}$
- (c) $\frac{[2\text{HCl}][2\text{Br}]}{[2\text{HBr}][2\text{Cl}]}$
- (d) $\frac{[\text{HBr}]^2 [\text{Cl}_2]}{[\text{HCl}]^2 [\text{Br}_2]}$

28. For a reversible reaction, at equilibrium :

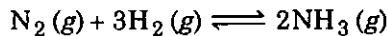
- (a) $\Delta G = 0$
- (b) $\Delta H = 0$
- (c) $\Delta E = 0$
- (d) None of these

29. Which of the following statements is incorrect :

- (a) reversible reactions proceed to completion
- (b) reversible reactions take place both in forward and backward direction.
- (c) irreversible reactions take place only in forward direction.
- (d) At equilibrium the amount of reactants and products do not undergo change.

30. When chlorine gas dissociates into atoms, then which of the following conditions are favourable for forward reaction :
(a) High temperature and low pressure
(b) High temperature and pressure
(c) Low temperature and pressure
(d) Low temperature and High pressure

31. In the synthesis of ammonia :



When 100 mL of N_2 have reacted the volume of H_2 , which has also reacted and ammonia produced are :

- (a) 100 mL H_2 and 100 mL NH_3 (b) 100 mL H_2 and 200 mL NH_3
(c) 300 mL H_2 and 200 mL NH_3 (d) 300 mL H_2 and 300 mL NH_3

ANSWERS

9. Ratio 10. Reciprocal 11. Decreases 12. Decreases 13. Changes 14. High
15. Increases 16. -13.2 J , Feasible 17. -1010.02 kJ 18. $1.42 \times 10^{-26}\text{ mol dm}^{-3}$

19. 12.1% 20. 0.213 atm 21. (c) 22. (c) 23. (c) 24. (d)
25. (c) 26. (a) 27. (b) 28. (a) 29. (a) 30. (a)
31. (c)



4

IONIC EQUILIBRIUM

LEARNING OBJECTIVES

- Nature of Electrolytes
- Ionization and Ionization Constant
- Ionization Constant and Ionic Product of Water
- Ionization of Weak Acids and Bases
- pH Scale
- Common Ion Effect
- Salt Hydrolysis
- pH for Different Salts
- Buffer Solutions
- Solubility and Solubility Product
 - Summary
 - Student Activity
 - Test Yourself

• 4.1. NATURE OF ELECTROLYTES

On the basis of degree of ionization, the electrolytes may be classified as :

(a) **Strong Electrolytes** are the electrolytes which dissociate almost completely into ions e.g., strong acids like HCl, HBr, HI, HNO₃, H₂SO₄, HClO₄, strong bases like NaOH, KOH, Ba(OH)₂ and salts like NaNO₃, Na₂SO₄ etc.

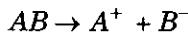
(b) **Weak Electrolytes** are the electrolytes which show poor dissociation into ions, e.g., HF, H₂CO₃, CH₃COOH, H₃PO₄, HNO₂, HCN, NH₄OH etc. (weak bases, weak acids and their salts).

(c) **Moderate Electrolytes** are the electrolytes which show dissociation moderately into ions i.e. neither very high nor very low such as strong and weak electrolytes.

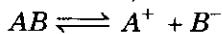
• 4.2. IONIZATION AND IONIZATION CONSTANT

Arrhenius (1887) put forward a theory to explain the behaviour of electrolytes in solution. This theory is known as **Theory of ionization or Theory of electrolytic dissociation**. According to this theory :

(i) When an electrolyte (acid, base or salt) is dissolved in water, it breaks up or dissociates into two types of particles, one carrying positive charge while one carrying negative but equal charge. These charged particles are called **ions**. The particles carrying positive charge are called **cations** and those carrying negative charge are called **anions**.



(ii) The ions present in solution are constantly re-combing to form neutral molecules which again dissociate. Thus there is a state of equilibrium set up between the ionized and unionized molecules. Thus,



Applying the law of mass action to the ionic equilibrium,

$$\frac{[A^+][B^-]}{[AB]} = K \text{ (Ionization constant)}$$

(iii) The extent to which an electrolyte dissociates into ions is known as degree of dissociation or ionization (α) and depends upon the following factors:

(a) Nature of the electrolyte : Strong acids, bases and their salts are almost completely ionized, while the weak acids, bases and their salts are feebly ionized.

(b) Temperature : Ionization increases with the increase of temperature.
 $[\alpha \propto T]$

(c) Dilution : Ionization also increases with the dilution at infinite dilution α is maximum.

(d) Nature of the solvent : It also affects ionization to a marked degree. It cuts the lines of forces binding the two ions and separates them in solution. This effect of the solvent is measured by its dielectric constant. The dielectric constant of a solvent may be defined as 'Its capacity to weaken the force of attraction between the dielectrical charges immersed in that solvent'. Water having a high dielectric constant (82) is a good and strong ionizing solvent.

(e) Presence of other ions : Degree of ionization of weak electrolytes is effected by the presence of other ions (common ion effect etc.) e.g., solubility of AgCl decreases in presence of NaCl.

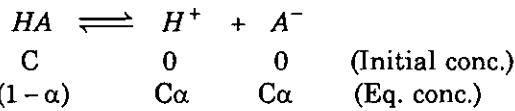
(iv) When an electric current is passed through the solution, negative ions (anions) move towards the anode and positive ions (cations) move towards the cathode.

The movement of the ions is thus responsible for the conduction of electricity through solution and hence explains the phenomenon of electrolysis. The electrical conductivity of a solution depends, therefore, on its power of ionization. Glucose, urea etc. which do not ionize are regarded as bad conductors of electricity and strong electrolytes e.g., NaCl, HNO₃ etc. which ionize almost completely are considered as good conductors.

(v) The ions behave as molecules in causing osmotic pressure, lowering of vapour pressure, depression of freezing point and elevation of boiling point whereby their abnormal values can be accounted for.

(vi) The properties of electrolytes in solution are the properties of the ions which they produce.

Ostwald's Dilution Law : Ostwald's dilution law is the application of the law of mass action to weak electrolytes in solution. Suppose an acid HA is dissolved in water, it will ionize as under :



Applying law of mass action,

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

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

where K_a is the ionization constant of the acid HA and α is its degree ionization.

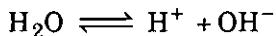
If $\alpha \ll 1$ then the above equation may be written as :

$$K_a = Ca^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{C}}$$

As $C \propto \frac{1}{V}$ then $\alpha = \sqrt{kV}$ or $\alpha \propto \sqrt{V}$ (at constant temperature)

• 4.3. IONIZATION CONSTANT AND IONIC PRODUCT OF WATER

Water ionizes as :



According to the law of mass action,

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \quad (K = \text{ionization constant of water})$$

$$\text{or } K \times [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

Water dissociates to a very small extent, so the concentration of undissociated water may be regarded as constant.

$$K_W = [\text{H}^+][\text{OH}^-]$$

where K_W is known as *ionic product of water*. Therefore,

'the product of hydrogen ion and hydroxyl ion concentrations in an aqueous solution is known as ionic product of water.' It is constant at a constant temperature. Its value can be measured from conductivity data as follows :

The specific conductivity of purest water is $5.54 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$. So, the conductivity of 1 litre of water will be $5.54 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3 = 5.54 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^2$. The equivalent conductivity of water, if it is completely ionised to give 1 g equivalent of H^+ ions and 1 g. equivalent of OH^- ions, can be obtained by adding the ionic conductance of H^+ and OH^- ions.

$$\text{So, conductivity of water} = \lambda_{\text{H}^+} + \lambda_{\text{OH}^-} = 349.8 + 198.5 = 548.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}.$$

As conductivity is proportional to the number of ions, it follows that when the conductivity of 1 litre of water is $5.54 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^2$, the number of g equivalent (or g moles) of hydrogen ions per litre

$$= \frac{5.54 \times 10^{-5}}{548.3} = 1.011 \times 10^{-7}$$

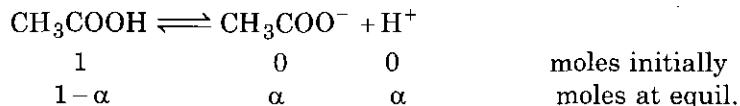
$$\therefore [\text{OH}^-] = [\text{H}^+] = 1.011 \times 10^{-7}$$

$$\begin{aligned} K_W &= [\text{H}^+][\text{OH}^-] \\ &= 1.011 \times 10^{-7} \times 1.011 \times 10^{-7} \\ &= 1.02 \times 10^{-14} \end{aligned}$$

$$\text{At } 25^\circ\text{C}, \quad K_W \approx 1.0 \times 10^{-14}$$

• 4.4. IONIZATION OF WEAK ACIDS AND BASES

Let us consider a weak acid, acetic acid (CH_3COOH). Its ionization may be given as :



where α is degree of ionization.

Let volume of the solution of CH_3COOH be VL .

$$\text{Therefore } [\text{CH}_3\text{COOH}] = \frac{1-\alpha}{V}, [\text{CH}_3\text{COO}^-] = [\text{H}^+] = \frac{\alpha}{V}$$

According to law of mass action,

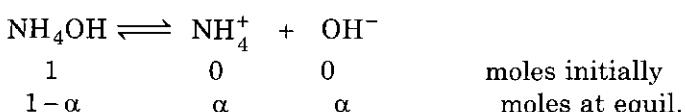
$$\begin{aligned} K &= \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad (K = \text{ionization constant}) \\ K &= \frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{(1-\alpha)V} \end{aligned}$$

If $\alpha \ll 1$ then, α may be neglected w.r.t. 1,

$$K = \frac{\alpha^2}{V}$$

or $\alpha = \sqrt{KV}$

Now we consider a weak base, ammonium hydroxide (NH_4OH). Its ionization may be given as :



where α is degree of ionization.

Let volume of the solution of NH_4OH be VL .

$$\text{Therefore, } [\text{NH}_4\text{OH}] = \frac{1-\alpha}{V}, \quad [\text{NH}_4^+] = [\text{OH}^-] = \frac{\alpha}{V}$$

According to law of mass action,

$$K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad (K = \text{ionization constant})$$

$$K = \frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{(1-\alpha)V}$$

If $\alpha \ll 1$ then, α may be neglected w.r.t. 1,

$$K = \frac{\alpha^2}{V}$$

or

$$\alpha = \sqrt{KV}.$$

• 4.5. pH SCALE

Since pure water is neutral, it follows that it contains equal concentration of hydrogen and hydroxyl ions. At a certain temperature, the product of the concentration of H^+ and OH^- ions in pure water is known as ionic product of water at that temperature. The ionic product of water at 25°C is approximately equal to 1×10^{-14} .

$$\therefore [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$\text{or } [\text{H}^+]^2 = 1 \times 10^{-14} \quad \{ \text{since } [\text{H}^+] = [\text{OH}^-] \}$$

$$[\text{H}^+] = 1 \times 10^{-7} = [\text{OH}^-].$$

It means that in pure water the concentration of H^+ and OH^- ions is 10^{-7} ion per litre each. Therefore, both the degree of acidity and the degree of alkalinity of a solution can be expressed quantitatively in terms of hydrogen ion concentration.

In neutral solution, $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$

In acidic solution, $[\text{H}^+] > 10^{-7}$

In alkaline solution, $[\text{H}^+] < 10^{-7}$.

Sorenson in 1909 expressed, hydrogen ion concentration in terms of *hydrogen ion exponent*, i.e., a number obtained by giving a positive value to the negative power of 10 in the expression 1×10^{-n} . This was originally represented as P_H but now most suitably written as pH. Thus,

pH of a solution is numerically equal to the negative power to which 10 must be raised in order to express the hydrogen ion concentration.

For example, if $[\text{H}^+] = 10^{-x}$, then $\text{pH} = x$.

Thus, we have a scale in which degree of acidity can be expressed in terms of pH.

Mathematically, we can write,

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

$$\text{or } \log [\text{H}^+] = -\text{pH} \log 10$$

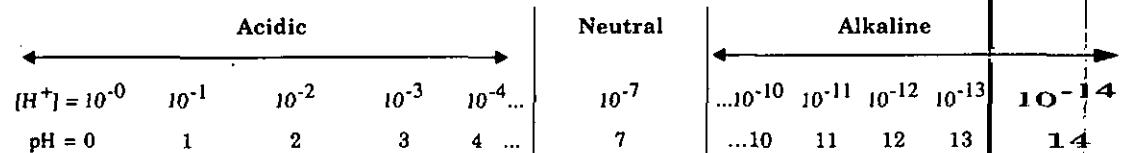
$$\text{pH} = \frac{-\log [\text{H}^+]}{\log 10}$$

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

$$[\because \log 10 = 1]$$

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

Thus, pH may also be defined as the *logarithm of the reciprocal of the hydrogen ion concentration*.



Since the pH value of pure water (neutral) is 7, any solution having pH less than 7 will be acidic and greater than 7 will be alkaline.

Ex. 1. Calculate the pH of N/1000 HCl and N/1000 NaOH, assuming both to be completely ionized.

Solution. For N/1000 HCl,

$$[\text{H}^+] = \frac{\text{N}}{1000} \text{ g eq / litre} = 10^{-3} \text{ g ion / litre}$$

$$\therefore \text{pH} = 3$$

$$\text{For N/1000 NaOH, } [\text{OH}^-] = \frac{\text{N}}{1000} \text{ g eq / litre} = 10^{-3} \text{ g ion / litre}$$

$$\therefore \text{pOH} = 3$$

$$\therefore \text{pH} = 14 - \text{pOH} = 14 - 13 = 11$$

Ex. 2. Calculate the pH of 0.001 M Ba(OH)₂ solution, assuming complete ionization.

Solution. $[\text{OH}^-] = 2 \times 0.001 \text{ M}$

$$\therefore [\text{H}^+] = \frac{10^{-14}}{2 \times 0.001} = 5.0 \times 10^{-12}$$

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log (5 \times 10^{-12}) \\ = 12 - 0.6990 = 11.3010.$$

Ex. 3. Calculate the pH of 0.001 N acetic acid, if it is 10% ionised.

Solution. $[\text{H}^+] = \text{Degree of dissociation} \times \text{normality}$

$$= \alpha \cdot N = \frac{10}{100} \times 0.001 = 10^{-4}$$

$$\therefore \text{pH} = 4.$$

Ex. 4. Calculate the pH of a solution containing 4 g/litre of NaOH.

Solution. Normality of NaOH solution = $\frac{4}{40} N = \frac{N}{10}$

For 0.1 N NaOH solution $[\text{OH}^-] = 10^{-1} \therefore \text{pOH} = 1$

$$\therefore \text{pH} = 14 - \text{pOH} = 14 - 1 = 13.$$

Ex. 5. The dissociation constant of acetic acid at 18°C is 1.8×10^{-5} . Calculate the pH of N/100 solution of acetic acid.

Solution. From Ostwald's dilution formula,

$$K = \frac{\alpha^2}{(1 - \alpha)V} \quad \text{or} \quad K = \frac{\alpha^2}{V}$$

$$\text{or} \quad \alpha = \sqrt{(KV)} = \sqrt{(1.8 \times 10^{-5} \times 100)} \quad \left(\text{For } \frac{N}{100}, V = 100 \text{ litres} \right)$$

$$\text{or} \quad \alpha = 0.0424 = 4.24 \times 10^{-2}$$

$$\therefore [\text{H}^+] = \frac{\alpha}{V} = \frac{4.24 \times 10^{-2}}{100} = 4.24 \times 10^{-4} \text{ g ion / litre}$$

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log (4.24 \times 10^{-4}) \\ = 4 - \log 4.24 = 4 - 0.6274$$

$$\text{or} \quad \text{pH} = 3.3726.$$

Ex. 6. Calculate the pH of the following :

(i) Solution containing 100 ml of $\frac{M}{100}$ HCl and 150 ml of $\frac{M}{500}$ H₂SO₄.

(ii) Solution containing 40 ml of 0.5 M HCl and 30 ml of 0.3 M NaOH.

(iii) Solution containing 60 ml of $\frac{M}{100}$ NaOH and 40 ml of $\frac{M}{50}$ Ba(OH)₂.

Solution. (i) 100 ml $\frac{M}{100}$ HCl = 1.0 ml N HCl

$$150 \text{ ml } \frac{M}{500} \text{ H}_2\text{SO}_4 \equiv \left(150 \times \frac{2}{500} \right) \text{ ml N H}_2\text{SO}_4 \equiv 0.6 \text{ ml N H}_2\text{SO}_4$$

$$\text{Total volume of the mixture} = (100 + 150) \text{ ml} = 250 \text{ ml}$$

$$\therefore \text{Strength of the mixture} = \left(\frac{1.0 + 0.6}{250} \right) N = \frac{1.6}{250} N = 0.0064 N$$

$$\therefore [H^+] = 0.0064 \text{ mol litre}^{-1} = 6.4 \times 10^{-3} \text{ M}$$

$$\therefore pH = -\log (6.4 \times 10^{-3}) = -(-3 + 0.8062) = 2.1938.$$

(ii) $40 \text{ ml } 0.5 \text{ M HCl} \equiv 40 \text{ ml } 0.5 \text{ N HCl} \equiv 20 \text{ ml N HCl}$
 $30 \text{ ml } 0.3 \text{ M NaOH} \equiv 30 \text{ ml } 0.3 \text{ N NaOH} \equiv 9 \text{ ml N NaOH}$

As HCl is in excess, the mixture now contains residual acid HCl
 $= (20 - 9) \text{ ml N HCl} = 11 \text{ ml N HCl}$

Total volume of the mixture = (40 + 30) ml = 70 ml

$$\therefore \text{Strength of the mixture} = \frac{11}{70} N$$

$$\therefore [H^+] = \frac{11}{70}$$

$$\therefore pH = -\log [H^+] = -\log \left(\frac{11}{70} \right) = -(\log 11 - \log 70)$$

$$= -(1.0414 - 1.8451) = 0.8037$$

(iii) $60 \text{ ml } \frac{M}{100} \text{ NaOH} \equiv 60 \text{ ml } \frac{N}{100} \text{ NaOH} \equiv 0.6 \text{ ml N NaOH}$
 $40 \text{ ml } \frac{M}{50} \text{ Ba(OH)}_2 \equiv 40 \text{ ml } \frac{2N}{50} \text{ Ba(OH)}_2$
 $\equiv 1.6 \text{ ml N Ba(OH)}_2$

Total volume of the mixture = (60 + 40) ml = 100 ml

$$\therefore \text{Strength of the mixture} = \left(\frac{0.6 + 1.6}{100} \right) N = 0.022 N$$

The mixture solution contains only alkalies, so

$$[OH^-] = 0.022 N$$

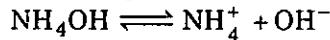
$$\therefore pOH = -\log (0.022) = -(\bar{2}.3424) = -(-1.6576) = 1.6576$$

$$\therefore pH = 14 - 1.6576 = 12.3424.$$

• 4.6. COMMON ION EFFECT

The degree of ionization of a weak electrolyte is suppressed by the addition of **strong** electrolyte containing a common ion. It is known as common ion effect.

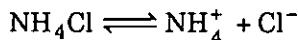
For example, ammonium hydroxide dissociates in solution as :



On applying the law of mass action, we get

$$\frac{[NH_4^+] [OH^-]}{[NH_4OH]} = K$$

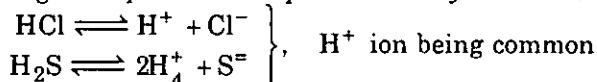
In the presence of ammonium chloride i.e., addition of ammonium ions (NH_4^+) to the solution and NH_4^+ ions are also obtained from the compound NH_4OH in the solution; hence it is named as common ion. Thus the concentration of NH_4^+ ion increases, but K is constant at a particular temperature, there must be an increase in the value of $[NH_4OH]$ or decrease in the value of $[OH^-]$.



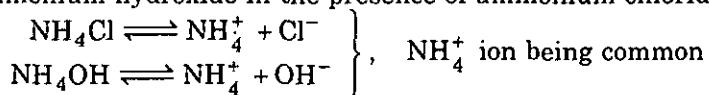
Thus the ionization of NH_4OH is diminished by the addition of NH_4Cl which furnishes the common ion NH_4^+ . In the same way the ionisation of CH_3COOH is diminished in the presence of CH_3COONa which furnishes the common ion CH_3COO^- .

The principle of common ion effect has a great importance in qualitative analysis.

Dissociation of hydrogen sulphide in the presence of hydrochloric acid.



Dissociation of ammonium hydroxide in the presence of ammonium chloride :



Thus, in above system $[\text{S}^{2-}]$ and $[\text{OH}^-]$ decreases in comparison the usual $[\text{S}^{2-}]$ and $[\text{OH}^-]$ obtained from H_2S and NH_4OH , respectively in water.

The common ion effect provides a valuable method for controlling the concentration of the ions furnished by a weak electrolyte.

• 4.7. SALT HYDROLYSIS

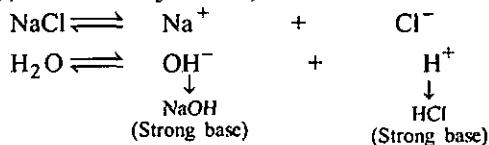
Pure water is neutral, as the concentration of H^+ and OH^- ions is the same. When water reacts with any salt and makes the solution either acidic or alkaline, then this phenomenon is called *salt hydrolysis*. It is defined as :

"The phenomenon of the interaction of the salt with water giving acidic or alkaline solution is known as salt hydrolysis."

We can explain the salt hydrolysis by taking the following examples :

[I] Salts of Strong Acid and Strong Base

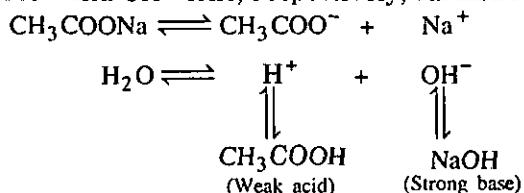
Salts like NaCl , KNO_3 , K_2SO_4 etc., belong to this category. For example, sodium chloride (salt) is obtained by the combination of strong acid (HCl) and strong base (NaOH). In solution, this salt gives Cl^- and Na^+ ions which combine with H^+ and OH^- ions, respectively, furnished by water, as follows :



Both the acid and base are strong, they ionize practically to a large extent and so there is neither an excess of H^+ ions nor OH^- ions. The solution is thus neutral, i.e., there is no effect on litmus. In other words, the pH remains nearly 7. So, NaCl does not hydrolyse.

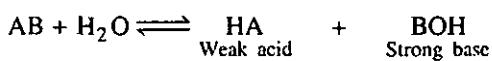
[II] Salts of Weak Acid and Strong Base

Salts like Na_2CO_3 , NaHCO_3 , CH_3COONa , KCN etc. belong to this category. For example, sodium acetate (salt) is obtained by the combination of weak acid (CH_3COOH) and strong base (NaOH). In solution, sodium acetate gives CH_3COO^- and Na^+ ions which combine with H^+ and OH^- ions, respectively, furnished by water, as follows :

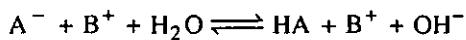


The base (NaOH) thus formed, being strong, ionizes to a large extent, while the acid (CH_3COOH) formed, being weak, ionizes to a very small extent. Thus, the solution contains an excess of free OH^- ions, whereby the solution becomes *alkaline*. So, aqueous solutions of all salts belonging to this category are alkaline in nature, i.e., turn red litmus to blue or the pH is greater than 7.

Relation between hydrolysis constant and ionization constant of the acid. The hydrolysis of a general salt AB of weak acid and strong base can be represented as :



In ionic form :



$$\text{or} \quad \text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^- \quad \dots (1)$$

According to the law of mass action,

$$K = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-][\text{H}_2\text{O}]} \quad (K = \text{constant})$$

The molar concentration of water remains constant, so

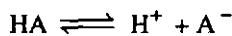
$$K \times [\text{H}_2\text{O}] = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

or

$$K_h = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \quad \dots (2)$$

where, K_h = hydrolysis constant.

The ionisation of the weak acid (HA) can be represented as :



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \dots (3)$$

where, K_a = ionization constant of the acid.

The ionic product of water (K_w) is given by

$$K_w = [\text{H}^+][\text{OH}^-] \quad \dots (4)$$

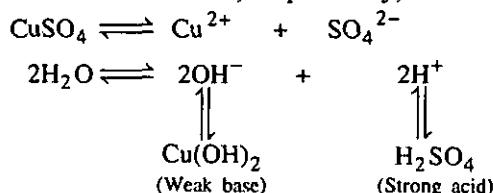
Dividing equation (4) by (3), we get

$$\frac{K_w}{K_a} = \frac{[\text{H}^+][\text{OH}^-][\text{HA}]}{[\text{H}^+][\text{A}^-][\text{HA}]} = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} = K_h$$

$$K_h = \frac{K_w}{K_a} \quad \dots (5)$$

[III] Salts of Strong Acid and Weak Base

Salts like NH_4Cl , CuSO_4 , FeCl_3 , aniline hydrochloride etc. belong to this category. For example, copper sulphate (salt) is obtained by the combination of strong acid (H_2SO_4) and weak base $[\text{Cu}(\text{OH})_2]$. In solution, copper sulphate gives Cu^{2+} and SO_4^{2-} ions which combine with OH^- and H^+ ions, respectively, furnished by water, as follows:



The acid H_2SO_4 thus formed, being strong, ionises to a large extent, while the base $\text{Cu}(\text{OH})_2$ formed being weak, ionises to a very small extent. Thus, the solution contains an excess of H^+ ions, whereby the solution becomes acidic. So, aqueous solutions of all salts belonging to this category are acidic in nature, i.e., turn blue litmus to red or the pH is less than 7.

Relation between hydrolysis constant and ionisation constant of the base. The hydrolysis of a general salt AB of this type can be represented as :



In ionic form :



or



According to the law of mass action,

$$K = \frac{[\text{H}^+][\text{BOH}]}{[\text{B}^+][\text{H}_2\text{O}]} \quad (\text{K} = \text{constant})$$

The molar concentration of water remains constant, so

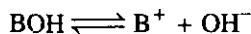
$$K \times [\text{H}_2\text{O}] = \frac{[\text{H}^+][\text{BOH}]}{[\text{B}^+]} \quad \dots (7)$$

or

$$K_h = \frac{[H^+][BOH]}{[B^+]} \quad \dots (7)$$

where, K_h = hydrolysis constant.

The ionization of weak base (BOH) can be represented as :



$$\therefore K_b = \frac{[B^+][OH^-]}{[BOH]} \quad \dots (8)$$

where, K_b = ionization constant of the base.

The ionic product of water (K_w) is given by

$$K_w = [H^+][OH^-] \quad \dots (9)$$

Dividing equation (9) by (8), we get

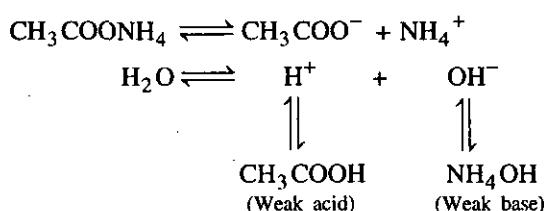
$$\frac{K_w}{K_b} = \frac{[H^+][OH^-][BOH]}{[B^+][OH^-]} = \frac{[H^+][BOH]}{[B^+]} = K_h$$

or

$$K_h = \frac{K_w}{K_b} \quad \dots (10)$$

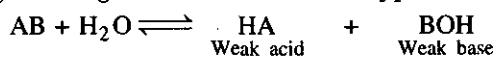
[IV] Salts of Weak Acid and Weak Base

Salts like $(NH_4)_2CO_3$, CH_3COONH_4 , aniline acetate belong to this category. For example, ammonium acetate (salt) is obtained by the combination of weak acid (CH_3COOH) and weak base (NH_4OH). In solution, ammonium acetate gives CH_3COO^- and NH_4^+ ions which combine with H^+ and OH^- ions, respectively, furnished by water as follows :



Both the acid (CH_3COOH) and base (NH_4OH) formed are weak and so are feebly ionised. Thus, the solution contains neither an excess of H^+ ions nor OH^- ions. So, the solution remains almost neutral. If the acid is slightly more ionised than the base, the solution will be acidic and if the base is slightly more ionised than the acid, the solution will be alkaline.

Relation between hydrolysis constant and ionisation constants of the acid and base. The hydrolysis of a general salt AB of this type can be represented as :



In ionic form :



According to the law of mass action,

$$K = \frac{[HA][BOH]}{[A^-][B^+][H_2O]}$$

$(K = \text{constant})$

The molecular concentration of water remains constant, so

$$K \times [H_2O] = \frac{[HA][BOH]}{[A^-][B^+]}$$

or

$$K_h = \frac{[HA][BOH]}{[A^-][B^+]} \quad \dots (12)$$

where, K_h = hydrolysis constant.

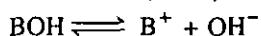
The ionization of the weak acid (HA) can be represented as :



$$\text{or } K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \dots (13)$$

where, K_a = ionization constant of the acid.

The ionization of the weak base (BOH) can be represented as :



$$\text{or } K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} \quad \dots (14)$$

where, K_b = ionization constant of the base.

The ionic product of water (K_w) is given by

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

Dividing the above equation by the product of equations (13) and (14), we get

$$\begin{aligned} \frac{K_w}{K_a \cdot K_b} &= \frac{[\text{H}^+][\text{OH}^-][\text{HA}][\text{BOH}]}{[\text{H}^+][\text{A}^-][\text{B}^+][\text{OH}^-]} \\ &= \frac{[\text{HA}][\text{BOH}]}{[\text{A}^-][\text{B}^+]} = K_h \end{aligned} \quad \dots (15)$$

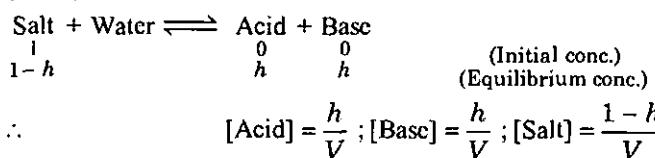
$$\text{or } K_h = \frac{K_w}{K_a \cdot K_b} \quad \dots (16)$$

Degree of Hydrolysis of Salt

Degree of hydrolysis of a salt is defined as, "the fraction of the total salt hydrolysed". It is represented by h and is generally expressed in percentage.

Effect of Dilution on Degree of Hydrolysis

Suppose 1 g mole of a salt is dissolved in V litre of solution, in which its degree of hydrolysis is h .



The value of hydrolysis constant (K_h) is written as

$$K_h = \frac{[\text{Acid}][\text{Base}]}{[\text{Salt}]} = \frac{\frac{h}{V} \times \frac{h}{V}}{\frac{1-h}{V}} = \frac{h^2}{(1-h)V}$$

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

As the value of h is very small, $(1-h)$ can be taken to be nearly equal to unity.

$$\therefore K_h = \frac{h^2}{V}$$

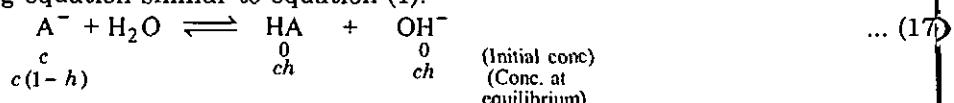
$$\text{or } h = \sqrt{(K_h V)} \quad \text{or} \quad h \propto \sqrt{V}$$

Therefore, the degree of hydrolysis is proportional to the square root of dilution.

• 4.8. pH OF SALT SOLUTIONS

We will derive expressions for different types of salt solutions as shown below.

(1) Salts of weak acid and strong base : Let c be the initial concentration of the salt AB in solution and let h be its degree of hydrolysis. We can thus represent the following equation similar to equation (1).



At equilibrium,

$$[\text{A}^-] = c(1-h), [\text{HA}] = ch, [\text{OH}^-] = ch$$

The hydrolysis constant (K_h) may be given as :

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

If h is small, then $1-h \approx 1$, so

$$K_h = ch^2$$

or $h = \sqrt{\frac{K_h}{c}}$... (18)

Substituting the value of h from equation (17) in equation (5), we get

$$h = \sqrt{\frac{K_w}{K_a \cdot c}} \quad \dots (19)$$

We know that in the hydrolysis of a salt of a weak acid and strong base, $[\text{OH}^-] = ch$.

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{K_w}{ch} \quad \dots (20)$$

Combining equations (19) and (20), we have

$$[\text{H}^+] = \frac{K_w}{c} \sqrt{\frac{K_a \cdot c}{K_w}} = \sqrt{\frac{K_w \cdot K_a}{c}} = \left(\frac{K_w \cdot K_a}{c} \right)^{1/2}$$

We know that,

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

Substituting the value of $[\text{H}^+]$ in the above equation, we get

$$\text{pH} = -\log \left(\frac{K_w \cdot K_a}{c} \right)^{1/2}$$

or $\text{pH} = -\frac{1}{2} \log K_w - \frac{1}{2} \log K_a + \frac{1}{2} \log c$

or $\text{pH} = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log c \quad \dots (21)$

$$(\because pK_w = -\log K_w, pK_a = -\log K_a)$$

Thus, we can calculate the pH of the salt solution from equation (21).

(2) Salts of strong acid and weak base : Let c be the initial concentration of the salt AB in solution and let h be its degree of hydrolysis. We can thus represent the following equation similar to equation (6).



c	0	0	(Initial conc.)
$c(1-h)$	ch	ch	(Conc. at equilibrium)

At equilibrium

$$[\text{B}^+] = c(1-h), [\text{H}^+] = ch, [\text{BOH}] = ch$$

Substituting the above values in equation (7), we get

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

If h is small, then $1-h \approx 1$, so

$$K_h = ch^2$$

or $h = \sqrt{\frac{K_h}{c}}$... (23)

Substituting the value of h from equation (23) in equation (10), we get

$$h = \sqrt{\frac{K_w}{K_b \cdot c}} \quad \dots (24)$$

We know that in the hydrolysis of a salt of a strong acid and weak base, $[\text{H}^+] = ch$.

Substituting the value of h from equation (24), we get

$$[\text{H}^+] = c \sqrt{\frac{K_w}{K_b \cdot c}}$$

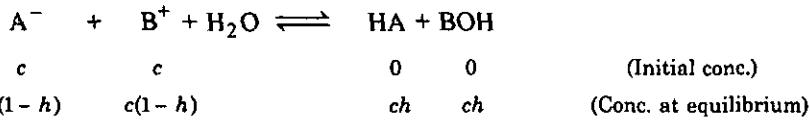
or $[\text{H}^+] = \sqrt{\frac{K_w \cdot c}{K_b}} \quad \dots (25)$

We know that,

$$\begin{aligned} \text{pH} &= -\log [\text{H}^+] \\ \therefore \text{pH} &= -\log \left(\frac{K_w \cdot c}{K_b} \right)^{1/2} \\ \text{or } \text{pH} &= -\frac{1}{2} \log K_w + \frac{1}{2} \log K_b - \frac{1}{2} \log c. \\ \text{or } \text{pH} &= \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log c \end{aligned} \quad \dots (26)$$

So, we can calculate the value of pH of the salt solution from equation (26).

(3) Salts of weak acid and weak base: Let c be the initial concentration of the salt AB in solution and let h be its degree of hydrolysis. We can thus represent the following equation similar to equation (11).



At equilibrium,

$$[\text{A}^-] = c(1-h), [\text{B}^+] = c(1-h), [\text{HA}] = ch, [\text{BOH}] = ch$$

Substituting the above values in equation (15),

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

If h is small, then $1-h \approx 1$, so

$$K_h = h^2$$

or $h = \sqrt{K_h} \quad \dots (27)$

Substituting the value of h from equation (27) in equation (16), we get

$$h = \sqrt{\frac{K_w}{K_a \cdot K_b}} \quad \dots (28)$$

From equation (13), we have

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

or $[\text{H}^+] = K_a \cdot \frac{[\text{HA}]}{[\text{A}^-]} \quad \dots (29)$

Substituting the values of $[\text{HA}]$ and $[\text{A}^-]$ in equation (29), we get

$$[\text{H}^+] = K_a \cdot \frac{ch}{c(1-h)} = K_a \cdot \left(\frac{h}{1-h} \right)$$

If h is small then $1-h \approx 1$, so

$$[\text{H}^+] = K_a \cdot h \quad \dots (30)$$

Substituting the value of h from equation (28) in equation (30), we have

$$[\text{H}^+] = K_a \cdot \sqrt{\frac{K_w}{K_a \cdot K_b}} = \sqrt{\frac{K_w \cdot K_a}{K_b}}$$

We know that,

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

$$\text{pH} = -\log \left(\frac{K_W \cdot K_a}{K_b} \right)^{1/2}$$

or $\text{pH} = -\frac{1}{2} \log K_W - \frac{1}{2} \log K_a + \frac{1}{2} \log K_b$

or $\text{pH} = \frac{1}{2} pK_W + \frac{1}{2} pK_a - \frac{1}{2} pK_b \quad \dots (31)$

So, the pH of the salt solution can be calculated from equation (31).

Ex. 1. Calculate the hydrolysis constant of NH_4Cl at 25°C , if dissociation constant of NH_4OH (K_b) = 1.4×10^{-5} and ionic product of water (K_W) = 14×10^{-14} .

Solution. Ammonium chloride is a salt of strong acid and weak base. Therefore,

$$K_h = \frac{K_W}{K_b} = \frac{1.4 \times 10^{-14}}{1.4 \times 10^{-5}} = 1 \times 10^{-9}$$

Ex. 2. At 25°C , the ionic product of water is 1×10^{-14} and dissociation constant of acetic acid is 2.00×10^{-5} . Calculate the hydrolysis constant for sodium acetate. What is the degree of hydrolysis of N/200 solution?

Solution. Sodium acetate is a salt of weak acid and strong base.

$$K_h = \frac{K_W}{K_a} = \frac{1 \times 10^{-14}}{2.00 \times 10^{-5}} = 5 \times 10^{-8}$$

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

or $K_h = \frac{h^2}{V} \quad (\because h \ll 1)$

$$h = \sqrt{(K_h \cdot V)} = \sqrt{(5 \times 10^{-8} \times 200)}$$

(For N/200 solution, $V = 200 \text{ L}$)

$$= 3.16 \times 10^{-3}$$

Degree of hydrolysis = 0.316%

Ex. 3. At 18°C , the dissociation constant of acetic acid is 18×10^{-5} and ionic product of water is 1.2×10^{-14} . Calculate the degree of hydrolysis of normal sodium acetate solution. Calculate the pH of the solution also.

Solution. CH_3COONa is a salt of weak acid and strong base.

$$K_h = \frac{K_W}{K_a} = \frac{1.2 \times 10^{-14}}{1.8 \times 10^{-5}} = 6.66 \times 10^{-10}$$

$$h = \sqrt{(K_h \cdot V)}$$

We have

$$h = \sqrt{(6.66 \times 10^{-10} \times 1)} = 2.58 \times 10^{-5}$$

Degree of hydrolysis = $2.58 \times 10^{-5} \times 100 = 2.58 \times 10^{-3}\%$

From equation (21), we have

$$\text{pH} = \frac{1}{2} pK_W + \frac{1}{2} pK_a + \frac{1}{2} \log c$$

or $\text{pH} = -\frac{1}{2} \log K_W - \frac{1}{2} \log K_a + \frac{1}{2} \log c$

$$= -\frac{1}{2} \log (1 \times 10^{-14}) - \frac{1}{2} \log (1.8 \times 10^{-5}) + \frac{1}{2} \log (1)$$

$$= 7 - \frac{1}{2} (\log 1.8 - 5 \log_{10}) + \frac{1}{2} \log (1)$$

$$= 7 - \frac{1}{2} (0.2553 - 5) + 0$$

$$= 7 + 2.3723 = 9.3723$$

Ex. 4. Calculate the degree of hydrolysis of N/100 NH₄Cl solution, if at 25°C, the ionic product of water is 1×10^{-14} and dissociation constant of NH₄OH is 1.7×10^{-5} . Calculate the pH of the solution also.

Solution. NH₄Cl is a salt of strong acid and weak base.

$$\therefore K_h = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10}$$

∴ From $h = \sqrt{(K_h \cdot V)}$, we have

$$h = \sqrt{(5.88 \times 10^{-10} \times 100)} = 2.42 \times 10^{-4}$$

∴ Degree of hydrolysis = $2.42 \times 10^{-2}\%$.

From equation (26), we have

$$\begin{aligned} \text{pH} &= \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log c \\ &= -\frac{1}{2} \log K_w + \frac{1}{2} \log K_b - \frac{1}{2} \log c \\ &= -\frac{1}{2} (\log 1 \times 10^{-14}) + \frac{1}{2} (\log 1.7 \times 10^{-5}) - \frac{1}{2} \log (0.01) \\ &= -\frac{1}{2} (-14) + \frac{1}{2} (\log 1.7 + \log 10^{-5}) - \frac{1}{2} (\log 1 - \log 100) \\ &= 7 + \frac{1}{2} (0.2304 - 5) - \frac{1}{2} (0 - 2) \\ &= 7 - 2.3848 + 1 = 5.6152. \end{aligned}$$

• 4.9. BUFFER SOLUTIONS

The pH value of pure water is 7, but it gradually changes on standing either due to the absorption of atmospheric CO₂ or impurities of the vessel. Moreover, the addition of a drop of HCl or NaOH in 1 litre of water, increases its H⁺ ion or OH⁻ ion concentration considerably.

But it is observed that the addition of HCl to a solution containing a mixture of weak acid and a salt of it with a strong base (i.e., CH₃COOH + CH₃COONa) is very slightly influenced and its pH value remains nearly the same. Similarly, a mixture of weak base and a salt of it with a strong acid (i.e., NH₄OH + NH₄Cl) is very slightly influenced and it maintains its pH value. Such combinations possess the following characteristics :

- (i) They possess a definite pH value.
- (ii) The pH value remains steady on keeping it for a long time or on dilution.
- (iii) The pH value is not appreciably changed on the addition of suitable quantity of either an acid or a base to the buffer solution.

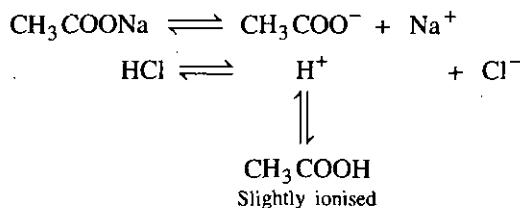
So, those solutions which have both reserve acidity and alkalinity are called buffer solutions.

Buffer solutions are of two types :

(i) **Acidic buffer solution :** It is a mixture of weak acid and a salt of it with a strong base, e.g., mixture of acetic acid and sodium acetate. The pH of this buffer solution is always less than 7.

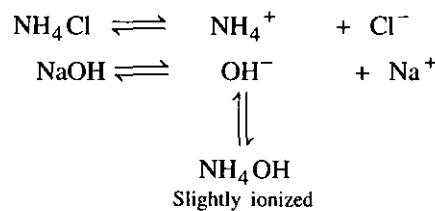
(ii) **Basic buffer solution :** It is a mixture of weak base and a salt of it with a strong acid, e.g., mixture of ammonium hydroxide and ammonium chloride. The pH of this buffer solution is always greater than 7.

Explanation : An acidic buffer solution like CH₃COOH + CH₃COONa contains a very small concentration of H⁺ ions. The formation of common acetate ion further suppresses the dissociation of acetic acid.



When a drop of an alkali, say NaOH , is added to the solution, it reacts with CH_3COOH to form CH_3COONa and water. Thus, the OH^- ions of the base are removed and the pH value of the solution remains nearly the same.

Moreover, the addition of NaOH to a basic buffer solution containing $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ does not change its pH value because the OH^- ions produced from it readily combine with NH_4^+ ions obtained from NH_4Cl to form slightly ionized NH_4OH .



Therefore, buffer solution contains actually a very small concentration of H^+ or OH^- ions, but they possess a large reserve of opposite ions. Hence, they are known as solutions with ***reserve acidity and reserve alkalinity***.

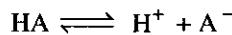
Buffer solutions find several applications in laboratory as well as in industries. A few important applications are given below :

- (i) In determining pH of unknown solution.
- (ii) In studying the rate of chemical reactions.
- (iii) In the removal of phosphate radical in qualitative analysis.
- (iv) In preparing cultures in biological specimens.
- (v) In the manufacture of ethyl alcohol from molasses (pH lies between 5 and 6.8)
- (vi) In paper manufacture, sugar manufacture, leather tanning etc.

Calculation of pH Value of Buffer Mixture (Henderson-Hasselbalch Equation)

Consider an acidic buffer solution of a weak acid (HA) and a salt (AB) of it with a strong base (BOH). Let c_1 and c_2 be the molar concentrations of the acid and the strongly ionized salt (AB), respectively.

Consider the dissociation of a weak acid HA as follows :



Applying the law of mass action,

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

or

$$[\text{H}^+] = K_a \cdot \frac{[\text{HA}]}{[\text{A}^-]} \quad \dots(1)$$

where, K_a = ionization constant of the acid.

The feeble dissociation of the weak acid is further suppressed by the presence of A^- ions with the result that the concentration of the unionised acid may be taken to be equal to the concentration of the total acid, i.e., $[\text{HA}] = c_1$. The concentration of $[\text{A}^-]$ ions may be taken to be equal to the concentration of the salt, as it is nearly totally dissociated, i.e., $[\text{A}^-] = c_2$.

∴ From equation (1),

$$[\text{H}^+] = K_a \cdot \frac{c_1}{c_2} = K_a \cdot \frac{[\text{Acid}]}{[\text{Salt}]}$$

Taking logarithm and then reversing the sign, we get

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

or

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \dots (2)$$

Equation (2) is known as *Henderson-Hasselbalch equation* from which we can calculate the pH of any acidic buffer solution.

Similarly, for a mixture of a weak base and its salt, Henderson-Hassel equation may be written as,

$$pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad \dots (3)$$

where, K_b = ionization constant of the base.

Knowing pOH, we can calculate the value of pH, from the equation
 $pH + pOH = pK_W = 14$

Ex. 1. What will be the pH value of a solution obtained by mixing 0.20 molles per litre sodium acetate with 0.15 moles per litre acetic acid? Dissociation constant of acetic acid is 1.8×10^{-5} .

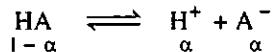
Solution. From Henderson's equation,

$$\begin{aligned} pH &= pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= -\log 1.8 \times 10^{-5} + \log \frac{0.20}{0.15} \\ &= 4.7448 + 0.1249 = 4.8697 \end{aligned}$$

Ex. 2. Prove that the pH of a solution of an acid with dissociation constant K and degree of dissociation α is given by

$$pH = \log_{10} \frac{I}{K} + \log_{10} \frac{\alpha}{1-\alpha}.$$

Solution. Consider the dissociation of an acid HA which occurs as follows :



(α = degree of dissociation)

On applying the law of mass action,

$$K = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (K = \text{dissociation constant})$$

or $\log_{10} K = \log_{10} [\text{H}^+] + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$

or $-\log_{10} [\text{H}^+] = -\log_{10} K + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$

or $pH = \log_{10} \frac{1}{K} + \log_{10} \frac{\alpha/V}{(1-\alpha)/V}$

or $pH = \log_{10} \frac{1}{K} + \log_{10} \frac{\alpha}{1-\alpha}$

• 4.10. SOLUBILITY AND SOLUBILITY PRODUCT

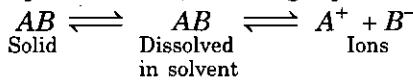
Solubility

Solubility is a property referring to the ability for a given substance (solid, liquid or gas), the solute, to dissolve in a solvent (water or non-aqueous) at a specific temperature and pressure. It is measured in terms of the maximum amount of solute dissolved in solvent at equilibrium. The resulting solution is called saturated solution. It is expressed in gram of solute per millilitre of solvent. It can be expressed in any mass unit of solute per any volume unit of solvent. It is an important parameter to achieve desired concentration of solution.

Solubility Product

When a sparingly soluble substance, say AB is kept in contact with water for some

time at a definite temperature the following equilibrium is established :



Applying the law of mass action,

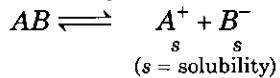
$$\frac{[A^+][B^-]}{[AB]} = K$$

But the concentration of the unionized $[AB]$ is constant at a given temperature; if excess of AB is present.

Hence $[A^+][B^-] = K [AB] = \text{constant } (K_{sp} \text{ or } S)$

Hence in saturated solution, the product of the ionic concentrations of sparingly soluble substance is constant at a given temperature. This constant product is called the solubility products (S or K_{sp}).

Relation between solubility ' s ' and solubility product (K_{sp}). Consider a reaction:

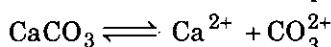
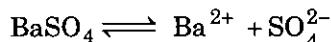
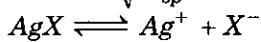


Now

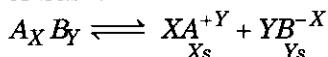
$$K_{sp} = [A^+][B^-]$$

$$K_{sp} = s^2 \quad \text{At constant temperature}$$

$$s = \sqrt{K_{sp}}$$



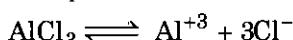
For $A_X B_Y$ type of Salt :



$$K_{sp} = (X.s)^x \cdot (Y.s)^y$$

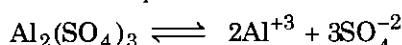
$$K_{sp} = X^x \cdot Y^y (s)^{x+y}$$

e.g., (i)



$$K_{sp} = s^1 (3s)^3 = 27s^4$$

e.g., (ii)



$$K_{sp} = 2^2 3^3 (s)^{2+3} = 108s^5.$$

When the ionic product exceeds the solubility product, the solution is super saturated and precipitation occurs and if the ionic product is less than the solubility product, the solution will be unsaturated and the precipitation will not occur.

This is also called the theory of precipitation.

Ionic product $<$ Solubility product, the salt dissolves.

Ionic product $< K_{sp}$, more salt can dissolve.

Ionic product $>$ Solubility product, precipitation takes place.

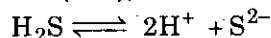
Ionic product $> K_{sp}$, the salt precipitates.

Since precipitation is governed by the principles of solubility product, the latter receives important applications in the field of analytical chemistry.

Precipitation as Sulphides of Radicals of Group II and IV : Precipitation of the sulphides can occur only when the ionic product $[M^{2+}][S^{2-}]$ exceeds the solubility product of the sulphide (MS) at that temperature i.e.,

$$[M^{2+}][S^{2-}] > \text{solubility product of MS.}$$

In the presence of acid (HCl), the ionization of H_2S is low,



i.e., suppressed due to the increase of H^+ ions (produced by acid). Due to low $[S^{2-}]$ in the solution, the solubility product of the sulphides of Group IV radicals is not reached. It is, however, enough to cause the precipitation of the II group radicals e.g. CuS, CdS,

PbS etc., which possess a low solubility product.

In the presence of NH_4OH the OH^- ions obtained from it [$\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$] combines with the H^+ ions produced from $\text{H}_2\text{S} (\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-})$ to give unionized water, so that more of H_2S ionizes and thus the concentration of S^{2-} ions in solution increases. In this way it becomes so high that the solubility product of IV group radicals e.g., ZnS , MnS etc. is exceeded and the precipitation takes place.

$$[\text{M}^{2+}] [\text{S}^{2-}] > \text{S} \text{ [Solubility product]} \\ \text{Precipitation occurs}$$

Since the solubility product governs all the precipitation reactions in qualitative analysis, it is of great importance and is intensively used in qualitative analysis.

Ex. 1. The concentration of Ni^{2+} ion in a given NiS solution is $2 \times 10^{-6} \text{ mol L}^{-1}$. Find the minimum concentration of S^{2-} ions necessary to cause precipitation of NiS . (Solubility product of NiS is 1.4×10^{-14}).

Solution. Since $K_{sp} = [\text{Ni}^{2+}] [\text{S}^{2-}]$

$$\therefore [\text{S}^{2-}] = \frac{K_{sp}}{[\text{Ni}^{2+}]} \\ = \frac{1.4 \times 10^{-14}}{2 \times 10^{-6}} \\ = 7 \times 10^{-7} \text{ mole L}^{-1}$$

Thus any concentration greater than 7×10^{-7} mole L^{-1} for S^{2-} ions will cause precipitation of NiS .

Ex. 2. Calculate the solubility product of silver chromate (molar mass = 332) if at 25°C it requires 0.0435 g of Ag_2CrO_4 to form its 1 litre saturated solution.

Solution. Conc. of $\text{Ag}_2\text{CrO}_4 = 0.0435 \text{ g L}^{-1}$

$$= \frac{0.0435}{332} \text{ mol L}^{-1} \\ = 1.31 \times 10^{-4} \text{ mol L}^{-1} \\ K_{sp} \text{ Ag}_2\text{CrO}_4 = 4s^3 = 4(1.31 \times 10^{-4})^3 \\ = 8.99 \times 10^{-12} \text{ mol}^3 \text{ L}^{-3}$$

Ex. 3. The solubility product of SrF_2 in water is 8×10^{-10} . Calculate its solubility in 0.1 M NaF aqueous solution.

Solution. For SrF_2

$$K_{sp} = [\text{Sr}^{2+}] [\text{F}^-]^2$$

Let the solubility of SrF_2 in 0.1 M NaF be x mol L^{-1} .

$$\therefore 8 \times 10^{-10} = (x)(2x + 0.1)^2 \\ = 4x^3 + 0.4x^2 + 0.01x$$

Neglecting x^2 and x^3 terms, we get

$$8 \times 10^{-10} = 0.01x$$

or

$$x = 8 \times 10^{-8} \text{ mol L}^{-1}$$

• SUMMARY

- Electrolytes are the substances which ionize in water into their ions. These are of three types strong, weak and moderate on the basis of their degree of ionization.
- Arrhenius put forward his theory of ionization for electrolytes.
- Degree of ionization depends upon nature of electrolytes, temperature, dilution, nature of solvent and presence of other ions.
- Ionization constant of water (K) may be given as :

$$K = \frac{[\text{H}^+] [\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Ionic product of water (K_w) may be given as :

$$K_W = [\text{H}^+] [\text{OH}^-]$$

- Degree of ionization of weak electrolytes (acid, base or salt) is directly proportion to square root of its dilution.
- pH value of solution indicates concentration of hydrogen ion $[\text{H}^+]$ and may be expressed as :

$$[\text{H}^+] = 10^{-\text{pH}} \quad \text{or} \quad \text{pH} = -\log_{10} [\text{H}^+]$$

- According to common ion effect, the degree of ionization of weak electrolytes is suppressed by the addition of strong electrolyte containing a common ion.
- Salt hydrolysis is a phenomenon of the interaction of the salt with water giving acidic or alkaline solution.
- Hydrolysis constant (K_h) is related with ionization constant of acid (K_a), of base (K_b) and both acid and base as :

$$K_h = \frac{K_W}{K_a} = \frac{K_W}{K_b} = \frac{K_W}{K_a K_b}$$

- pH value for different types of salts may be given as :

(i) Salt of weak acid and strong base :

$$\text{pH} = \frac{1}{2} pK_W + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

(ii) Salt of strong acid and weak base :

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

(iii) Salt of weak acid and weak base.

$$\text{pH} = \frac{1}{2} pK_W + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

- Buffer solutions are the solutions which have both reserve acidity and alkalinity. These are of two types acidic and basic buffer solutions.
- The pH and pOH of acidic and basic buffer solutions may be given as :

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

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

- Solubility is a phenomenon which refer the ability of solute dissolve in solvent at a specific temperature.
- Solubility product is used for sparingly soluble electrolytes at a given temperature. It is represented by K_{sp} . For an electrolyte $A_x B_y$, $K_{sp} = x^x \cdot y^y s^{x+y}$. This phenomenon is very useful in analytical chemistry.

• STUDENT ACTIVITY

- Describe briefly Arrhenius theory of ionization.

- Discuss ionization constant and ionic product of water.

- Explain pH value of an acid.

4. What is common ion effect ?

5. What do you know about salt hydrolysis ? Why the solution of copper sulphate is acidic in nature ?

6. Derive an equation for pH value of a salt of weak acid and strong base.

7. What do you mean by buffer solutions ?

8. Derive Henderson-Hassel equation for a buffer solution.

9. What is solubility product of a sparingly soluble salt ?

• TEST YOURSELF

Answer the following questions :

1. What do you understand by pH value of a solution?
2. Define buffer solution.
3. Define hydrolysis. Find out a relation between hydrolysis constant and ionization constant for :
 - (a) Salts of strong acid and weak base
 - (b) Salts of weak acid and strong base
 - (c) Salts of weak acid and weak base
4. Derive Henderson-Hasselbalch equation.
5. Define degree of hydrolysis.
6. Derive a relation between K_h , K_w and K_b for the hydrolysis of a salt of strong acid and weak base.

- (c) 10^{-3} mole/litre (d) 10^{-2} mole/litre
33. Which of the following is not a buffer solution ?
 (a) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ (b) $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$
 (c) $\text{CH}_3\text{COONH}_4$ (d) Borax + boric acid
34. What is the $[\text{H}^+]$ of a solution which is obtained by mixing 100 mL 1.0 M ~~HNC~~ with 100 mL 0.1 M KOH ?
 (a) 0.5 (b) 0.45 (c) 0.55 (d) 0.40
35. Solutions with reserve acidity or alkalinity are known as :
 (a) Isohydric solutions (b) Colloid
 (c) Buffer solutions (d) True solutions
36. Which one of the pairs will form a buffer solution?
 (a) CH_3COONa and NaOH (b) $\text{CH}_3\text{COONH}_4$ and NH_4Cl
 (c) NH_4Cl and NH_4OH (d) CH_3COONa and HCl
37. 20 mL of 0.1N HCl is mixed with 20 mL of 0.1N KOH solution, the pH of the solution will be :
 (a) 1 (b) 7 (c) 2 (d) 9
38. An acidic buffer solution can be prepared by mixing solution of :
 (a) CH_3COONa and CH_3COOH (b) NH_4Cl and NH_4OH
 (c) H_2SO_4 and Na_2SO_4 (d) NaCl and NaOH
39. At 90°C pure water has $\text{H}_3\text{O}^+ = 10^{-6}$ mole/litre, what is the value of K_w at 90°C ?
 (a) 10^{-6} (b) 10^{-12} (c) 10^{-14} (d) 10^{-8}
40. The dissociation constant of an acid HA is 1×10^{-5} . The pH of 0.1 molar solution of the acid will be approximately :
 (a) Three (b) Five (c) One (d) Six
41. The pH of a 0.001 M solution of hydrochloric acid is :
 (a) 1.0 (b) 3.0 (c) 5.0 (d) 10.0
42. The pH of a solution containing N/10 NaOH is :
 (a) 10^{-12} (b) 10^{-1} (c) 2 (d) 13
43. As aqueous solution of K_2CO_3 is :
 (a) Alkaline (b) Acidic (c) Neutral (d) Highly acidic
44. The pH of 0.05 N solution of HCl is :
 (a) 5.0 (b) 0.5 (c) 1.3 (d) 3.0
45. The pOH of a solution is 4, the H^+ ion concentration will be :
 (a) 10^{-4} (b) 10^{-10} (c) 10^{10} (d) 10^4
46. The pH of a neutral solution is
 47. The ionic product of water is
 48. The aqueous solution of CuSO_4 is in water.
 49. An aqueous solution of CH_3COONa is in nature.
 50. The fraction of the total salt hydrolysis is known as

ANSWERS

16. 3.37 17. 2.7 18. 12, 3 19. 4.569 20. 5.56×10^{-10} , 7.45×10^{-5} , 5.13
 21. 0.582 m 0.763, 9.14 22. 1.82 moles 23. 2.45 24. 11.3, 2.7 25. 5.96
 26. (b) 27. (c) 28. (d) 29. (d) 30. (b) 31. (b) 32. (a) 33. (b) 34. (b)
 35. (c) 36. (c) 37. (b) 38. (a) 39. (b) 40. (a) 41. (b) 42. (d) 43. (a)
 44. (c) 45. (b) 46. 7 47. 10^{-14} 48. acidic 49. alkaline 50. degree of hydrolysis

5

BENZENE AND AROMATICITY**LEARNING OBJECTIVES**

- Aromaticity : The Huckel Rule
- Electrophilic Reagents or Electrophiles
- Halogenation of Benzene
- Nitration of Benzene
- Sulphonation of Benzene
- Friedal-Crafts Reaction
- Directing Effects of the Groups
- Preparation of Benzene
- Reactions
 - Summary
 - Student Activity
 - Test Yourself

• 5.1. AROMATICITY : THE HUCKEL RULE

It is clear that benzene is an especially stable compound. A number of other compounds have a similar special stability, which is called aromaticity. To be aromatic a compound must conform to *all* of the following criteria :

- (i) Aromatic compounds have a cyclic arrangement of *p* orbitals. Thus aromaticity is a property of certain cyclic compounds.
- (ii) There is a *p*-orbital on every atom of an aromatic ring.
- (iii) Aromatic rings are planar; this planarity allows the *p*-orbitals on every atom to overlap.
- (iv) The cyclic arrangement of *p* orbitals in an aromatic compounds, must contain $(4n + 2)\pi$ electrons, where *n* is any integer (0, 1, 2, 3, 4, ...). In other words, aromatic compounds have 2, 6, 10, 18, ..., *pi* electrons.

These criteria for aromatic behaviour were first recognised by Erich Hückel. They are often called collectively the **Hückel $4n + 2$ rule** or simply the **$4n + 2$ rule**.

On the other hand, if such system contains $(4n)\pi$ electrons it will be antiaromatic. Antiaromatic systems are specially unstable. Thus in antiaromatic compounds delocalisation of the *pi* electrons over the ring results in an increase in the electronic energy. Thus in antiaromatic compounds delocalisation decreases stability of the system by increase in energy. Antiaromatic compounds are much less stable even than similar nonaromatic compounds.

Hückel rule can be applied to simple annulenes.

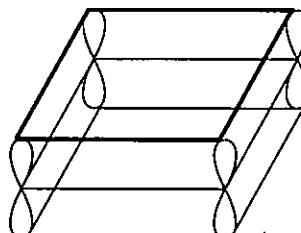
Application of Hückel Rule to Simple Annulenes

An annulene is monocyclic hydrocarbon with alternating single and double bonds. Since carbon atoms occur as doubly bonded pairs, an annulene must have an even number of carbon atoms. Annulenes are named [x] annulene where *x* is the number of carbons in the ring. Thus, cyclooctatetraene becomes [8]annulene, cyclodecapentaene

becomes [10]annulene and so on. Hückel rule is easily used to determine whether an annulene is aromatic or antiaromatic.

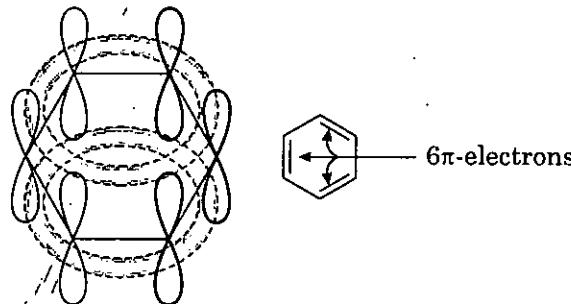
Cyclobutadiene : The simplest annulene is [4]annulene or [4]Annulene

Cyclobutadiene has four sp^2 hybrid carbon atoms with the four unhybridised p orbitals forming a continuous ring. There are four π electrons (two π bonds in the classical structure), so it is a $4n$ system, with $n = 1$. Thus cyclobutadiene is antiaromatic and its conjugation should make it less stable.



Cyclobutadiene is an antiaromatic system with four π electrons.

Benzene : Benzene is [6]annulene. It is a cyclic compound with the ring composed of sp^2 hybrid carbon atoms. The molecule can easily achieve a planar structure with a continuous ring of overlapping p orbitals. There are six π electrons in benzene, so it is a $(4n + 2)\pi$ system with $n = 1$. Thus benzene is aromatic.

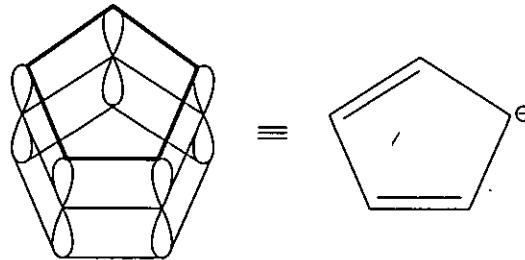


Overlapping p -orbitals in benzene
Benzene is an aromatic system
with six π electrons

Aromatic Ions

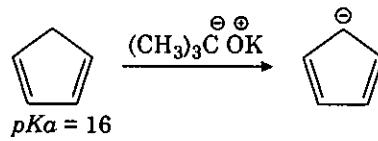
Up to this point we have discussed aromaticity using the annulenes as examples. Annulenes are uncharged molecules having even number of carbon atoms. Hückel rule also applies to the systems having odd number of carbon atoms and bearing positive or negative charges.

The Cyclopentadienyl Ions : Cyclopentadienyl anion with six π electrons is aromatic.

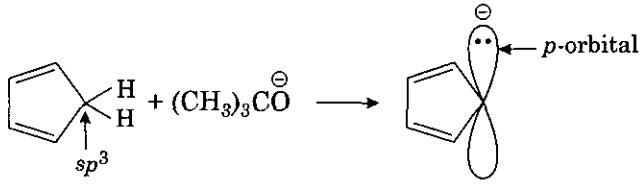


Cyclopentadienyl anion

It is prepared from cyclopentadiene. Cyclopentadiene is 10^8 times more acidic than a terminal alkyne. In fact, cyclopentadiene is nearly as acidic as water and more acidic than any alcohol. It can be deprotonated by potassium *tert*-butoxide.

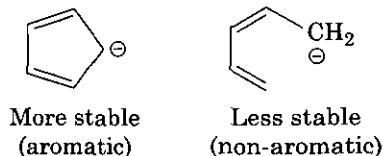


Hückel rule predicts that the cyclopentadienyl anion is aromatic, and this explains why cyclopentadiene is much more acidic than other hydrocarbons. Cyclopentadiene is neither aromatic nor antiaromatic because its ring contains an sp^3 hybrid ($-\text{CH}_2-$) carbon atom. This carbon has no unhybridised p orbital, so there can be no continuous ring of p orbitals. Deprotonation of the $-\text{CH}_2-$ group leaves an orbital occupied by a pair of electrons. This orbital can rehybridise to a p orbital, completing a ring of p orbitals containing six π electrons; the two electrons on the deprotonated carbon, plus the four electrons in the original double bonds. Thus, the cyclopentadienyl anion is aromatic.

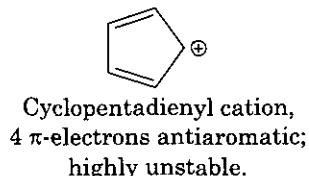


Cyclopentadienyl anion

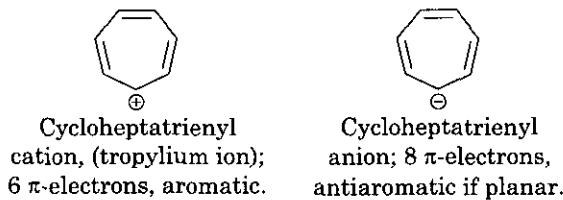
When we say that the cyclopentadienyl anion is aromatic, this does not imply that it is as stable as benzene. The fact that this ion is aromatic implies that it is more stable than the corresponding open chain ion.



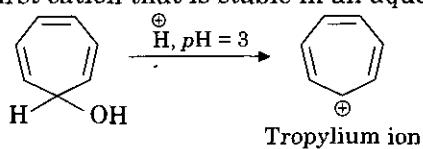
Cyclopentadienyl Cation]



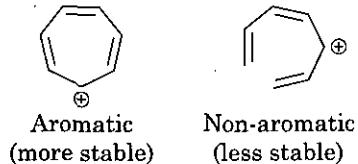
The Cycloheptatrienyl Ions



Cycloheptatrienyl cation is prepared from cycloheptatrienol. When this compound is treated with sulphuric acid, the formation of cycloheptatrienyl cation takes place very readily. This is the first cation that is stable in an aqueous solution.



Some tropylium salts can be isolated and stored for months without decomposition. Aromatic tropylium ion is not necessarily as stable as benzene. The tropylium ion's aromaticity implies that the cyclic ion is more stable than the corresponding open-chain ion.



In contrast to the easy formation of the tropylium cation, the corresponding anion is difficult to prepare because it is antiaromatic, hence highly unstable. Cycloheptatriene is about as acidic as propene ($pK_a = 53$).

Cyclopropenyl ions



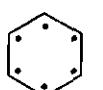
Cyclopropenyl cation,
 2π -electrons aromatic



Cyclopropenyl anion,
 4π -electrons anti-aromatic

Cyclopropenyl cation is prepared from cyclopropenyl bromide. When this compound is treated with water, it ionises and gives cyclopropenyl cation.

Since aromatic properties in the molecule are due to the presence of aromatic sextet hence some *heterocyclic compounds* like pyridine, thiophene, pyrrole, furan exhibits aromatic properties.



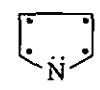
Benzene



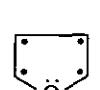
Pyridine



Thiophene



H
Pyrrole



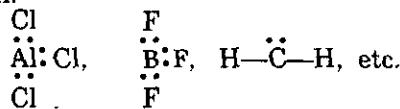
Furan

• 5.2. ELECTROMERIC AROMATIC SUBSTITUTIONS

Electrophilic Reagents or Electrophiles

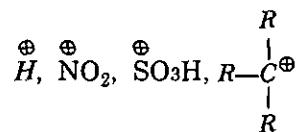
An electrophile (electron loving) is a reagent that is electron deficient and the deficiency accounts for its affinity for electrons. Electrophiles can be of two types :

(i) **Neutral Electrophiles** : The neutral electrophiles, through electron deficient do not carry positive charge. They have incomplete valence shells. The example are AlCl_3 , BF_3 , CH_2 (carbene), etc. They are electron deficient due to incomplete outermost shell.

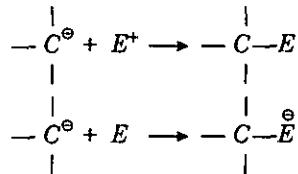


(Only six electrons instead of eight electrons in the outermost shell)

(ii) **Positive Electrophiles** : The positive electrophiles are those which carry a positive charge on central atom and have incomplete octet.



The positive electrophile attacks the substrate (negative nucleophile) and accepts an electron pair for sharing, thus forming a neutral molecule. On the other hand, a neutral electrophile will attack an electron rich substrate (negative nucleophile) to produce a negatively charged molecule.



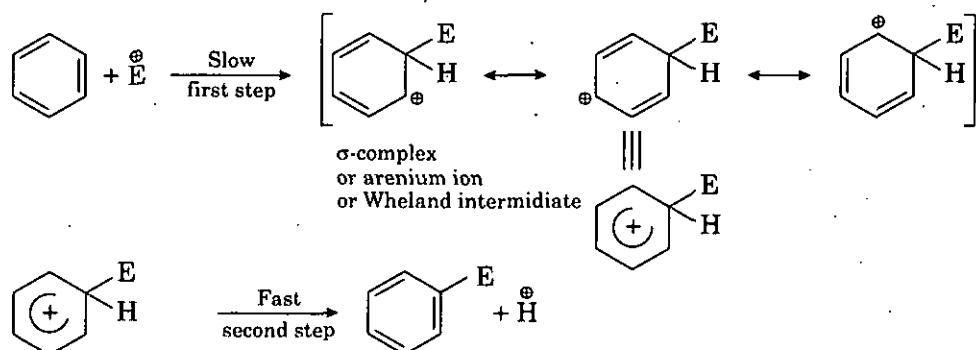
Substitution Reactions

Substitution reactions are characteristic of benzene and many other aromatic compounds. In these reactions a hydrogen on the ring is replaced by an electrophile

formed in the presence of a suitable catalyst (usually, a Lewis acid). These reactions are grouped as **aromatic electrophilic substitutions** (e.g., halogenation, nitration, sulphonation and Friedel-Crafts reactions), as all of them are initiated by electrophiles. Aromatic electrophilic substitution reactions have been discussed in detail ahead.

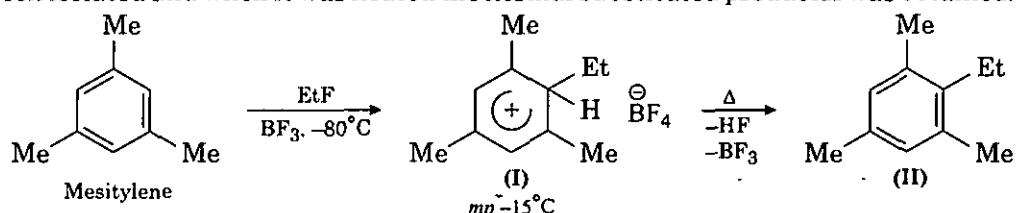
General Pattern of the Mechanism

According to the most accepted theory of aromatic electrophilic substitution, it proceeds by a bimolecular mechanism via the formation of an intermediate and that the formation of this intermediate is the rate-determining step. In this mechanism, which is called the **arenium ion mechanism**, the electrophile attacks in the first step giving rise to a **carbocation intermediate [known as arenium (benzenium) ion or Wheland intermediate or σ complex]** and the leaving group (H) departs in the second step. The second step is (nearly always) faster than the first step. The attacking electrophile may be a positive ion or a positive end of a dipole or induced dipole. The σ complex is stabilised by resonance. The resonance energy of the arenium ion intermediate will be much less than that of benzene, but by expulsion of a proton the molecule can revert to the more stable benzenoid (aromatic) state. Sometimes this mechanism is called SE₂ mechanism, as it is bimolecular.



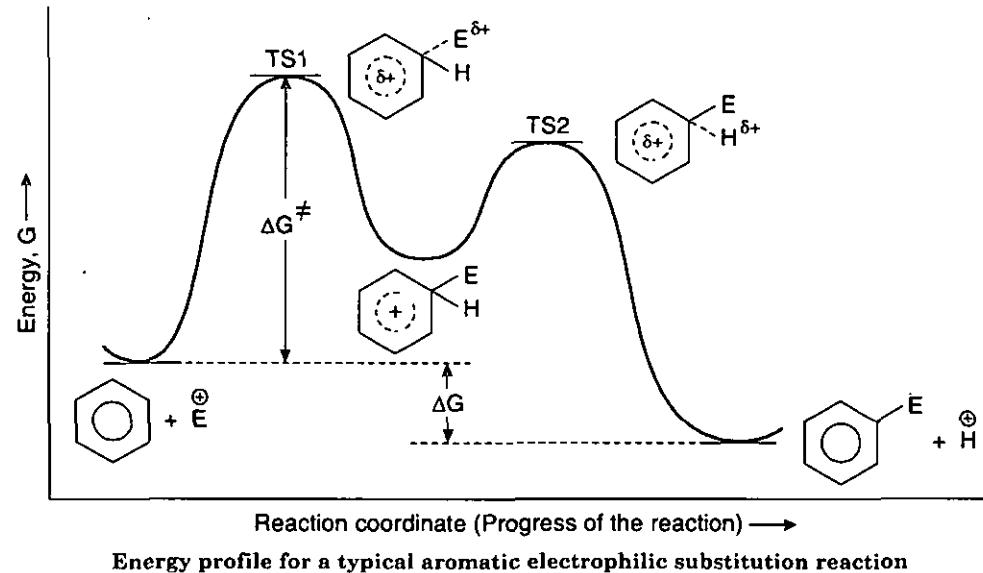
Evidence in support of the arenium ion mechanism

(1) **Isolation of arenium ion intermediates :** The intermediate arenium ions have not only been detected but also have been isolated in many cases. This gives a very strong evidence for the arenium ion mechanism. For example, the arenium ion I has been isolated and when it was heated the normal substituted product II was obtained.



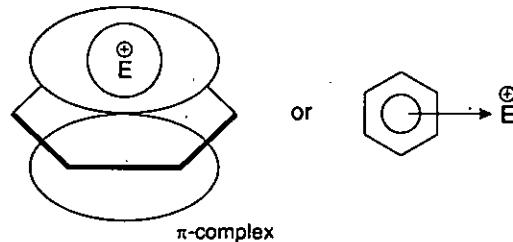
(2) **Isotope effect :** In the arenium ion mechanism the C—H bond is not broken in the rate-determining step, hence no isotope effect should be observed. This is the case also because in general, aromatic electrophilic substitutions do not exhibit isotope effect. For example, the rates of nitration of deuterio- and tritiobenzenes are the same as the rate for benzene. Thus, the removal of proton is not the rate-determining step of the reaction therefore, an aromatic electrophilic substitution is not a single step process.

A more detailed picture of the arenium ion mechanism may be presented by its energy profile. Similar energy profiles can be constructed for substituted benzenes also.



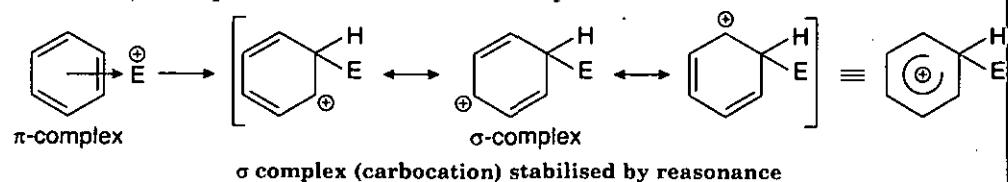
Role of σ and π Complexes in Aromatic Electrophilic Substitution

The intermediates in aromatic electrophilic substitutions are commonly called σ complexes. In σ complexes there is a covalent bond between the electrophile to a ring carbon. Experimental evidence suggests that the formation of a σ complex takes place after the initial formation of a π complex. A π complex does not involve actual bonding but the electrophile is held near the π electron cloud of the aromatic ring, i.e., the electrophile is strongly attracted to the electron rich π electron cloud of the aromatic ring and π complex is formed.

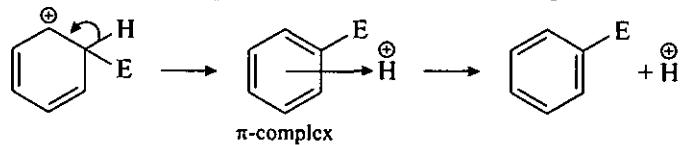


Attraction of electrophile to π electron cloud of benzene to form π complex

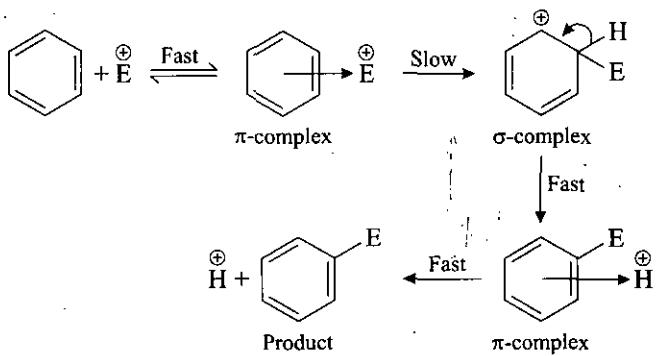
As the electrophile penetrates the π electron cloud and approaches bonding distance, it acquires two electrons from the π system and bonds to benzene ring. In other words, π complex is converted into σ complex.



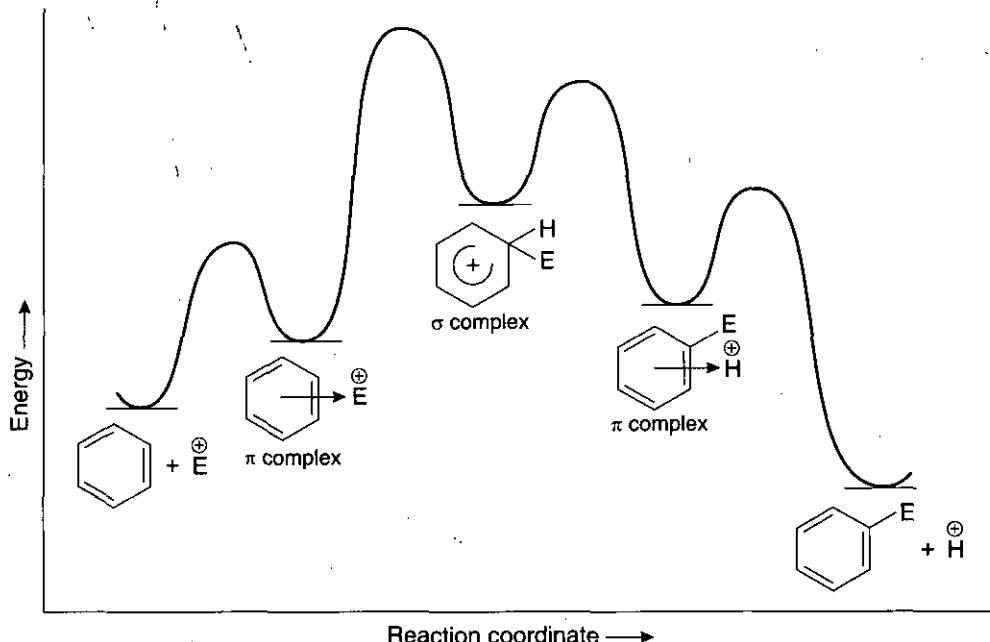
This σ complex loses a proton which before departing from the σ complex again forms a π complex. This π complex then converts into the product.



Thus the overall mechanism can be written as shown ahead.



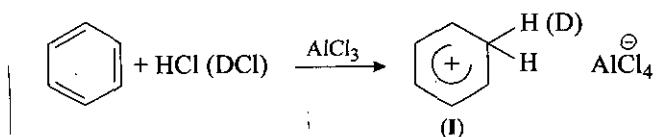
Available data suggest that in most of the aromatic substitutions the first step is the rapid reversible formation of the π complex and a high energy transition state is reached during the conversion of the π complex to the σ complex. This conversion is rate determining step. The energy profile of the substitution is shown below.



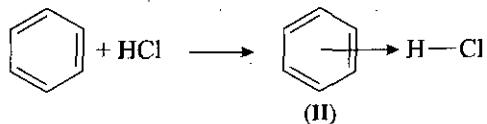
Energy profile showing π and σ complex formation in aromatic electrophilic substitutions where the σ complex is the rate-determining step.

Evidence for the formation of σ and π complexes

In the presence of $AlCl_3$, benzene forms a complex with HCl . The complex is coloured and its solution conducts electricity showing its ionic character. Moreover, when DCl is used in place of HCl , the deuterium exchanges with the benzene protons. This can only be explained if there is the formation of a σ complex I as shown below.



In the absence of $AlCl_3$, benzene still forms a 1 : 1 complex with HCl , but in contrast to the σ complex, the solution of this complex is colourless and does not conduct electricity. In this case when DCl is used in place of HCl , the recovered benzene is not found to contain any deuterium. This type of complex is called a π complex.

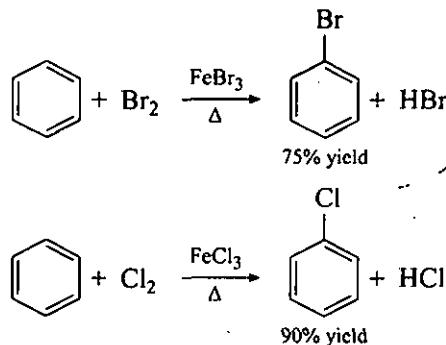


It is formed by the loose association of a proton (or any other electrophile) with the π electron cloud of the benzene ring (II). There is no actual bonding in this case, hence deuterium exchange does not occur.

• 5.3. HALOGENATION OF BENZENE

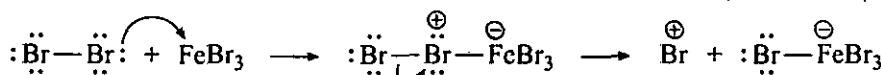
Benzene does not react with chlorine or bromine unless a Lewis acid is used as catalyst. In the presence of Lewis acid, benzene reacts readily with bromine and chlorine to give bromobenzene and chlorobenzene, respectively in good yield.

The most common catalyst for the halogenation reaction is anhydrous FeX_3 and anhydrous AlX_3 .

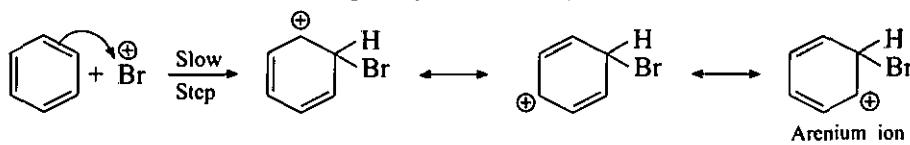


Mechanism of Bromination

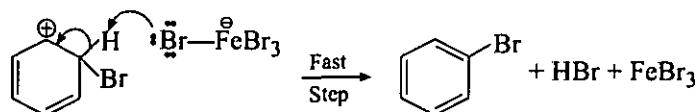
Step I : In the first step of the reaction bromine donates a lone pair of electrons to the Lewis acid to form a complex. This complex on dissociation gives Br^- and $\overset{\oplus}{\text{FeBr}_3}$.



Step II : The positive end of the halogen-Lewis acid complex (halogen dipole) or $\overset{\oplus}{\text{Br}}$ attacks benzene to form σ complex (arenium ion).

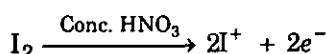


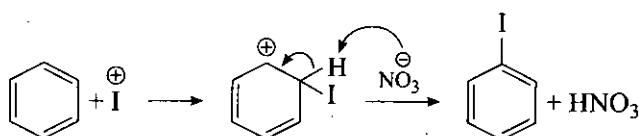
Step III : In this step a proton is removed from the arenium ion by FeBr_4^- . This results in the formation of bromobenzene and hydrogen bromide. At the same time catalyst FeBr_3 regenerates in this step.



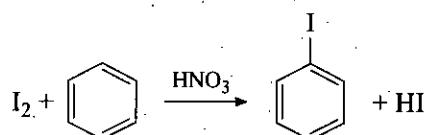
Note :

- Fluorine is highly reactive. It reacts so rapidly with benzene that aromatic fluorination requires special conditions and special types of apparatus.
- The mechanism of the chlorination of benzene in the presence of FeCl_3 is analogous to the one for bromination.
- Iodine is so unreactive that a special technique has to be used to effect direct iodination. The iodination is carried out in the presence of an oxidising agent such as HNO_3 .





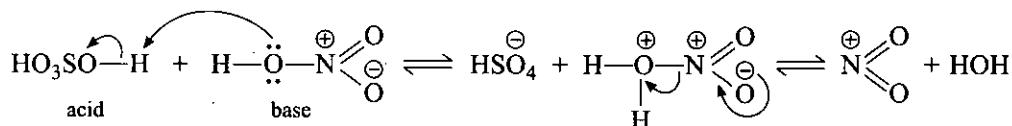
Thus the overall reaction is



• 5.4. NITRATION OF BENZENE

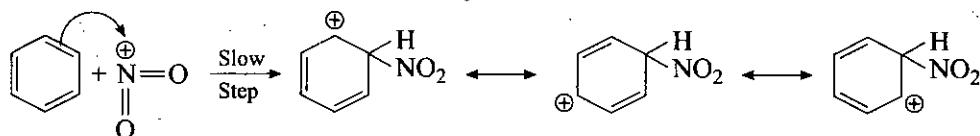
Nitration of benzene requires sulphuric acid as a catalyst. Sulphuric acid protonates nitric acid. Loss of water from the protonated nitric acid forms a nitronium ion, the electrophile required for nitration.

Step I :

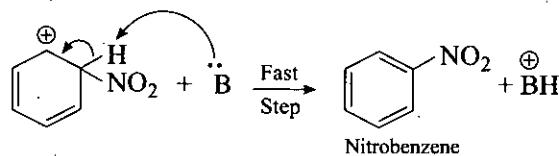


Here nitric acid acts as a base.

Step II : The electrophile, $\overset{\oplus}{NO}_2$, attacks benzene ring to form σ complex or arenium ion. Arenium ion is stabilised by resonance.



Step III : In the third step the arenium ion loses a proton to a Lewis base (HOH or $\overset{\oplus}{NO}_3^-$ or HSO_4^-) and gives nitrobenzene.



Besides mixed acids ($HNO_3 + H_2SO_4$), nitration can also be performed with conc. HNO_3 alone which also occurs via nitronium ion. Here HNO_3 acts as both as an acid and a base.

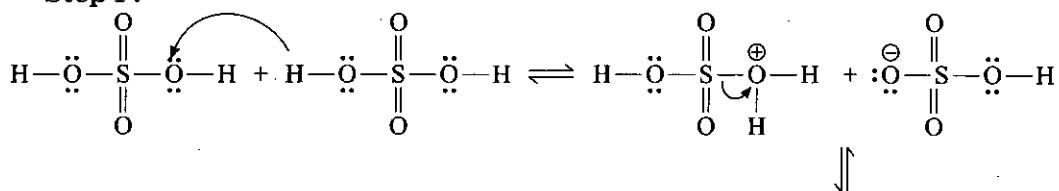
Salts of nitronium ion, e.g., $\overset{\oplus}{NO}_2ClO_4^-$ and $\overset{\oplus}{NO}_2BF_4^-$ have been isolated and used as nitrating agents. This is a very strong evidence for the existence of nitronium ion.

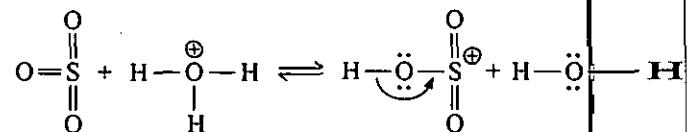
• 5.5. SULPHONATION OF BENZENE

Fuming sulphuric acid or concentrated sulphuric acid is used to sulphonate benzene. Fuming sulphuric acid is sulphuric acid that contains added sulphur trioxide (SO_3).

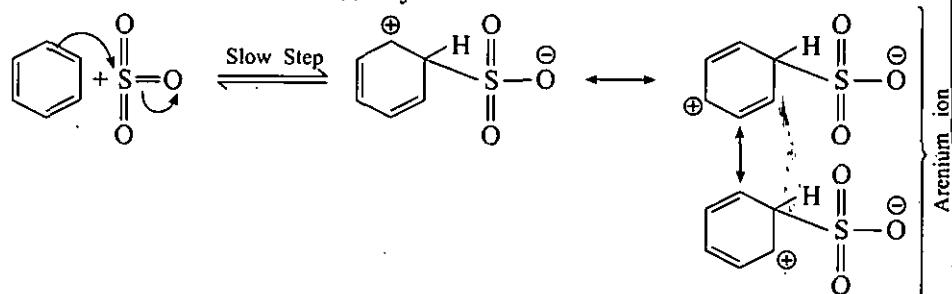
In either reaction the electrophile appears to be sulphur trioxide. In concentrated sulphuric acid, sulphur trioxide is produced in an equilibrium in which H_2SO_4 acts as both an acid and a base.

Step I :

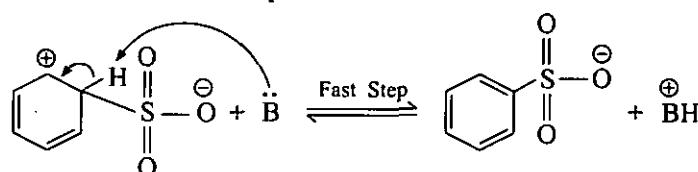




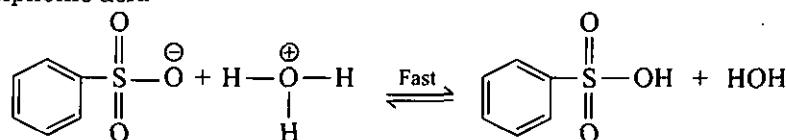
Step II : Sulphur trioxide is the actual electrophile that reacts with benzene to **form** an arenium ion which is stabilised by resonance.



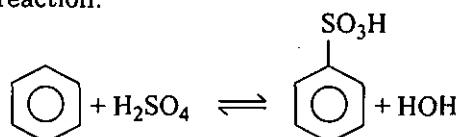
Step III : In the third step a proton is removed by base (HOH or HSO4-) from **the** arenium ion to form the benzenesulphonate anion.



Step IV : The benzenesulphonate anion accepts a proton to **become** benzenesulphonic acid



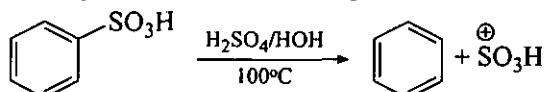
All the steps (Step I to Step IV) are reversible steps. Therefore, sulphonation of benzene is a reversible reaction.



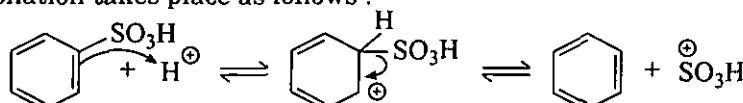
Because all of the steps are reversible, the position of equilibrium can be influenced by the conditions we employ. For example :

(i) If we want to sulphonate benzene we use concentrated sulphuric acid **or** better fuming sulphuric acid under these conditions the position of equilibrium **lies** appreciably to the right and we obtain benzenesulphonic acid in good yield.

(ii) On the other hand, we may want to remove a sulphonic acid group from **the** benzene ring. To do this we employ dilute sulphuric acid and usually pass steam through the mixture. Under these conditions with a high concentration of water **the** equilibrium lies appreciably to the left and desulphonation occurs.



Desulphonation takes place as follows :

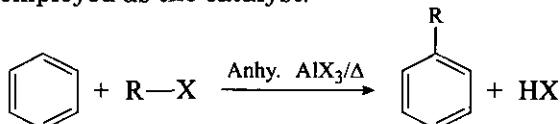


• 5.6. FRIEDEL-CRAFTS REACTION

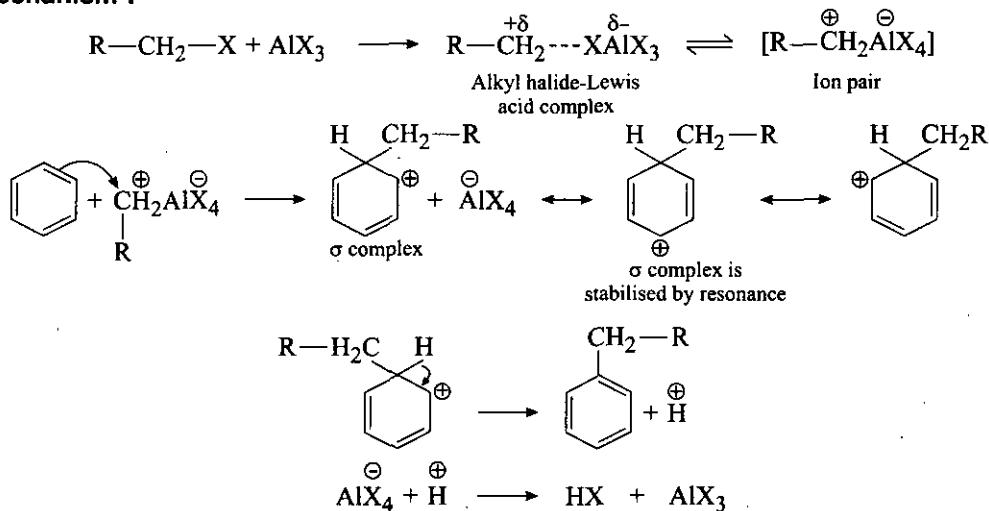
Alkylation of aromatic compounds with aliphatic compounds like halides, alcohols, esters, ethers, alkenes, aldehydes and ketones in the presence of Lewis acid **or**

proton acid as catalyst is known as Friedel-Crafts alkylation. This reaction is an example of aromatic electrophilic substitution reaction. If alkylating agent is halide, alcohol, ester or ether then catalyst is Lewis acid, but when alkylating agent is alkene, aldehyde and ketone, catalyst is proton acid.

Halides are the reagents of most frequent choice in alkylation and aluminium halides are usually employed as the catalyst.

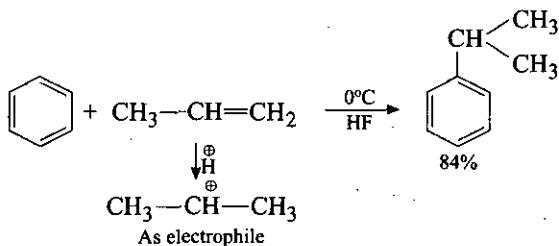
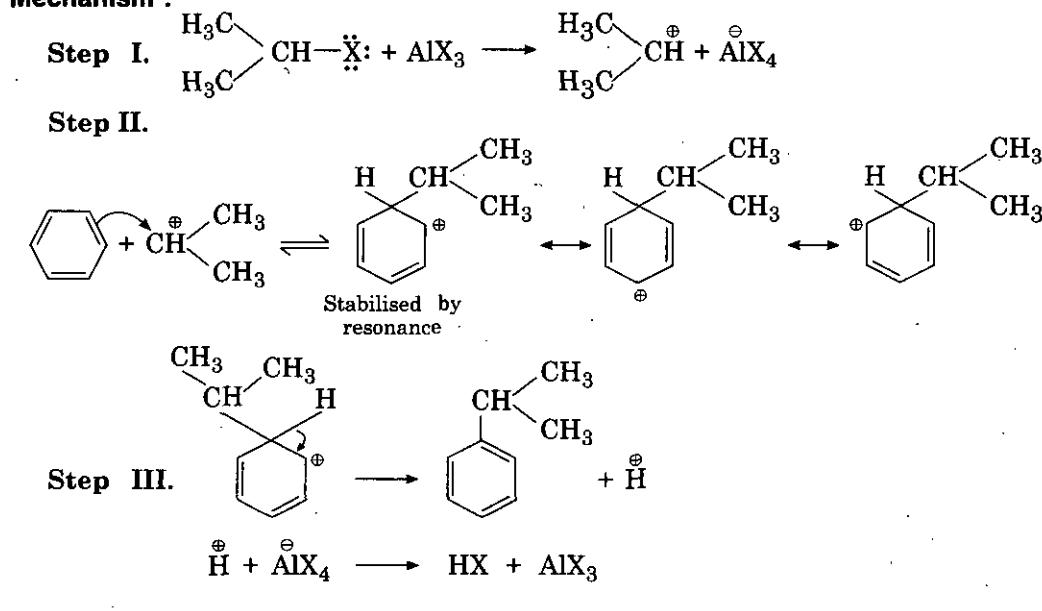


Mechanism :



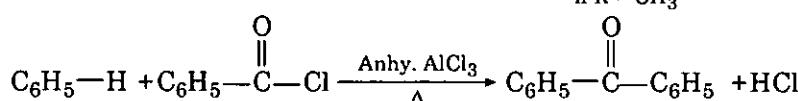
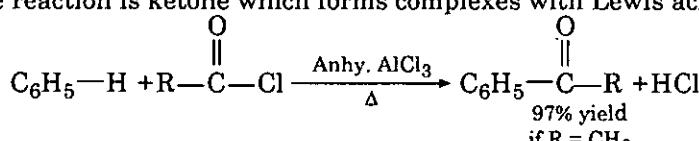
If alkyl halide is tertiary, then reaction starts with the formation of carbocation and this carbocation acts as the electrophile. With primary alkyl halide the electrophile is an alkyl halide-Lewis acid complex with a positively polarised carbon.

Mechanism :

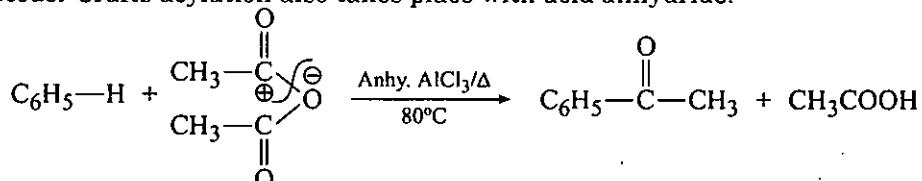


Acylation

The $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{-}$ group is called an acyl group and a reaction whereby an acyl group is introduced into a compound is called acylation reaction. Acylation of aromatic compounds takes place in the presence of excess amount of Lewis acid because the product of the reaction is ketone which forms complexes with Lewis acid.

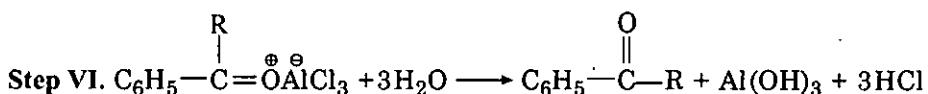
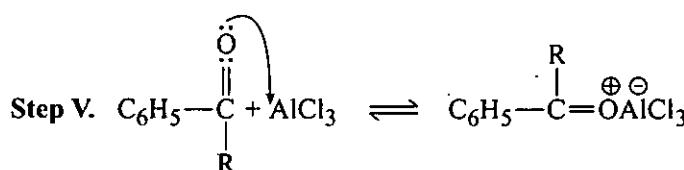
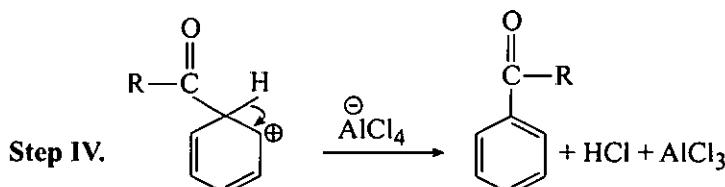
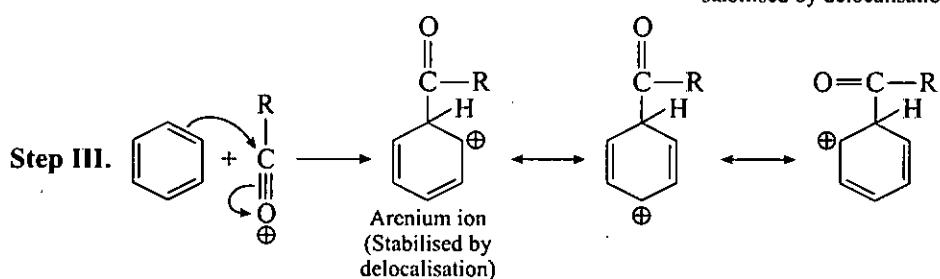
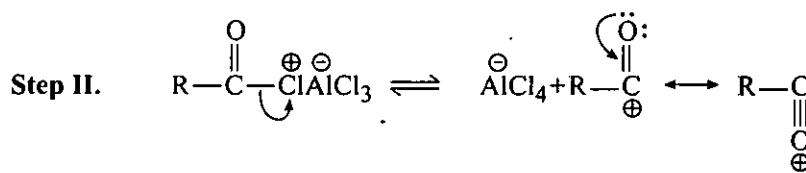
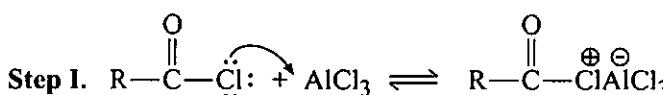


Friedel-Crafts acylation also takes place with acid anhydride.



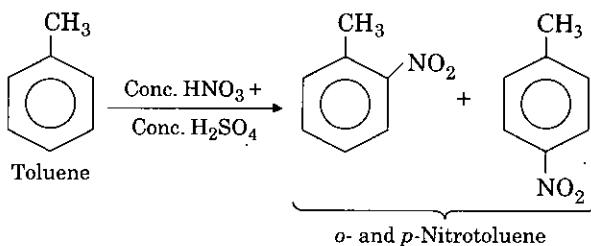
Friedel-Crafts acylation also takes place with acid anhydride.

Mechanism :

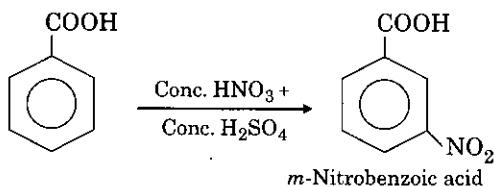


• 5.7. DIRECTING EFFECTS OF THE GROUPS

When a monosubstituted derivative of benzene is converted into a disubstituted derivative, the product is either a mixture of *ortho* and *para* derivatives or it is a *meta* derivative. Thus, when toluene is nitrated, the $-\text{NO}_2$ group enters the *ortho* and *para* positions and a mixture of *ortho* and *para* nitrotoluenes is obtained.



But when benzoic acid is nitrated, the $-\text{NO}_2$ group enters in the *meta* position and *m*-nitrobenzoic acid is obtained.



From the above, it is clear that the group already present in the benzene ring is responsible for the position taken by incoming group. This is known as **directive influence of groups in aromatic substitution**.

It has also been observed that *o*- and *p*-directive groups possess activating effect on the substituent reactions, whereas *meta* directive groups deactivate the whole ring so that further substitution becomes difficult.

Certain empirical rules have been given to explain the nature of the groups already present in the ring. These are :

(1) **Crum-Brown-Gibson's rule (1892)** : According to this rule,

If the substituent X already present in the benzene ring forms a compound HX with hydrogen which can be directly oxidised to HXO, then X is *meta*-directive group, otherwise it is *ortho* and *para* directing.

Group X	HX	HXO	Oxidation	Directive influence
$-\text{CH}_3$	CH_4	CH_3OH	Difficult	<i>o</i> , <i>p</i> -
$-\text{OH}$	H_2O	H_2O_2	Difficult	<i>o</i> , <i>p</i> -
$-\text{NH}_2$	NH_3	NH_2OH	Difficult	<i>o</i> , <i>p</i> -
$-\text{Cl}$	HCl	HOCl	Difficult	<i>o</i> , <i>p</i> -
$-\text{NO}_2$	HNO_2	HNO_3	Easy	<i>m</i> -
$-\text{COOH}$	H.COOH	H_2CO_3	Easy	<i>m</i> -
$-\text{SO}_3\text{H}$	H_2SO_3	H_2SO_4	Easy	<i>m</i> -
$-\text{CHO}$	HCHO	HCOOH	Easy	<i>m</i> -

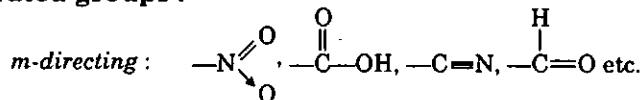
Objections : The main objection against the rule was that the word 'direct oxidation' was vague. For example, $-\text{CN}$ forms HCN which is oxidised to HCNO but not easily and so it should be *o*, *p*-directive but actually it is *m*-directive. This rule is silent about the orientation of a trisubstituted product formed from a disubstituted product containing two different groups. This rule also does not give the proportions of *ortho* and *para*-isomers.

(2) **Vorlander's rule (1902)** : According to this rule,

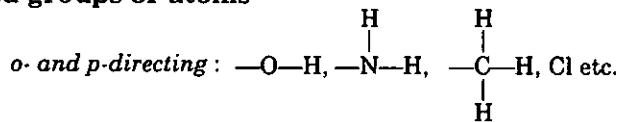
Unsaturated groups are *meta* directing, whereas saturated groups are *ortho* and *para* directing.

Objections : This rule had exceptions, e.g., in cinnamic acid $C_6H_5CH=CHCOOH$, the group — CH = CH.COOH is unsaturated but it is *o*-, *p*-directing.

(i) Unsaturated groups :



(ii) Saturated groups or atoms



(3) Hammic-Illingworth's rule (1930) : According to this rule, in the benzene derivative C_6H_5XY ,

- If Y belongs to a higher group in the periodic table than X, the group already present is *meta* directing
- If Y belongs to a lower group in the periodic table than X, the group already present is *ortho* and *para* directing.
- If X and Y belong to the same group in the periodic table and Y has lower atomic weight than X, the group already present is *meta* directing.
- If there is no Y, the group already present is *ortho* and *para* directing.

Group	X and its group	Y and its group	Directive influence
$-NO_2$	N (Group V)	O (Group VI)	<i>m</i> -directing
$-NH_2$	N (Group V)	H (Group I)	<i>o</i> -, <i>p</i> -directing
$-CH_3$	C (Group IV)	H (Group I)	<i>o</i> -, <i>p</i> -directing
$-CN$	C (Group IV)	N (Group V)	<i>m</i> -directing
$-OH$	O (Group VI)	H (Group I)	<i>o</i> -, <i>p</i> -directing
$-COOH$	C (Group IV)	O (Group VI)	<i>m</i> -directing
$-SO_3H$	S (Group VI) <small>(At. wt. = 32)</small>	O (Group VI) <small>(At. wt. = 16)</small>	<i>m</i> -directing
Cl			<i>o</i> -, <i>p</i> -directing

Modern view : According to modern view, the directive influence and the activating or deactivating effect of substituents on the benzene ring can be accounted for in terms of the mechanism of aromatic substitution and electron displacement effect of the substituent already present.

Introduction of a Third Substituent Into the Benzene Ring

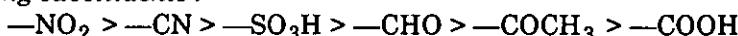
When a third group enters in the benzene ring, its position is ascertained by the nature of the two substituents already present in it.

- If the two substituents already present have the same directive influence, then directive influence will be in the following order.

Ortho-and para-directing substituents :



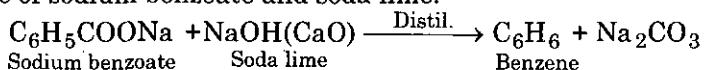
Meta directing substituents :



- When the two substituents already present have different directive influence, then the influence of *o*- and *p*-directing groups predominates. In case, the influence of the two substituents reinforce each other, the third substituent will enter almost entirely in reinforced position.

• 5.8. PREPARATION OF BENZENE

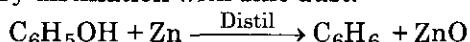
(i) Laboratory method : Benzene is prepared in laboratory by the distillation of a mixture of sodium benzoate and soda lime.



Experiment: A mixture of 20 g of sodium benzoate and 30 g of soda lime is taken in a round-bottom flask fitted with a thermometer and a delivery tube attached to a water condenser. On heating, benzene is formed and is collected in a receiver along with water. Benzene is then separated using a separating funnel. It is then dried over anhydrous calcium chloride and finally obtained in the pure form by distillation.

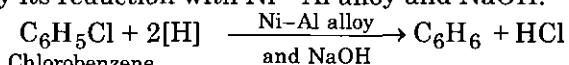
(ii) From derivatives of benzene :

(a) **From phenol**: By distillation with zinc dust.

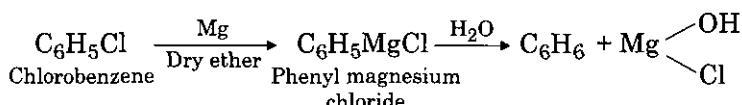


(b) *From chlorobenzene* : There are two ways :

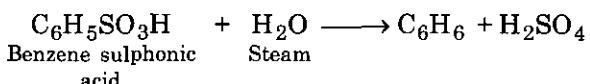
(i) By its reduction with Ni-Al alloy and NaOH.



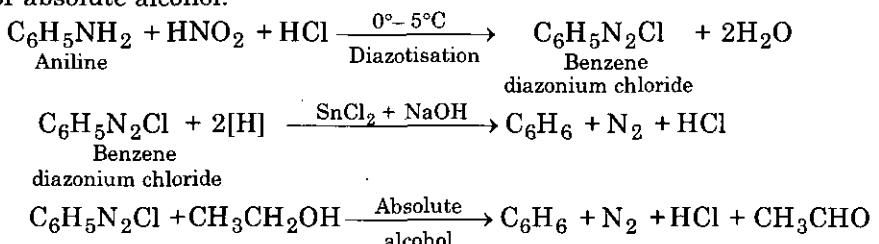
(ii) By first preparing Grignard's reagent and then hydrolysing it.



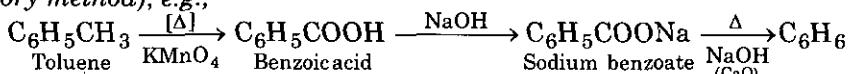
(c) *From benzene sulphonic acid* : By its hydrolysis with super heated steam.



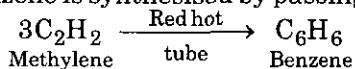
(d) From aniline or benzene diazonium chloride : Aniline on diazotisation forms benzene diazonium chloride which is then reduced to benzene by SnCl_2 and NaOH or absolute alcohol.



(e) **From homologues of benzene** : Monoalkyl benzenes, on oxidation with KMnO_4 , form benzoic acid which is then decarboxylated by heating with soda lime (See laboratory method), e.g.,



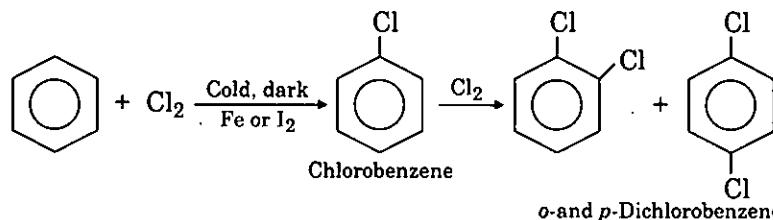
(iii) **Synthesis** : Benzene is synthesised by passing acetylene through red hot tube.



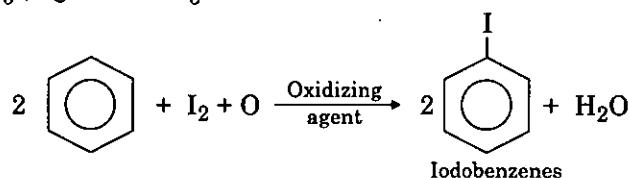
• 5.9. REACTIONS

Electrophilic Substitution

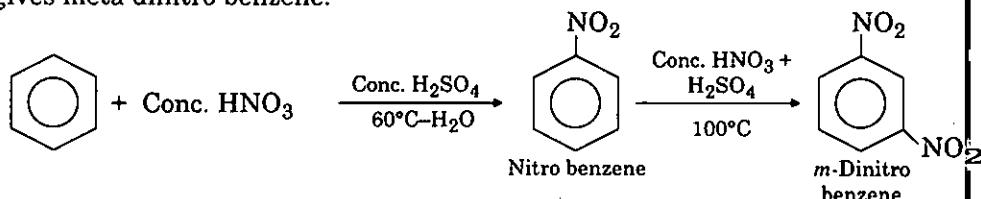
(1) Halogenation : The phenomenon of replacement of one or more hydrogen atoms from benzene nucleus by halogen atom is known as **halogenation**. Thus, benzene reacts with chlorine in presence of halogen carrier Fe or I_2 and in cold dark to form chloro substitution products.



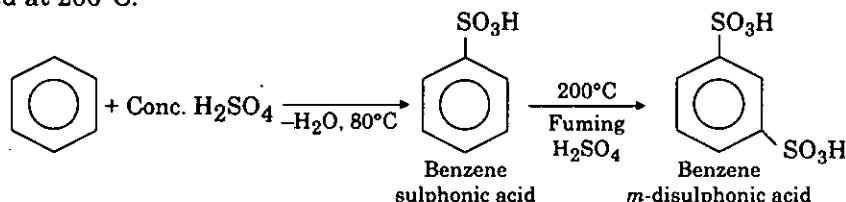
Bromine reacts similarly but with iodine the reaction is reversible. In order to make the reaction irreversible, the reaction is carried out in the presence of an oxidizing agent conc. HNO_3 , HgO or HIO_3 .



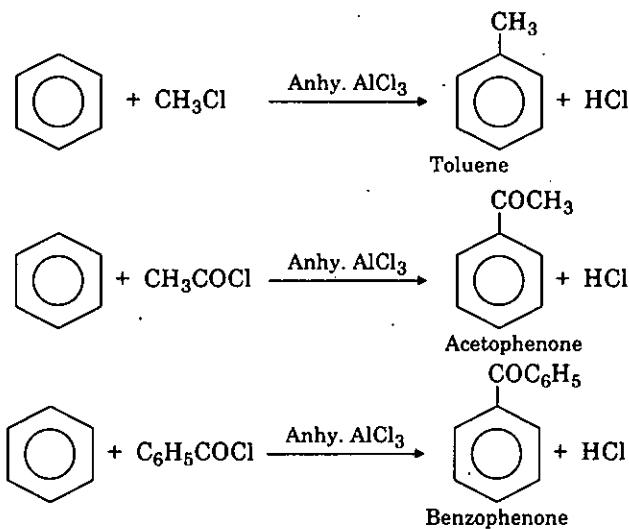
(b) Nitration : The phenomenon of replacement of one or more hydrogen atoms from benzene nucleus by nitro group is known as *nitration*. Thus, benzene reacts with a mixture of conc. HNO_3 and conc. H_2SO_4 at 60°C to give nitrobenzene whereas at 100°C it gives meta dinitro benzene.



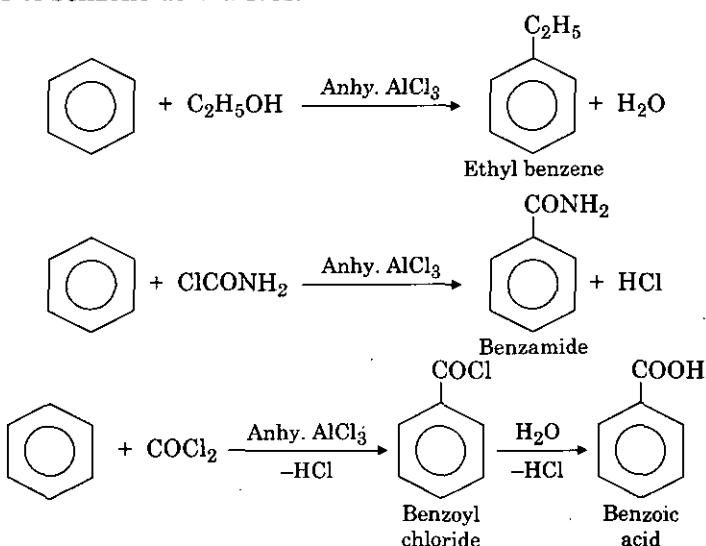
(c) Sulphonation : The phenomenon of replacement of one or more hydrogen atoms from benzene nucleus by $-\text{SO}_3\text{H}$ group is known as *sulphonation*. Thus, benzene reacts with conc. H_2SO_4 at 80°C to form benzene sulphonic acid. If fuming sulphuric acid is used, the reaction takes place further and benzene *m*-disulphonic acid is formed at 200°C .



(d) Friedel-Craft's reaction : The reaction involves the introduction of an alkyl or acyl group into the benzene nucleus in the presence of anhydrous AlCl_3 as catalyst.



Benzene also shows the following reactions in the presence of anhydrous AlCl_3 to form a number of benzene derivatives.



• SUMMARY

- The unique property of aromatic compounds is called aromaticity.
- Hückel's ($4n + 2$) rule:** A cyclic compound which has $(4n + 2)\pi$ electrons (where $n =$ an integer) should be markedly stable, typical of benzenoid aromatics.
- Cyclic compounds which have $(4n)\pi$ electrons are called anti-aromatic compounds and this quality is known as anti-aromaticity.
- A group already present in the benzene ring is responsible for the position taken by the incoming group during substitution. This is known as directive influence of groups in aromatic substitution. It is governed by three rules, namely Cum-Brown-Gibson's rule, Vorlander's rule and Hammick-Illingworth rule.
- An electrophile is a reagent that is electron deficient. These are of two types
 - (i) Neutral electrophile (e.g., AlCl_3 , BF_3 , CH_2 etc. and (ii) Positive electrophile (e.g., H^+ , Cl^+ , NO_2^+ , SO_3 etc.)
- During electrophilic substitution reactions σ and π complexes are formed. The energy of the product is lower than that of reactants.
- Benzene is prepared in laboratory by the distillation of a mixture of sodium benzoate and sodalime.
- Benzene can also be prepared from the derivatives of benzene such as phenol, chlorobenzene, aniline etc.

• STUDENT ACTIVITY

- Write a short note on aromaticity.
-
-

- What is aromatic sextet?
-
-

- What is $(4n + 2)$ rule?
-
-

- Discuss the mechanism of halogenation of benzene.

- Write a note on Friedel-Craft's alkylation process.

- Describe the preparation of benzene.

- TEST YOURSELF

21

In the Friedel-Crafts acylation of an aromatic ring, the role of AlCl_3 is:

to :



- (a) form a $\text{CH}_3 - \text{C}^+$ ion
 (b) function as Lewis base
 (c) chloronation of aromatic ring
 (d) withdraw electrons from the aromatic ring
22. In sulphonation of benzene, following species is used :
 (a) SO_2 (b) SO_3 (c) SO_3^+ (d) SO_2^+
23. Benzene reacts with benzoyl chloride in the presence of anhydrous AlCl_3 to form
 24. The directive influence of nitro group is
 25. The directive influence of methyl group is
 26. The catalyst used in Friedel Crafts reaction is
 27. Benzene reacts with acetyl chloride in the presence of anhydrous AlCl_3 to give
 28. According to Huckel rule in aromatic compounds number of π electrons is
 29. In the preparation of benzene by laboratory method is heated with sodalime.
 30. Benzene on sulphonation gives

ANSWERS

- | | | | | | |
|------------------|--------------|--------------------|-----------------------------|---------|---------|
| 12. (b) | 13. (d) | 14. (a) | 15. (a) | 16. (b) | 17. (d) |
| 18. (c) | 19. (b) | 20. (b) | 21. (a) | 22. (b) | |
| 23. Benzophenone | 24. meta | 25. ortho and para | 26. anhyd. AlCl_3 | | |
| 27. Acetophenone | 28. $4n + 2$ | 29. Sodium | 30. Benzene sulphonic acid. | | |
| | | benzoate | | | |



6

ALKYL AND ARYL HALIDES

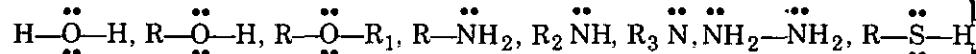
LEARNING OBJECTIVES

- Nucleophilic Reagents
- Nucleophilic Substitution Reactions
- Reactions of Alkyl Halide
- Preparation of Aryl Halides
- Reactions of Chlorobenzene
 - Summary
 - Student Activity
 - Test Yourself

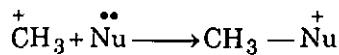
• 6.1. NUCLEOPHILIC REAGENTS OR NUCLEOPHILES

Reagents having an unshared pair of electrons are known as nucleophilic reagents or nucleophiles. Because they have a tendency to share this pair of electrons with electron deficient substrate. These nucleus loving species are known as nucleophiles. Nucleophiles can be classified into three groups :

(i) **Neutral Nucleophiles** : Electron rich species due to the presence of non-bonding electrons are known as neutral nucleophiles. Central atom of such species should have complete octet. They are not charged and are electrically neutral. For example



The addition of neutral nucleophile to a positively charged substrate will give a positively charged product.

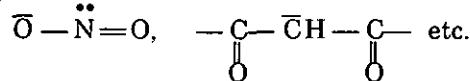


(ii) **Negative Nucleophiles** : Negative nucleophiles are those which carry an electron pair and are negatively charged because of one extra electron. For example $\overline{\text{X}}$, $\text{R}-\overline{\text{O}}$, $-\overline{\text{NO}}_2$, $\overline{\text{OH}}$, $\text{R}_3\overline{\text{C}}$, RCOO^- , $\overline{\text{CH}}_3$

Addition of a negative nucleophile to a positively charged substrate results in a neutral molecule.

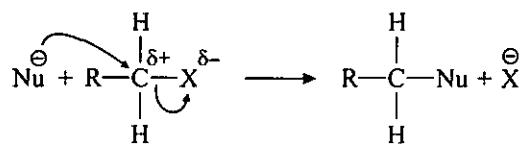


(iii) **Ambident Nucleophiles** : The nucleophiles which can attack through two or more atoms are called ambident nucleophiles. For example, CN^- can attack through N or C to give cyanide ($\text{R}-\text{CN}$) or isocyanide ($\text{R}-\text{NC}$). Other examples of ambident nucleophiles are :



• 6.2. NUCLEOPHILIC SUBSTITUTION REACTIONS

The $\text{C}-\text{X}$ bond in alkyl halides is polar, withdrawal of electron pair towards halogen makes the carbon electron deficient, hence it becomes a good target for attack by nucleophiles.



In nucleophilic substitution two changes occur—breaking of the bond with **leaving group** and formation of bond with **nucleophile**. The principal mechanistic variations are associated with changes in the timing of the two processes. The following are the possible mechanisms of nucleophilic substitutions :

(1) Two steps reaction (S_N1 Mechanism, Substitution Nucleophilic Unimolecular)

First Step : Breaking of the C—X bond

Second Step : Making of the C—Nu bond

(2) One step reaction (S_N2 Mechanism, Substitution Nucleophilic Bimolecular) : In this reaction the bond breaking and bond making are simultaneous.

Before discussing one step and two steps reactions let us first discuss leaving group and incoming nucleophile of the reaction.

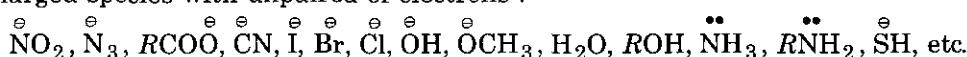
A general nucleophilic substitution reaction may be schematically represented as:



where L is a leaving group (or leaving nucleophile or nucleofuge) and Nu is an incoming nucleophile.

Incoming Nucleophile

An incoming nucleophile may either be negatively charged or it may be an uncharged species with unpaired of electrons :

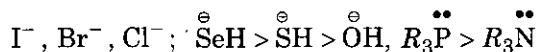


The reactivity of nucleophile is called its nucleophilicity. The nucleophilicity increases with increasing polarisability. Nucleophilicity can be compared as given below :

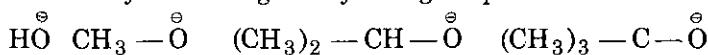
(1) A species with a negative charge is a stronger nucleophile than a similar species without a negative charge. In particular, a base is a stronger nucleophile than its conjugate acid. Therefore, $\overset{\ominus}{\text{OH}}$ is a stronger nucleophile than HOH and $\overset{\ominus}{\text{SH}}$ is a stronger nucleophile than $\text{CH}_3-\overset{\ominus}{\text{S}-\text{H}}$.

(2) Nucleophilicity decreases on going from left to right in the period of the periodic table. Therefore, $\overset{\ominus}{\text{OH}}$ is more nucleophilic than $\overset{\ominus}{\text{F}}$; NH_3 is more nucleophilic than HOH; and $\overset{\ominus}{\text{CH}_3}$ is more nucleophilic than $\overset{\ominus}{\text{NH}_2}$.

(3) Nucleophilicity increases on going down in the group of the periodic table. Therefore,



(4) Bulky group present on nucleophilic centre decreases nucleophilicity and increases basicity of the negatively charged species.



Basicity in increasing order; nucleophilicity in decreasing order →

Leaving Groups or Leaving Nucleophiles

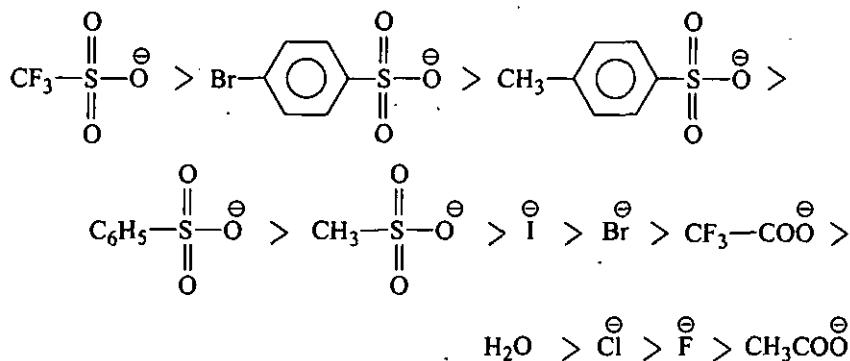
The leaving group must have the following three important characteristics :

(1) A leaving group is electron-withdrawing so that it creates a partial positive charge on the carbon atom.

(2) The leaving group should be stable after leaving with the bonding pair of electrons. In general, good leaving groups should be **weak bases**, and therefore, they are the conjugate bases of strong acids.

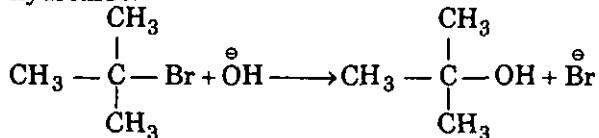
(3) Finally, the ability of a species to act as a good leaving group depends on its polarisability. That is its ability to continue bonding with a carbon atom while it is leaving. This bonding stabilises the transition state, minimising the activation energy.

The leaving power of some nucleophilic groups are given below in decreasing order :



• 6.3. SN1 MECHANISM OR SN1 REACTION : TWO STEP PROCESS

A typical example of this process is the hydrolysis of tertiary butyl bromide in the presence of sodium hydroxide.

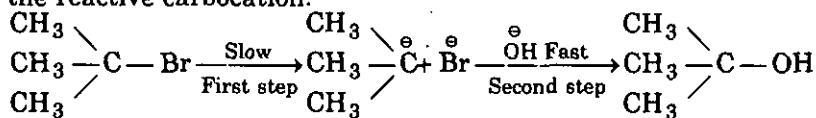


In this reaction, the rate of reaction is not increased by addition of NaOH even though hydroxide ions are consumed in the reaction. The rate of the reaction depends only on the concentration of the organic halide and hence, the first-order rate law is followed :

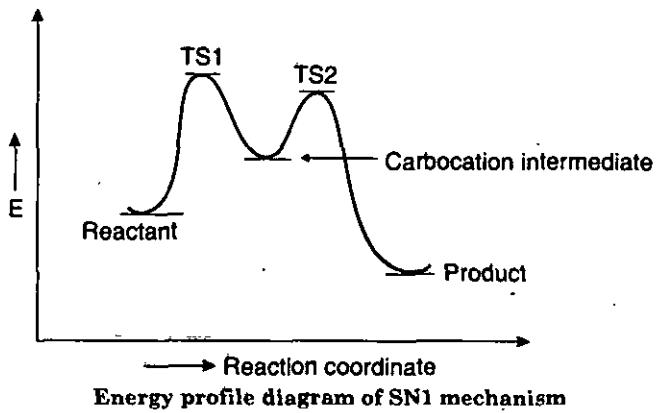
$$\text{Rate} = K \left[\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{Br} \\ | \\ \text{CH}_3 \end{array} \right]$$

This can be explained, if it is assumed that the reaction takes place in two steps. The first one being the ionization of alkyl halide producing carbocation. This will obviously be a slow (rate determining) step as it involves breaking of a covalent bond.

This is followed by the fast (non-rate determining) step which involves addition of nucleophile to the reactive carbocation.

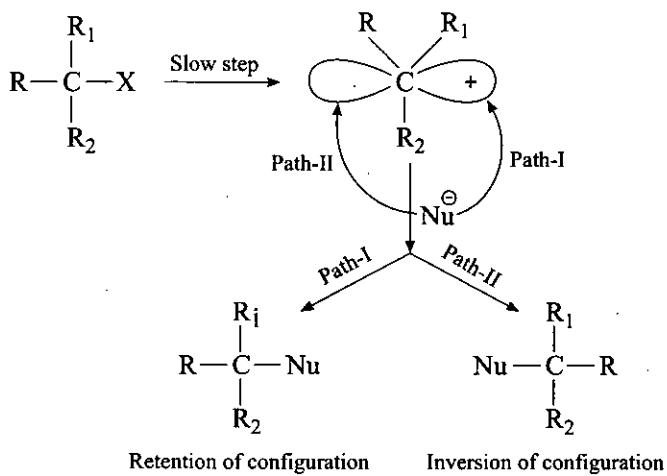


The energy profile diagram of SN1 mechanism is depicted below :



This two step mechanism (SN1 mechanism) of nucleophilic substitution is unimolecular because in the rate-determining step (slow first step) only the alkyl halide is undergoing covalency change. The nucleophile does not come into play until the fast second step.

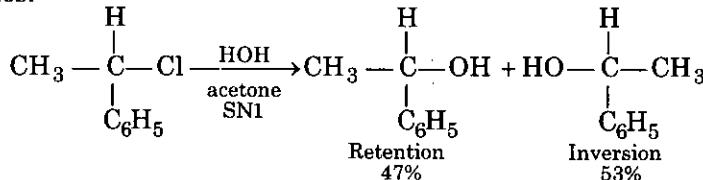
Stereochemistry of SN1 Reaction : The reaction of alkyl halide in which halogen is bonded to a chiral carbon leads to the formation of enantiomers. One with the same relative configuration as the reacting alkyl halide and other with the inverted configuration.



Formation of enantiomeric pair is due to the formation of carbocation whose geometry is planar.

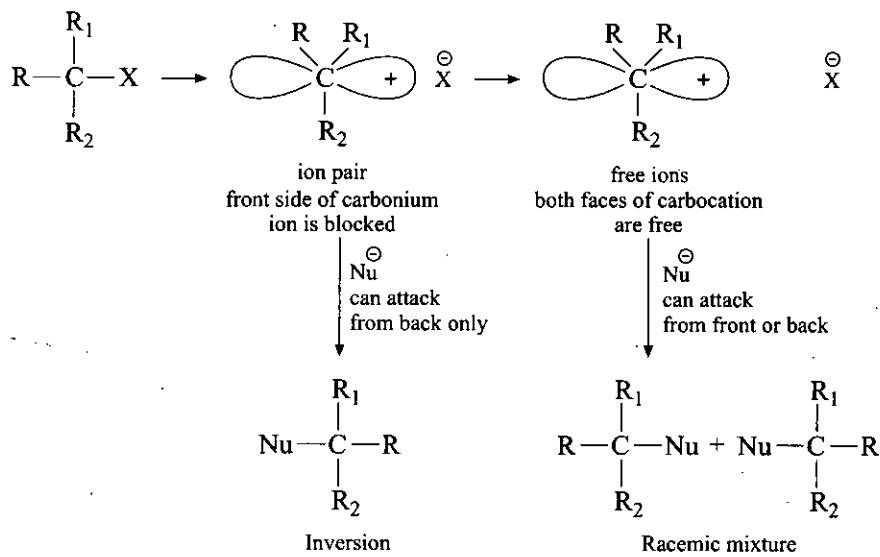
The SN1 reaction that transforms an optically active substrate into an enantiomeric pair or racemic mixture is said to proceed with **racemisation**. If enantiomers are formed in equal amounts then reaction is said to proceed with complete racemisation. In the case of complete racemisation no optical activity is detected in the mixture.

Only very few reactions are known where optically active alkyl halides undergo complete racemisation (i.e. 50% retention of configuration and 50% inversion of configuration). In most of the cases optically active alkyl halides undergoing SN1 reaction give partially racemised products instead of completely racemised products. The products usually consist of more inversion product than retention product. In most of the cases the product usually consists of 5–20% inverted product and 80–95% racemised species.



This result may occur if the carbocation is not sufficiently stable and if the leaving group is not far enough removed from the carbocation (it is present as ion pair). Ion pair blocks front face of carbocation for the attack of nucleophile. Thus attack of nucleophile on the ion pair can occur more easily at the backside producing more of inversion product and less of retention product.

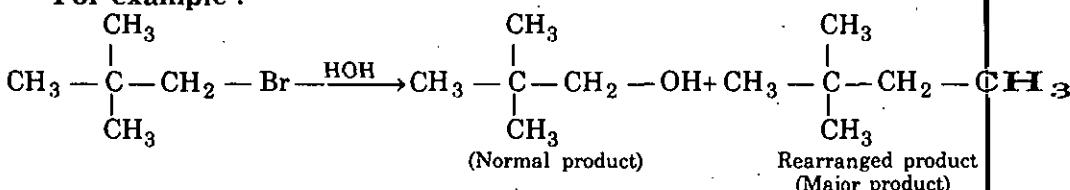
Partial racemisation proceeds as follows :



SN1 Reactions are Accompanied by Rearrangement

If carbocation is primary or secondary having at least three carbons then rearrangement takes place in carbocation. This leads to the formation of two or more products, one is normal and others are rearranged products.

For example :



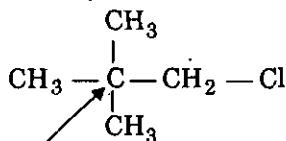
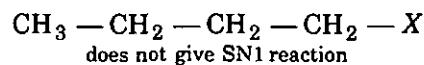
Factors Influencing SN1 Reaction Rate

1. Effect of Substrate Structure on Rate : A carbocation being intermediate in an S_N1 reaction, its stability determines the rate of the reaction. The greater the carbocation stability, the higher is the rate. This is reflected in reactivity order of alkyl halides towards S_N1 reaction. The reactivity order is:

$$3^\circ >> 2^\circ > 1^\circ > \text{CH}_3$$

Thus the SN1 mechanism will be most preferred in *tert*-halides and least preferred in case of primary alkyl halides.

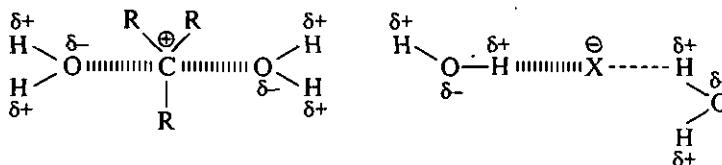
If the carbon site having leaving group is highly crowded with bulky groups, it tends to get relief from the steric strain with 109° bond angle (sp^3) and it does so when it approaches 120° bond angle in the carbocation intermediate. In other words, the greater the crowding around the carbon having leaving group, the greater is the possibility of SN1 reaction.



Crowding around α -carbon gives SN1 reaction

2. Effect of Solvents on Rate : A solvent with high ionising power (*i.e.*, polar protic solvent) enhances the rate of SN1 reactions. Thus polar hydroxyl solvents like HOH, ROH, CH₃COOH, etc. are good solvents for SN1 reaction.

This is because the negative pole of such species interacts with the incipient positive charge; while hydrogen bond is formed with the incipient negative charge through the $H^{δ+}$ pole. In other words, polar protic solvent stabilises carbocation and hence increases rate of the reaction.



Ion-solvent interactions

Non-polar, non-hydroxylic solvents retard the rate of an SN1 reaction.

3. Effect of Nucleophiles on Rate : Since the rate determining step of an S_N1 reaction does not involve the incoming nucleophile, neither its nucleophilicity, nor its concentration has any effect on the rate of the reaction. So an S_N1 reaction can proceed with weak nucleophiles of low concentration.

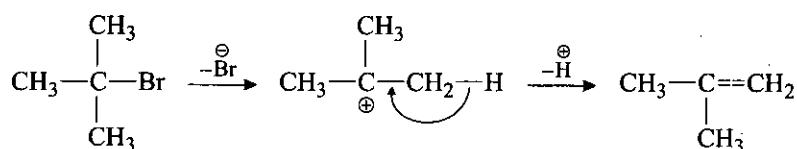
4. Effect of Leaving Groups on Rate : More is the leaving power of the group, more will be reactivity of the substrate for S_N1 reaction. Thus reactivity order among the halide ions is :

$$\text{I} > \text{Br} > \text{Cl} > \text{F}$$

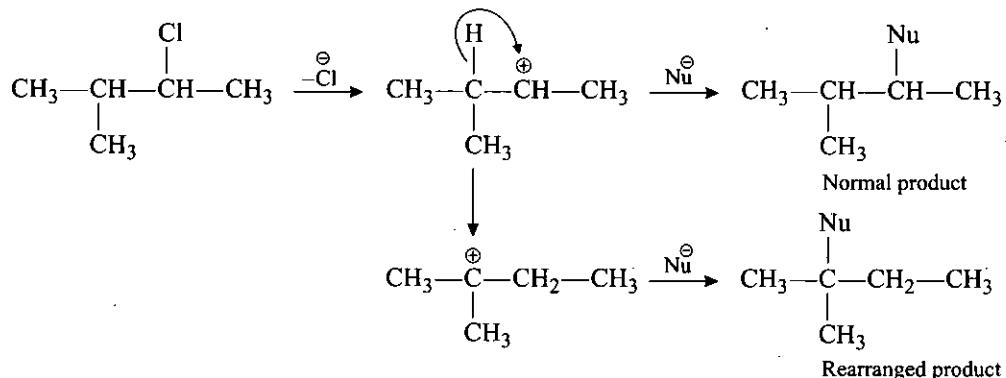
(1) Competitive Reactions: Carbocation is the intermediate in SN1 reaction.

It may give up a β -H from the β -position with respect to the leaving group. This leads

to the formation of a double bond and then the reaction is an elimination reaction.



On the other hand, a carbocation may rearrange to give a stable carbocation.



Thus elimination and rearrangement reactions complete with substitution in SN1 reaction.

Strong nucleophiles being strong bases, they can abstract a H^+ and thus favour elimination reaction. It is therefore, better to use weak nucleophiles in SN1 reactions.

• 6.4. SN2 MECHANISM OR SN2 REACTION : ONE STEP PROCESS

A typical example of this process is the hydrolysis of methyl bromide in the presence of NaOH.



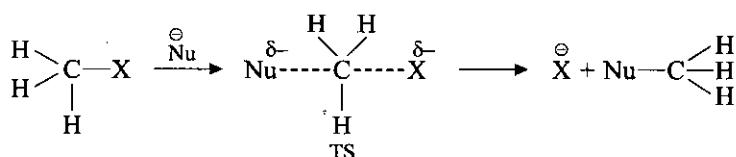
Kinetic studies have revealed that the reaction rate depends on the concentration of alkyl halide (CH_3Br) as well as the concentration of the nucleophile. Both the reactants being involved in the rate determining step.

$$\text{Rate} = K [\text{CH}_3\text{Br}] [\text{OH}^-]$$

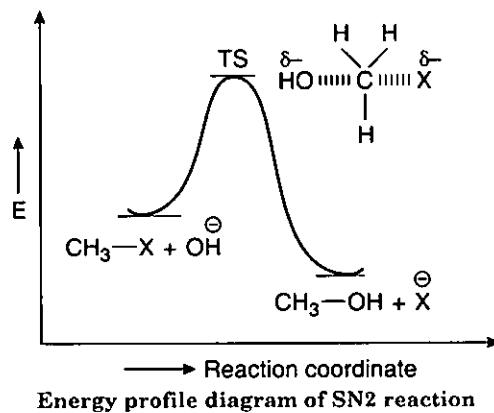
Increasing the concentration of either species will increase the reaction rate and vice-versa.

In this mechanism, the formation of carbon-nucleophile bond and cleavage of the carbon-halogen bond occurs simultaneously. In other words, the bond between carbon and nucleophile starts forming and at the same time the bond between carbon and halogen starts breaking. Such a reaction, therefore, involves a transition state in which the carbon atom appears to be pentavalent, i.e., it is attached to three hydrogens by full covalent bonds and to the nucleophile and halide atom by partial bonds. The three hydrogens acquire a coplanar geometry.

The nucleophile attacks the carbon from the side just opposite to that from which the halide is leaving. This is sterically favourable in that the nucleophile and halide do not hinder movement of each other as well as there is minimum repulsion between them.

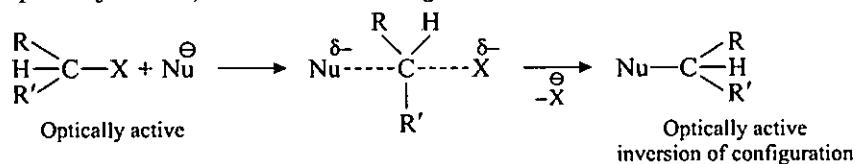


The SN2 mechanism is bimolecular because both reacting species are undergoing covalency change in the rate determining step. The energy profile diagram of SN2 reaction is shown below :



Stereochemistry of SN2 Reactions

In an SN2 reaction, the nucleophile enters as the halide is leaving. Consequently, the nucleophile attacks from the rear to avoid the path of the leaving group. If the alkyl halides is optically active, inversion of configuration will occur.

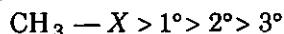


The nucleophile is attached just opposite side to the leaving group. Thus, the substitution product is still optically active but of opposite configuration to the alkyl halide.

Thus it can be said that as SN2 reaction proceeds with complete inversion of configuration usually referred to as **Walden inversion**.

Factors Influencing SN2 Reaction Rate

(1) Effect of Substrate Structure on Rate : Electrical effect on the carbon site has the minimum to do with the SN2 reaction rate. The carbon atom usually bears a partial positive charge owing to the bond dipole of the C—X bond. Any thing that decreases the positive charge on the carbon site by giving electrons, decreases the reaction rate while anything that increases positive charge on the same withdrawing electron, increases the rate of the reaction. Thus the reactivity order is :

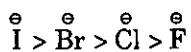


On the other hand, steric factor has profound effect on SN2 reaction rate. Availability of space for attack on the carbon site by the nucleophile decreases with the increasing steric hindrance and consequently the rate of the reaction diminishes largely. Since alkyl groups are larger than hydrogen atom, steric crowding increases in the direction from primary to tertiary alkyl halides and thus primary will be most reactive.

(2) Effect of Solvents on Rate : Polar hydroxyl solvents form hydrogen bond with the incoming nucleophile. Thus solvent molecules envelop the nucleophile. It becomes difficult for the nucleophile to attack the carbon site. Hence hydroxyl solvents retard the rate of an SN2 reaction. The rate, however, increases to a large extent in the presence of polar non-hydroxyl solvents like DMF (dimethylformamide) DMSO (dimethyl sulphoxide) and acetone.

(3) Effect of Nucleophiles on Rate : Since the single step SN2 reaction involves the substrate and the nucleophile, the rate of the reaction depends largely on the concentration of the nucleophile and on its nucleophilicity. Strong nucleophiles increase the rate of the SN2 reaction while weak nucleophiles decrease it.

(4) Effect of Leaving Groups on Rate : The rate of an SN2 reaction is dependant on the nature of the leaving group. Groups of lower basicity and higher polarisability increase the rate of the reaction. Thus the reactivity order among the halide ions is :



Comparison of SN1 and SN2 Substitutions

Alkyl and Aryl Halides

	SN2		SN1
(1)	One step mechanism.	(1)	Two step mechanism.
(2)	Bimolecular reaction	(2)	Unimolecular reaction
(3)	Product formation takes place by TS	(3)	Product formation takes place by carbocation intermediate
(4)	No carbocation rearrangement	(4)	Carbocation rearrangement
(5)	Reaction is favoured by polar aprotic solvents	(5)	Reaction is favoured by polar protic solvents
(6)	Given mainly by methyl halides	(6)	Given mainly by tertiary alkyl halides
(7)	Reactivity of RX; $\text{CH}_3\text{X} > 1^\circ > 2^\circ > 3^\circ$	(7)	Reactivity of RX; $3^\circ > 2^\circ > 1^\circ >$ methyl
(8)	Mechanism is favoured when nucleophile is an anion	(8)	Mechanism is favoured when nucleophile is neutral
(9)	Reaction velocity depends on the concentration of nucleophile, i.e., mechanism is favoured by high concentration of nucleophile	(9)	Reaction velocity is independent of the concentration of nucleophile.
(10)	Inversion of configuration.	(10)	Racemisation

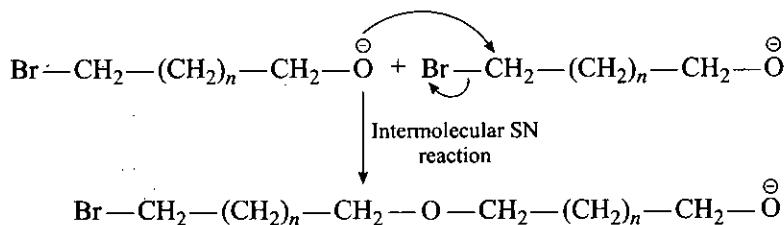
• 6.5. SN1 MECHANISM INTER- AND INTRAMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTIONS

Bifunctional compound that contains both a nucleophile and a leaving group gives either intermolecular or intramolecular nucleophilic substitution reaction.

(A) Intermolecular Nucleophilic Substitution Reactions :

(1) In intermolecular (inter means between) nucleophilic substitution reactions, the nucleophile of one molecule displaces the leaving group of a second molecule of the compound.

(2) Higher concentration of reactant favours intermolecular nucleophilic substitution reaction.



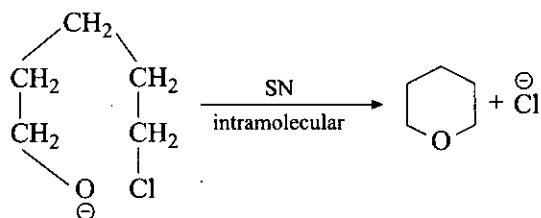
(B) Intramolecular Nucleophilic Substitution Reactions :

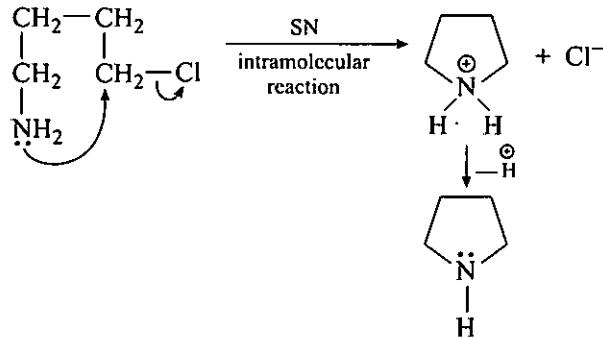
(1) An intramolecular (Intra means within or single) nucleophilic substitution takes place within the molecule.

(2) Low concentration of the reactant favours intramolecular reaction.

(3) Intramolecular reaction gives cyclic product. If intramolecular reaction would form a five or six membered ring, it would be highly favoured over the intermolecular reaction because of the stability.

(4) Intramolecular reactions are less favourable for other size of the ring (i.e., three, four, seven, etc.)

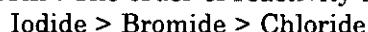




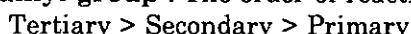
• 6.6. REACTIONS

The alkyl halides are reactive compounds. The reactivity depends upon the nature of halogen atom as well as the nature of alkyl group.

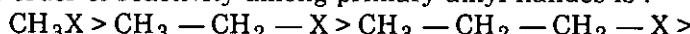
Nature of halogen atom : The order of reactivity is :



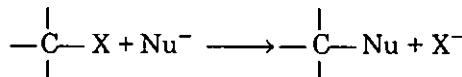
Nature of alkyl group : The order of reactivity is :



The order of reactivity among primary alkyl halides is :

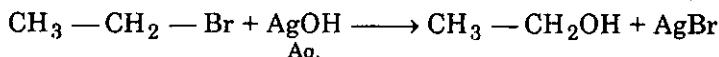


The high reactivity of alkyl halides is due to the polarity of C—X bond. The C—X bond is highly polarized covalent bond ($\delta^+ \text{C} - \delta^- \text{X}$) due to the large electronegativity difference between carbon and halogen atoms. Due to partial positive charge nucleophiles (electron rich species) attack at the carbon atom to which the halogen atom is attached and replace the halide ion. Such reactions in which a stronger nucleophile replaces a weaker nucleophile are known as **nucleophilic substitution reactions**.



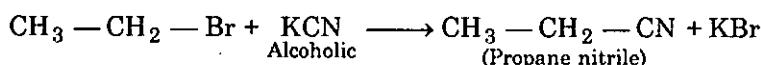
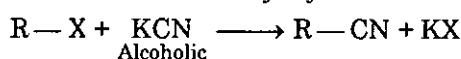
Hydrolysis

Reaction with aq. NaOH or aq. KOH or aq. AgOH : Alcohol is obtained.

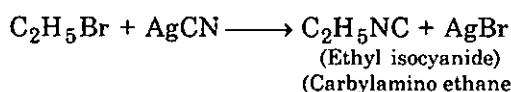


Nitrile and Isonitrile Formation

Reaction with alcoholic KCN : Alkyl cyanide or nitrile is obtained.

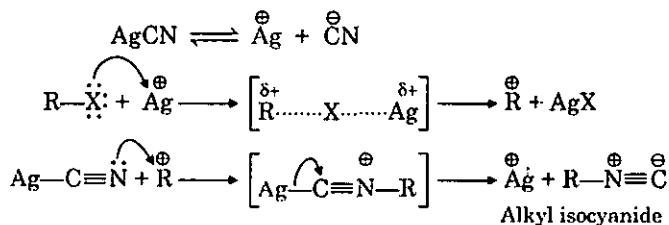


Reaction with alcoholic AgCN : Alkyl isocyanide or carbylamine is obtained.



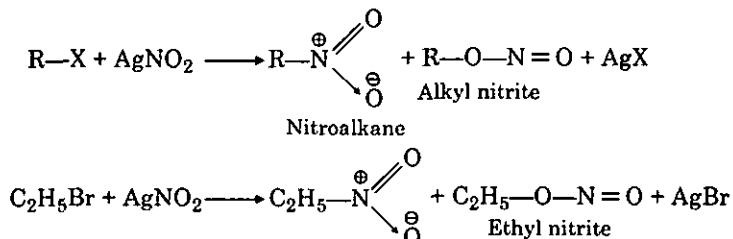
When silver cyanide is used in place of KCN, the major product is alkyl isocyanide.

Silver cyanide though covalent in nature, contains traces of Ag^\oplus which attacks at the halogen atom generating a carbocation. The carbocation reacts with silver cyanide forming the isocyanide.

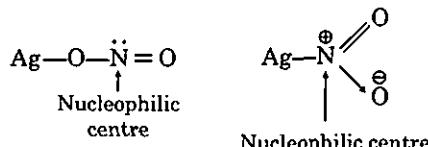


Nitro and Nitrite Formation :

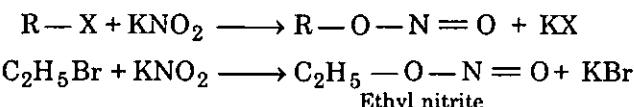
Reaction with AgNO_2 : When alkyl halides are treated with alcoholic AgNO_2 , a mixture of nitroalkane and alkyl nitrite is obtained.



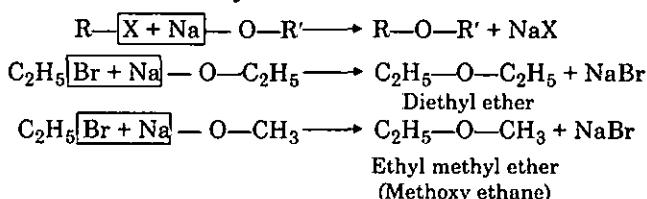
Treatment with silver nitrite gives a mixture of alkyl nitrite and nitroalkane because silver nitrite exists in two forms:



Reaction with KNO_2 : When alkyl halides are heated with KNO_2 in the presence of alcohol, alkyl nitrites are obtained.

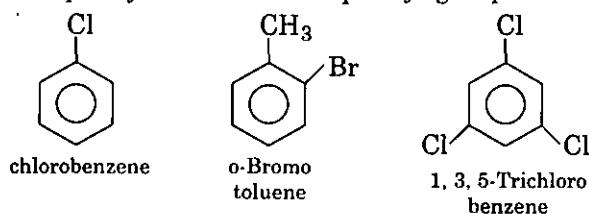


Williamson's Ether Synthesis : Reaction with sodium alkoxide : Ether is obtained. The reaction is known as Williamson's ether synthesis and is used for the preparation of symmetrical and unsymmetrical ethers.



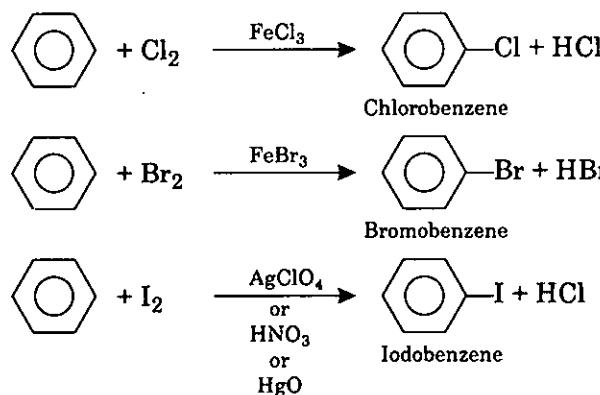
• 6.7. ARYL HALIDES

Aryl halides : These are nucleus substituted aromatic halogen compounds in which the halogen atom is directly attached to the aromatic nucleus. The general formula is ArX (Ar = phenyl or substituted phenyl group and X = halogen atom) e.g.

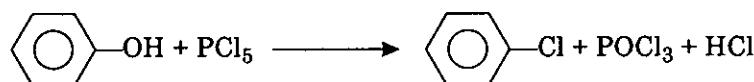


Preparations :

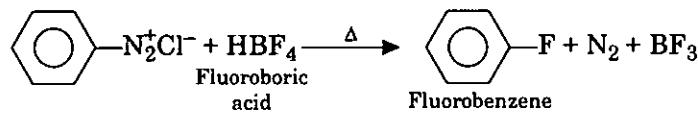
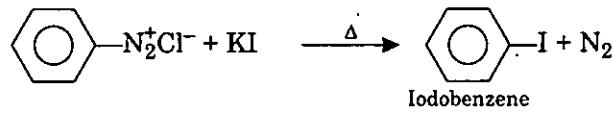
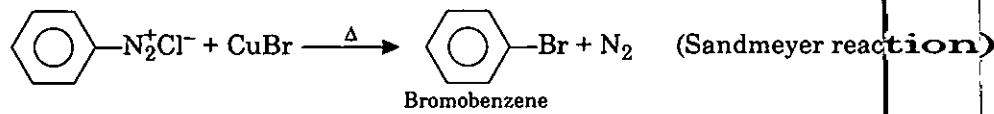
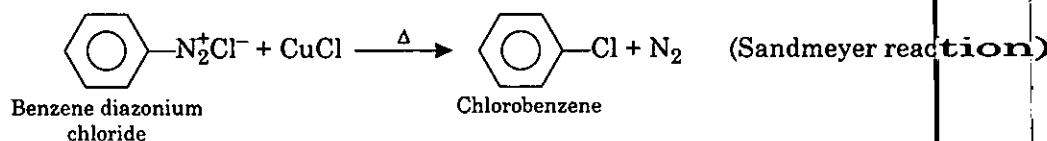
(1) By direct halogenation : Aryl chlorides and aryl bromides are prepared from benzene by the reaction with chlorine or bromine in the presence of a catalyst such as FeCl_3 , FeBr_3 or AlCl_3 .



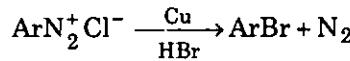
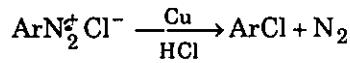
(2) From Phenol : Phenol reacts with PCl_5 to form chlorobenzene.



(3) By Sandmeyer Reaction : Aryl halides can be prepared most satisfactorily by the decomposition of aryl diazonium salts in the presence of suitable metal halides.



(4) By Gatterman Reaction : In this reaction aryl halides are prepared by the decomposition of aryl diazonium salts in the presence of copper powder and suitable acid

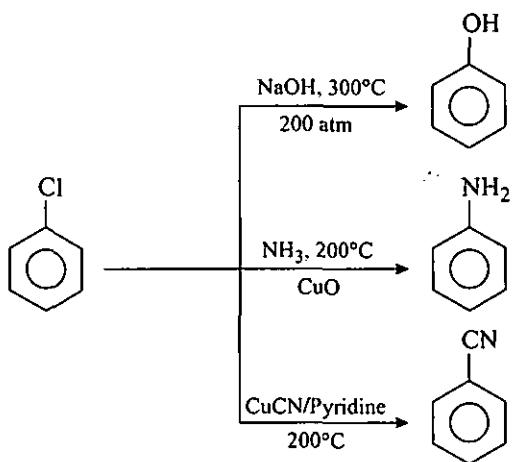


Reactions :

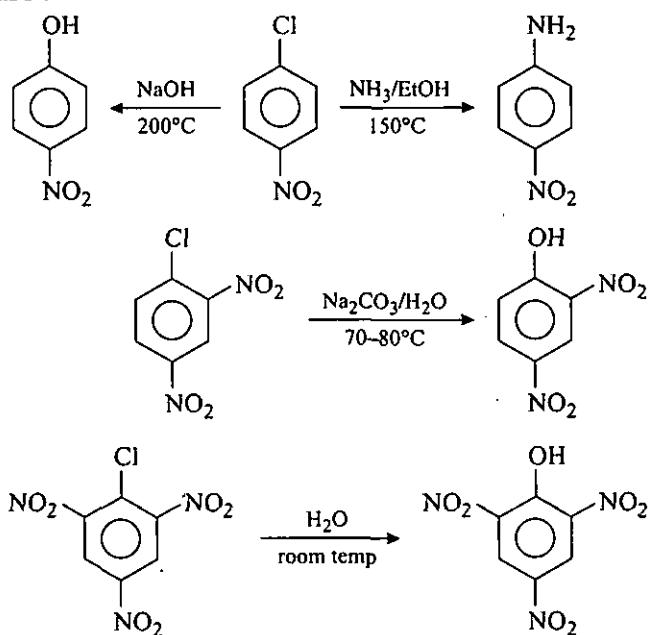
Unlike alkyl halides, aryl halides do not undergo nucleophilic substitution reactions under ordinary conditions. Because halogen atom in aryl halides is very firmly held by the benzene nucleus and cannot be easily replaced by nucleophiles.

Another reason for the low activity of aryl halides towards nucleophilic substitution reaction is the presence of six electrons in the delocalised π electron cloud in aromatic ring. This discourages the nucleophile from attacking the ring carbon bearing halogen.

But under drastic conditions, halogen atom can be replaced by a suitable nucleophile.



On the other hand, when a powerful electron-withdrawing group (*m*-director) is present at *ortho* and/or *para* to the halogen atom, replacement of X by nucleophilic reagents is facilitated. Thus *m*-directors activate nucleophilic substitution reaction. Some examples are :



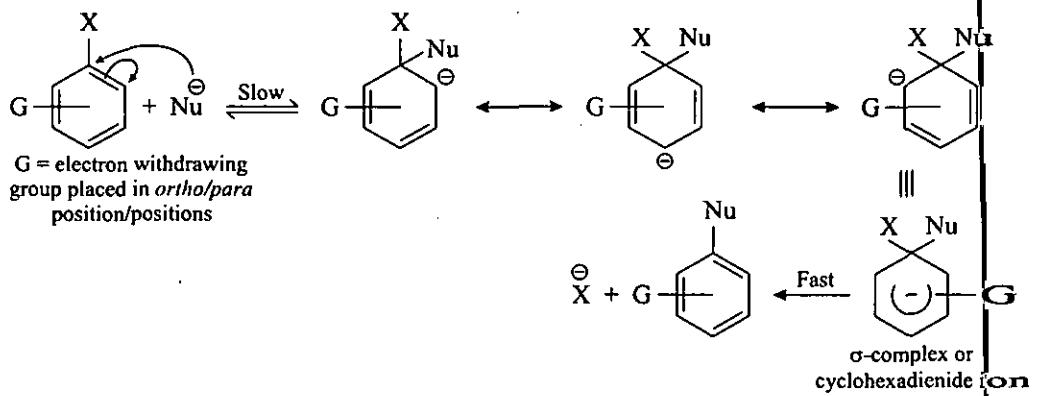
Mechanism of Nucleophilic Aromatic Substitutions

Nucleophilic substitutions involving replacement of $\overset{\ominus}{\text{H}}$ by a nucleophile in aromatic hydrocarbons do not occur because $\overset{\ominus}{\text{H}}$ is one of the strongest nucleophiles. However, if there is suitable leaving group in the ring (halogen atoms or other groups) nucleophilic substitution may take place by one of the following mechanisms :

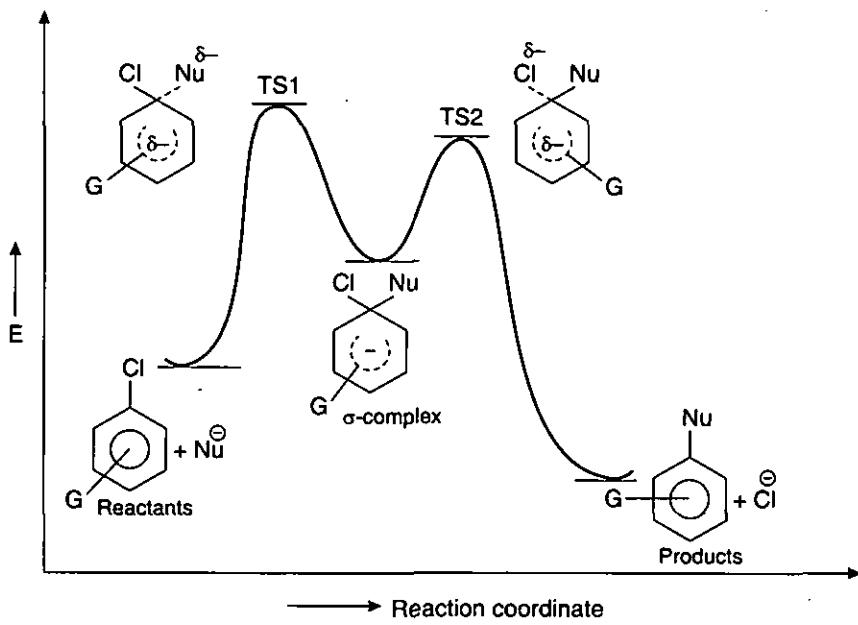
(1) **Bimolecular mechanism or Addition-elimination mechanism** : If the benzene ring bears strongly electron withdrawing substituents as well as a good leaving group, nucleophilic substitution reactions take place under mild conditions. Kinetic studies have revealed that the reaction rate depends on the concentration of aromatic substrate and the nucleophile. Thus both the reactants being involved in the rate-determining step.

$$\text{Rate} = K [\text{Aromatic substrate}] \times [\text{Nucleophile}]$$

Available evidence suggests that the reaction takes place by addition-elimination process involving attack by nucleophile in the first step, which in many cases is the rate-determining step.



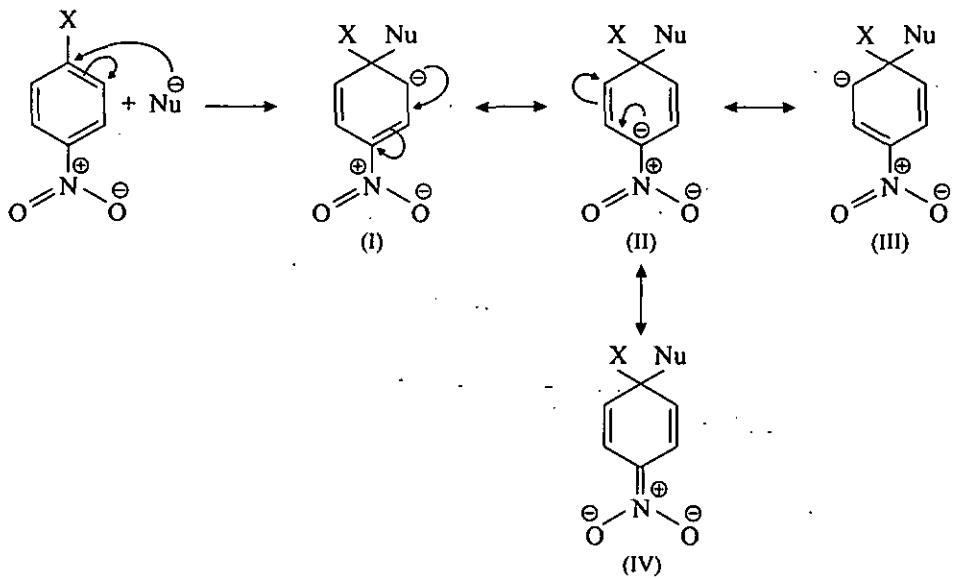
The energy profile diagram is similar to aromatic electrophilic substitution reactions.

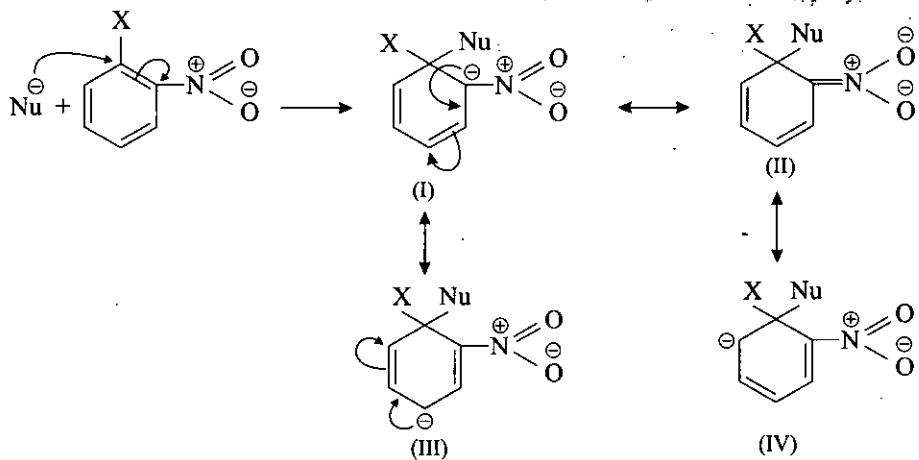
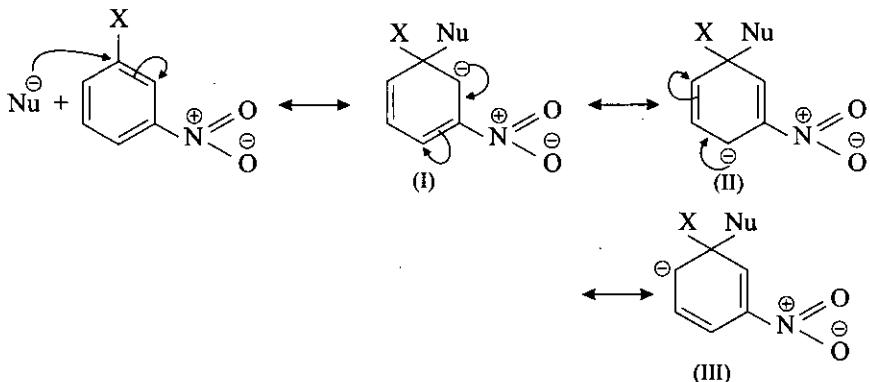


Energy profile diagram of aromatic nucleophilic substitution reaction.

The formation of σ -complex is not possible unless some group capable of accommodating the negative charge is present in the *o*- or *p*-position. Such group stabilises the intermediate carbanion.

Para



ortho*meta*

Since the delocalisation of the negative charge via structures (II) to (IV) in the case of *ortho* and *para* derivatives is not possible with *meta* derivatives, they do not undergo such reactions.

• SUMMARY

- Nucleophiles have an unshared pair of electrons. These are neutral, negatively charged and ambident.
- Nucleophilic substitution reactions are of three types e.g. SN1, SN2 and SN1.
- SN1 type reactions take place in two steps while SN2 type reactions take place in one step.
- The alkyl halides are reactive compounds. The reactivity depends upon the nature of halogen atom and alkyl group. The order of reactivity is :
 - Iodide > Bromide > Chloride
 - Tertiary > Secondary > Primary > Methyl $\text{CH}_3\text{X} > \text{CH}_3\text{CH}_2\text{X} > \text{CH}_3\text{CH}_2\text{CH}_2\text{X} > \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{X}$
- Alkyl halides react with KCN to form nitrile compounds while with AgCN to form isonitrile compounds.
- Alkyl halides react with KNO_2 to form nitrite compounds while with AgNO_2 to form nitro compounds.
- Aryl halides are the compounds in which halogen atom is directly attached to the aromatic nucleus and represented as ArX .
- Aryl halides can be prepared satisfactorily by the decomposition of aryl diazonium salts in the presence of copper powder or cuprous salts.
- Aryl halides show low activity because halogen atom directly attached with the arene ring as well as the presence of six delocalised π -electrons in the ring.
-

• STUDENT ACTIVITY

1. Discuss the nucleophilic substitution reactions in ethyl halides.

2. Differentiate between SN1 and SN2 reactions.

3. Discuss the formation of nitro and nitrite alkyl compounds.

4. Describe any two preparations of aryl halides.

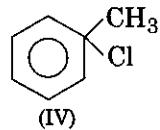
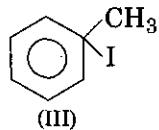
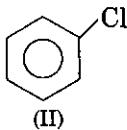
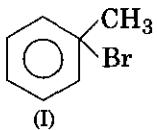
5. Discuss the nucleophilic substitution reactions of aryl halides.

• TEST YOURSELF

Answer the following questions :

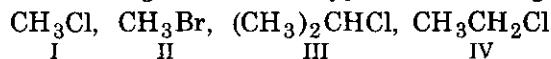
1. What are the nucleophiles ? Classify them.
2. Describe briefly nucleophilic substitution reactions.
3. Discuss the SN1 type reactions with suitable example.
4. Describe the SN2 type reaction with proper example.
5. Explain stereochemistry of SN1 reaction.
6. What are the factors which influence SN2 reaction rate.
7. Compare SN1 and SN2 reactions.
8. What do you know about SNi reactions.
9. What happens when :
 - (i) Bromoethane reacts with KOH (aq.)
 - (ii) Chloroethane reacts with alcoholic KCN and AgCN separately.
 - (iii) Ethyl bromide reacts with KNO_2 and AgNO_2 separately.
 - (iv) Ethyl bromide reacts with sodium ethoxide.
10. Describe Williamson's ether synthesis.
11. What are the aryl halides ? Give examples.
12. How do you prepare aryl halides by Sandmeyer's as well as Gattermann reactions?
13. Describe atleast three methods for the preparation of aryl halides.

14. Why do aryl halides are less reactive than alkyl halides.
15. Show that *p*-nitrochlorobenzene is more reactive than chlorobenzene.
16. Describe nucleophilic substitution reaction of chlorobenzene and nitro derivatives of chlorobenzene.
17. Explain the order of reactivity of alkyl halides with respect to halogens and alkyl groups.
18. Arrange different primary alkyl halides in the increasing order of their reactivity.
19. When ethyl iodide reacts with sodium methoxide it gives :
- (a) ethyl iodide
 - (b) ethyl methyl ether
 - (c) ethyl ether
 - (d) methyl ether
20. An alkyl halide can be converted into alcohol by reaction.
- (a) Addition
 - (b) Elimination
 - (c) Substitution
 - (d) Dehydration
21. The decreasing order of reactivity of the following compounds towards SN1 reactions is :



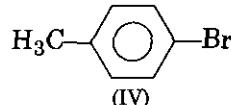
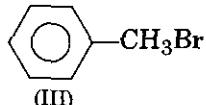
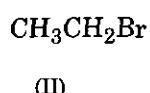
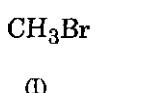
- (a) II > I > III > IV
- (b) III > I > IV > II
- (c) IV > II > III > I
- (d) I > IV > II > III

22. The order of decreasing SN2 reactivity of the following alkyl halides is :



- (a) I > II > IV > III
- (b) I > II > IV > III
- (c) IV > II > I > III
- (d) I > IV > II > III

23. The order of reactivity of the following halides with alcoholic AgNO_2 is :



- (a) I > II > IV > III
- (b) I > II > III > IV
- (c) III > II > I > IV
- (d) IV > III > I > II

24. Chlorobenzene is prepared by :

- (a) Dow's process
- (b) Williamson's method
- (c) Friedel-Crafts reaction
- (d) Sandmeyer's reaction

25. Which of the following alkyl halide is most reactive ?

- (a) R—F
- (b) R—Cl
- (c) R—Br
- (d) R—I

26. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to :

- (a) Large carbon-halogen bond
- (b) Resonance stabilisation
- (c) Formation of less stable carbonion ion
- (d) Inductive effect

27. Which of the following does not undergo nucleophilic substitution reaction so readily under ordinary conditions :

- (a) Chlorobenzene
- (b) Benzylchloride
- (c) Alkyl chloride
- (d) Tetrabutyl chloride

28. Alkyl halide on treatment with alcoholic AgNO_2 forms

29. Alkyl halide on treatment with alcoholic KCN forms

30. Ether is an example of nucleophile.

31. Cyanide ion (CN^-) is an example of nucleophile.

32. SN1 mechanism is of step process.

ANSWERS

19. (b) 20. (c) 21. (b) 22. (a) 23. (c) 24. (d) 25. (d) 26. (b) 27. (a)
28. Nitro alkane 29. Nitrile 30. Neutral 31. Ambident 32. Two



7

ALCOHOLS AND PHENOLS

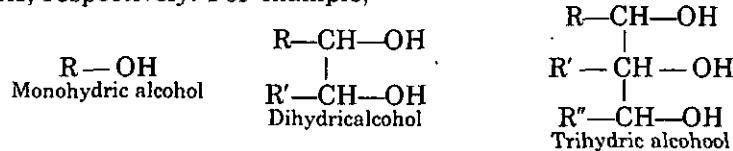
LEARNING OBJECTIVES

- Introduction
- Primary, Secondary and Tertiary Alcohols
- Method of Preparation of Alcohols
- Reactions of Alcohols
- Oxidation of Diols
- Pinacol-Pinacolone Rearrangement
- Phenols
- Preparation of Phenol
- Reaction of Phenol
 - Summary
 - Student Activity
 - Test Yourself

• 7.1. INTRODUCTION

Alcohols are compounds of the general formula ROH, where R is any alkyl or substituted alkyl group. The hydroxyl group ($-OH$) is the functional group of alcohols. The hydroxyl group in alcohol is usually attached to a carbon atom whose other valencies are satisfied by hydrogen or other carbon atoms and not by any other atom or group.

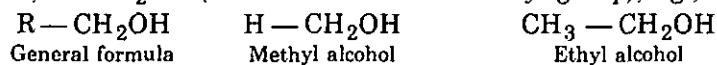
Those alcohols which contain one hydroxyl group are called monohydric alcohols. Alcohols with two, three or more hydroxyl groups are called dihydric, trihydric and polyhydric alcohols, respectively. For example,



• 7.2. PRIMARY, SECONDARY AND TERTIARY ALCOHOLS AND THEIR INTERCONVERSIONS

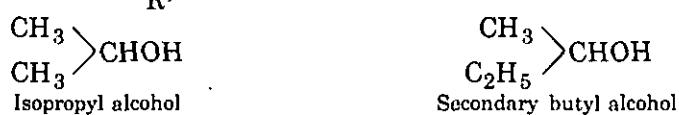
[I] Primary, Secondary and Tertiary Alcohols

(i) **Primary alcohol** : Primary alcohols contain $-CH_2OH$ group. They have the general formula, $R-CH_2OH$ (where R is H atom or alkyl group), e.g.,



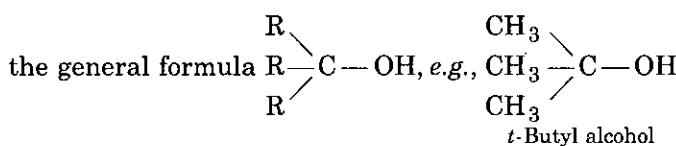
They are also known as 1° alcohols, because $-OH$ group is attached to primary carbon atom.

(ii) **Secondary alcohol** : Secondary alcohols contain $>CHOH$ group. They have the general formula $\overset{R}{\underset{R}{>}}CHOH$, e.g.,

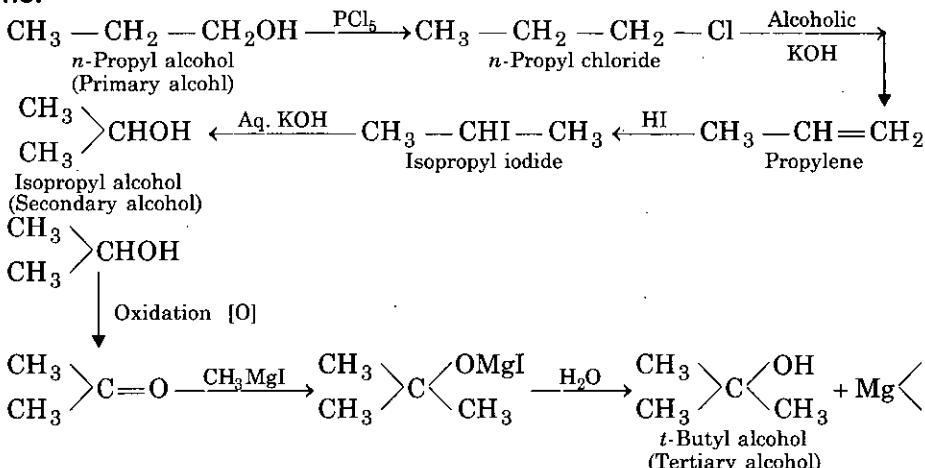


They are also known as 2° alcohols, because —OH group is attached to secondary carbon atom.

(iii) Tertiary alcohol : Tertiary alcohols contain $\text{C}(\text{---})\text{---}\text{OH}$ group. They have



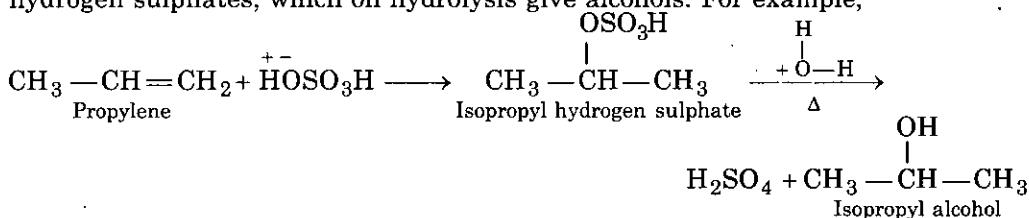
[ii] Conversion of Primary Alcohol into Secondary Alcohol and then to Tertiary Alcohol



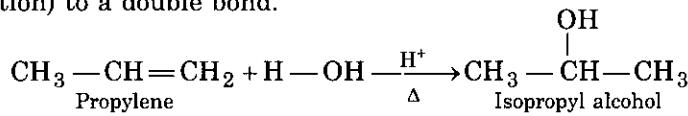
• 7.3. METHODS OF PREPARATION OF ALCOHOLS

Alcohols are prepared by the following methods :

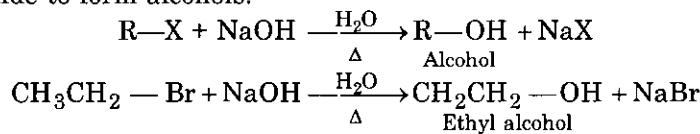
(1) **Hydration of alkenes** : Alkenes react with sulphuric acid to form alkyl hydrogen sulphates, which on hydrolysis give alcohols. For example,



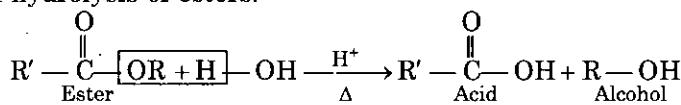
The overall result of the above reaction appears to be Markownikoff's addition of H_2O (hydration) to a double bond.



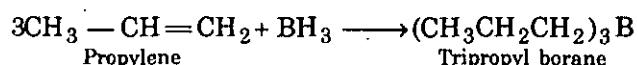
(2) Hydrolysis of alkyl halides : Alkyl halides react with aqueous sodium hydroxide to form alcohols.



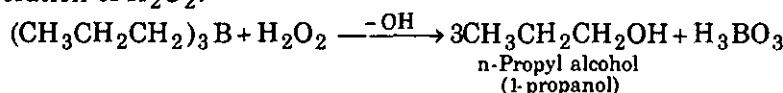
(3) Hydrolysis of esters : Alcohols may be prepared by acidic or basic catalysed hydrolysis of esters.



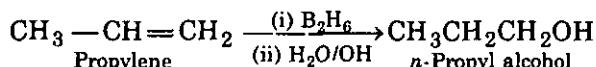
(4) Hydroboration-oxidation of alkenes : Alkenes react with diborane, B_2H_6 to form trialkylboranes. Diborane adds as borane, BH_3 . The positive part of BH_3 is the boron, the negative part is hydrogen. For example,



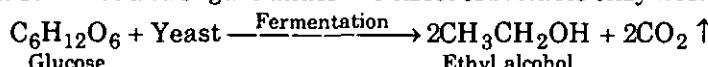
Trialkylboranes are used to prepare primary alcohols by reaction with alkaline aqueous solution of H_2O_2 .



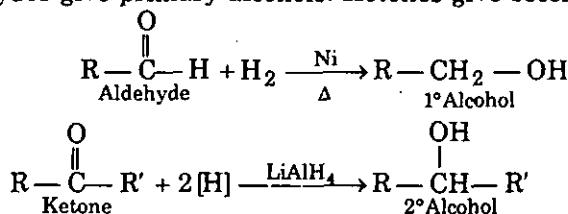
The overall result of the above reaction appears to be anti-Markownikoff addition of H₂O to a double bond.



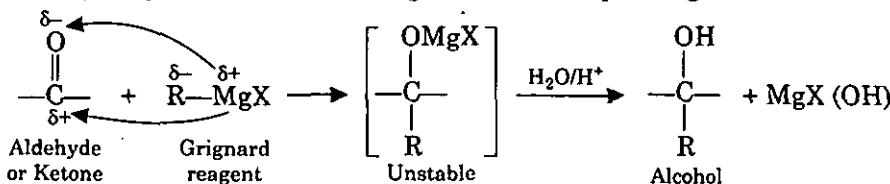
(5) **Fermentation of carbohydrates** : Some alcohols can be prepared by fermentation of starches and sugars under the effect of suitable enzymes. For example,



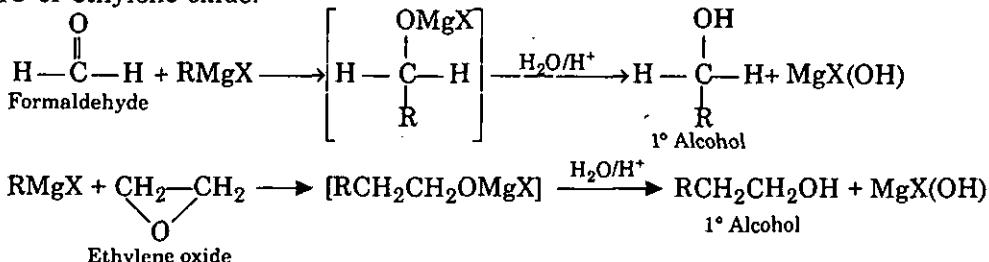
(6) Reduction of aldehydes and ketones : Aldehydes and ketones can be reduced with H_2/Ni or lithium aluminium hydride ($LiAlH_4$) to form the corresponding alcohols. Aldehydes give primary alcohols. Ketones give secondary alcohols.



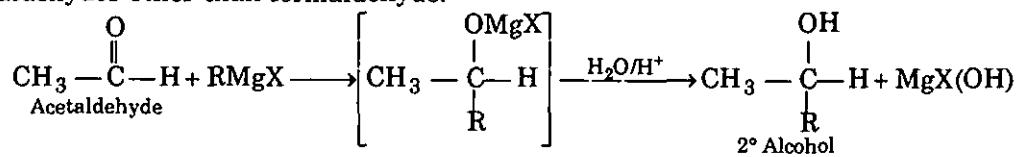
(7) **Addition of Grignard reagent to aldehydes and ketones :**
Grignard reagents react with aldehydes or ketones to form the addition compound which on hydrolysis with dilute acid gives the corresponding alcohols.



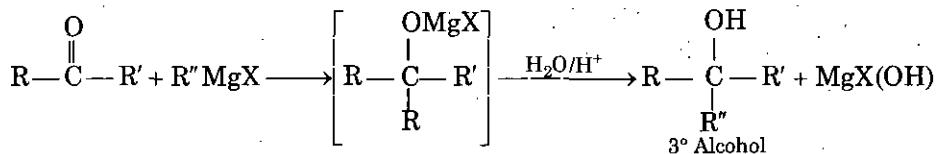
(i) Primary alcohols are obtained by treating a Grignard reagent with HCHO or ethylene oxide.



(ii) Secondary alcohols are obtained by treating a Grignard reagent with aldehydes other than formaldehyde.



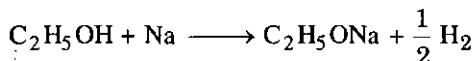
(iii) Tertiary alcohols are obtained by treating a Grignard reagent with ketones.



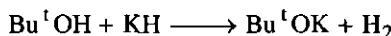
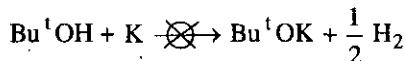
• 7.4. REACTIONS OF ALCOHOLS

1. Reaction with Alkali Metals :

Because of the presence of lone pair of electrons on the oxygen of the —OH group, alcohols behave as bases. However, they also behave as weak acids. The acidity of alcohols can be explained on the basis of the fact that hydrogen atom is attached to electronegative oxygen atom, which attracts the pair of electrons of the O—H bond, hence there is tendency for the loss of hydrogen as proton. In other words, the acidic nature of alcohols is due to the ability of oxygen to accommodate the negative charge after the loss of proton. Thus alcohols react with strongly electropositive metals like Li, Na, K with evolution of hydrogen to form alkoxides.

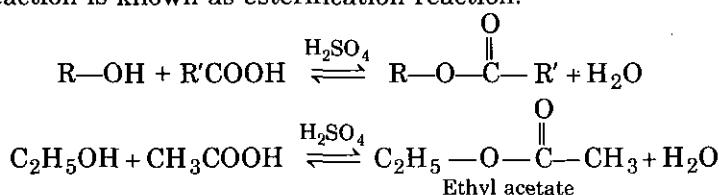


Alkoxides are also obtained from alcohols and metal hydride. With the relatively unreactive tertiary alcohols, KH is particularly effective.

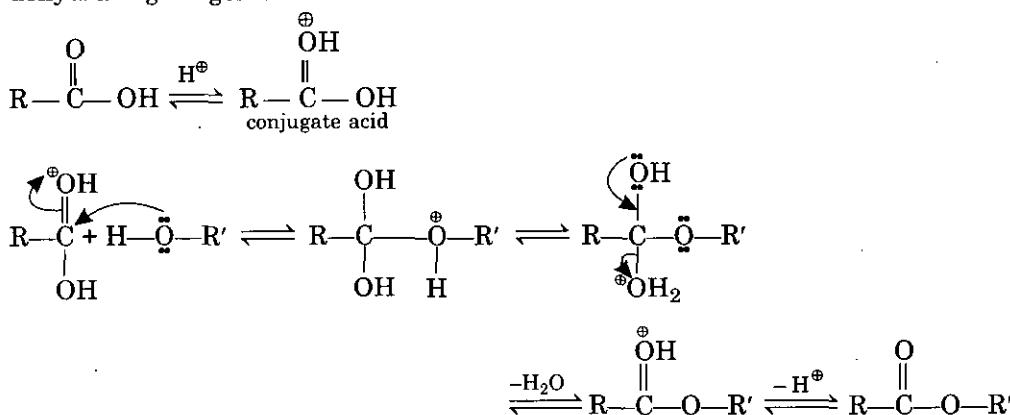


2. Reaction with carboxylic acids: Esterification

Alcohols react with acids in the presence of catalyst (conc. H_2SO_4) to form esters. This reaction is known as esterification reaction.



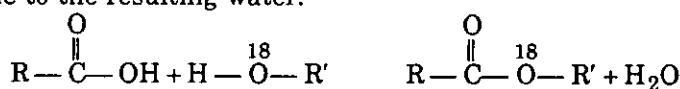
The esterification is a reversible process and is carried out in the presence of dehydrating reagent.



The reaction is acid catalysed, the function of the strong acid is to convert carboxylic acid into its conjugate acid. The mechanism of the reaction is as follows:

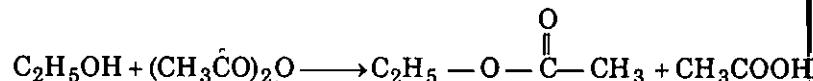
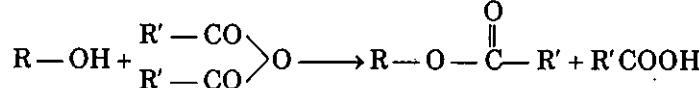
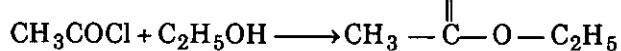
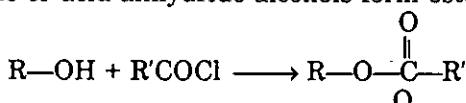
Isotopic tracer technique has established that esterification involves the cleavage of O—H bond of the alcohol. The reaction is carried out with alcohol having O^{18} and the resulting ester contains this radioactive isotope of oxygen. This confirms that ester formation is taking place due to the breaking of O—H bond. If the C—Obond of alcohol

would have cleaved during esterification, O¹⁸ should have not been present in ester, it would have gone to the resulting water.

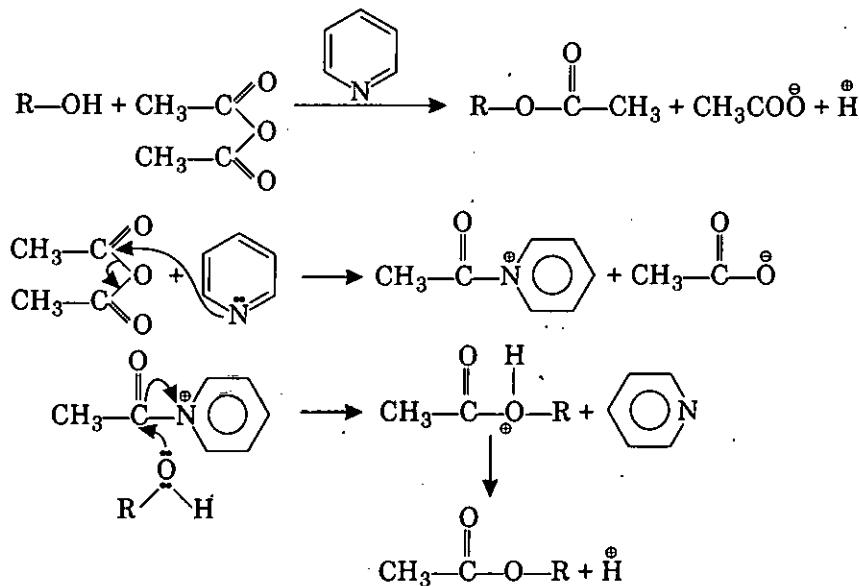


Reaction with acid chloride and acid anhydride:

With acid chloride or acid anhydride alcohols form esters:

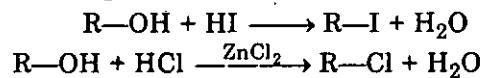


When alcohols are treated with acetyl chloride or acetic anhydride, the hydrogen of the —OH group is replaced by an acetyl group (—COCH₃) and the reaction is known as **acetylation reaction**. This reaction is catalysed by pyridine. The mechanism of the acetylation reaction is as follows:



3. Reaction with HX (Lucas Test)

Alcohols react with HX to form the corresponding alkyl halides. The order of reactivity of HX is HI > HBr > HCl. Hence HCl reacts only in the presence of a catalyst (anhydrous AlCl₃ or ZnCl₂). No catalyst is required in the case of HI and HBr.



Reaction with HCl in the presence of anhydrous NiCl₂ Lucas Reaction

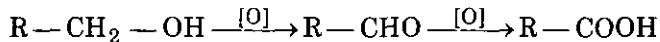
Primary and secondary alcohols are less reactive and require the help of catalyst before they can undergo reaction with less reactive HCl in a reasonable period of time.

In Lucas test Lucas reagent (anhydrous ZnCl₂ and conc. HCl) is used. When an alcohol is mixed with Lucas reagent, an alkyl chloride is formed. Since alkyl chlorides are insoluble in water, a turbidity is obtained. At room temperature, a *tertiary alcohol* gives the turbidity immediately, a *secondary alcohol* gives the turbidity within 5 minutes, while a *primary alcohol* does not give any turbidity at room temperature.

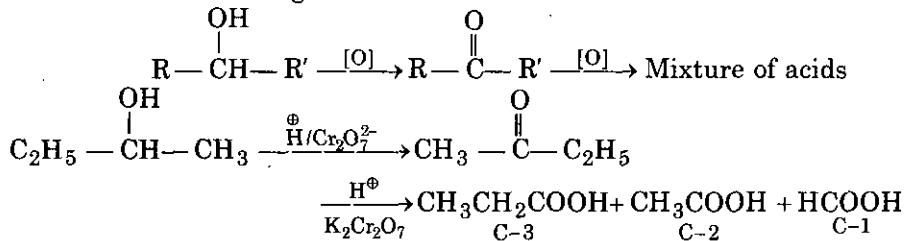
4. Oxidation

The compound that is formed by oxidation depends upon the nature of alcohol. The main oxidising agents are acidic and alkaline KMnO_4 and dil. HNO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ and CrO_3 .

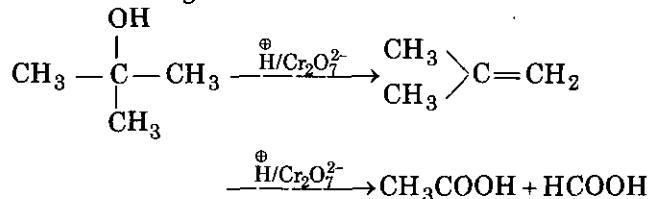
(i) **Primary alcohols** are oxidised to aldehydes which are, in turn, easily oxidised to carboxylic acid containing the same number of carbon atoms as the parent alcohol.



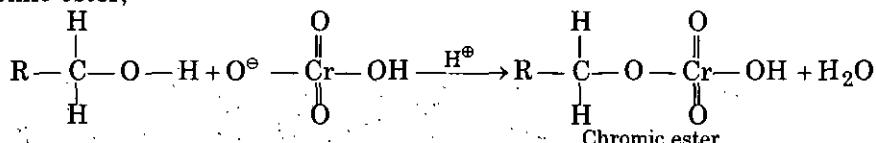
(ii) **Secondary alcohols** are oxidised to ketones containing the same number of carbon atoms. This, on further oxidation under drastic condition, form mixture of acids each having lesser number of carbon atoms than the alcohol.



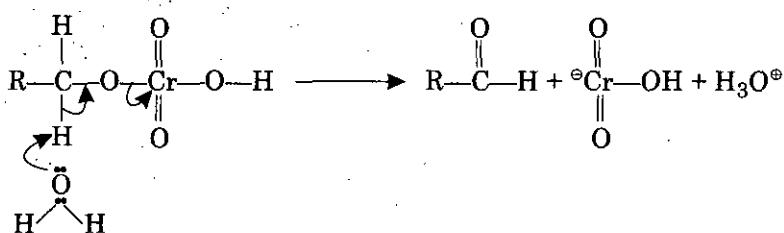
(iii) **Tertiary alcohols** do not undergo oxidation, rather in the presence of acid along with the oxidising agent they undergo dehydration forming alkenes which are oxidised to acids having fewer number of carbon atoms than the parent alcohol.



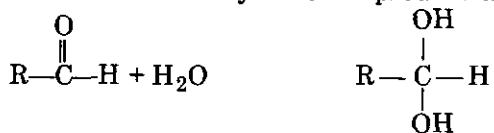
The oxidation of the primary alcohol with chromic acid begins with the formation of chromic ester,



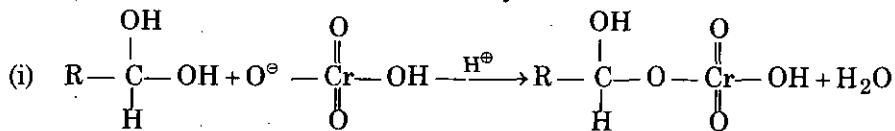
In the next step this chromic ester undergoes an elimination reaction. This elimination reaction forms a carbon-oxygen double bond instead of carbon-carbon double bond.

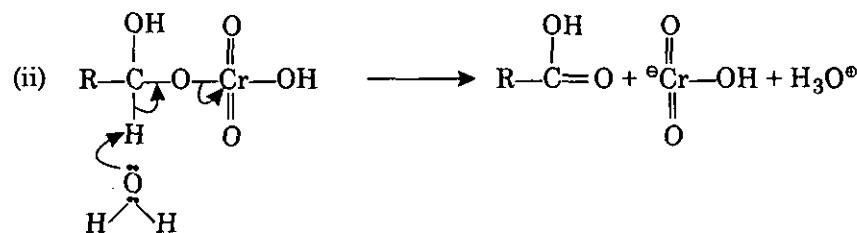


The aldehyde which is formed is hydrated to produce a 1, 1-diol,



This *gem*-diol is then oxidised to carboxylic acid as follows :

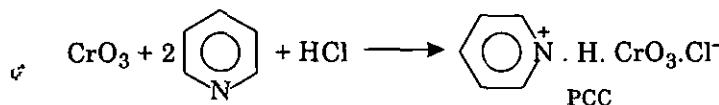




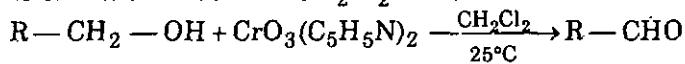
Aldehyde can also be prepared in excellent yield by the oxidation of a primary alcohol with Pyridinium Chlorochromate (PCC) and Pyridinium Dichromate (PDC, Sarret reagent) both are used in CH_2Cl_2 . This reagent is prepared as follows :



PCC is obtained by adding pyridine to a solution of chromium (VI) oxide in HCl.

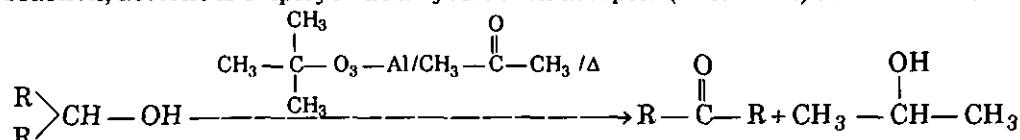


The oxidation is done in CH_2Cl_2 solvent at 25°C .

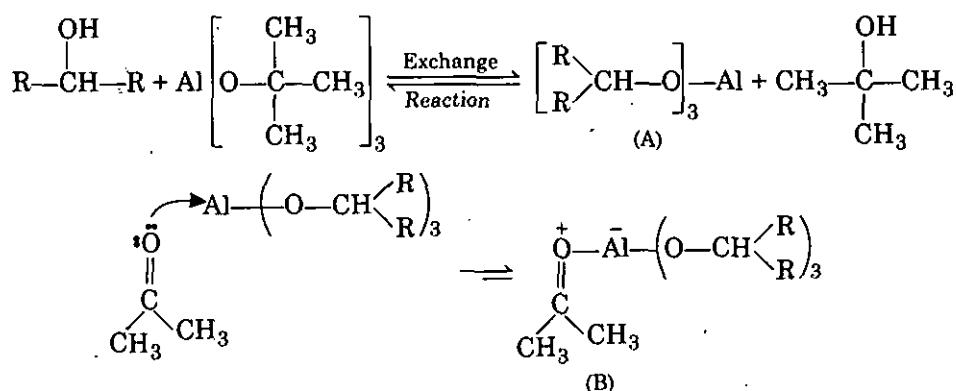


5. Oppenauer Oxidation

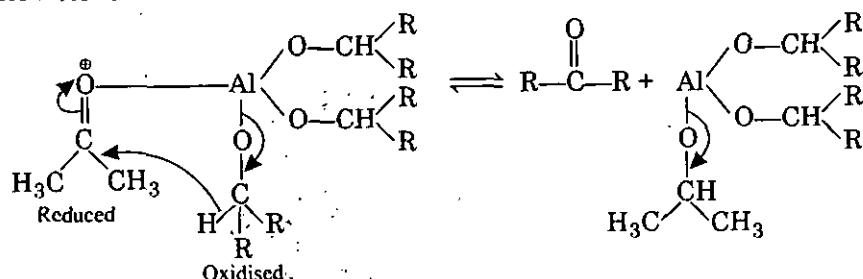
Oxidation of secondary alcohols into ketones by aluminium ter. butoxide in presence of acetone or cyclopropanone is known as Oppenauer oxidation. In this reaction, acetone is employed as a hydride ion acceptor (as oxidant) as well as a solvent.



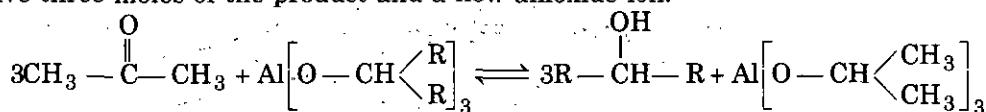
Mechanism



This new complex (B) is set up for an intramolecular transfer of hydrogen in the form of hydride ion which simultaneously reduces acetone and oxidises secondary alcohol into ketone.



Thus, three moles of acetone (solvent) react with one mole of the new complex (A) to give three moles of the product and a new alkoxide ion.

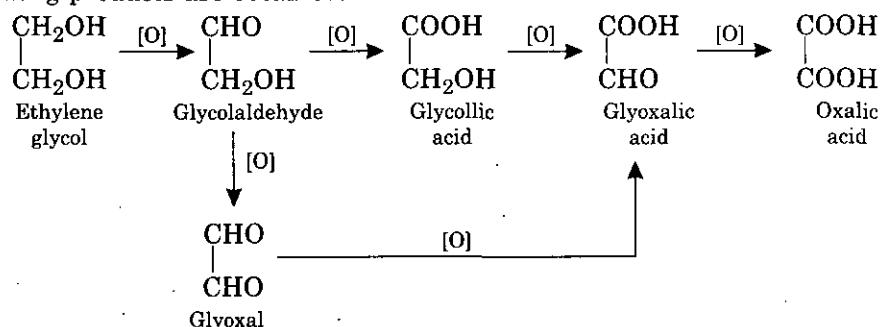


Since reaction is reversible, the oxidant i.e. acetone is usually added in excess amount so that the equilibrium mixture favours the desired product.

• 7.5. OXIDATION OF DIOLS

On oxidation, glycols give a variety of products which depend on the nature of oxidising agent and other reaction conditions. The product may arise with or without the breaking of carbon-carbon bond. This has been illustrated below by taking the example of ethylene glycol.

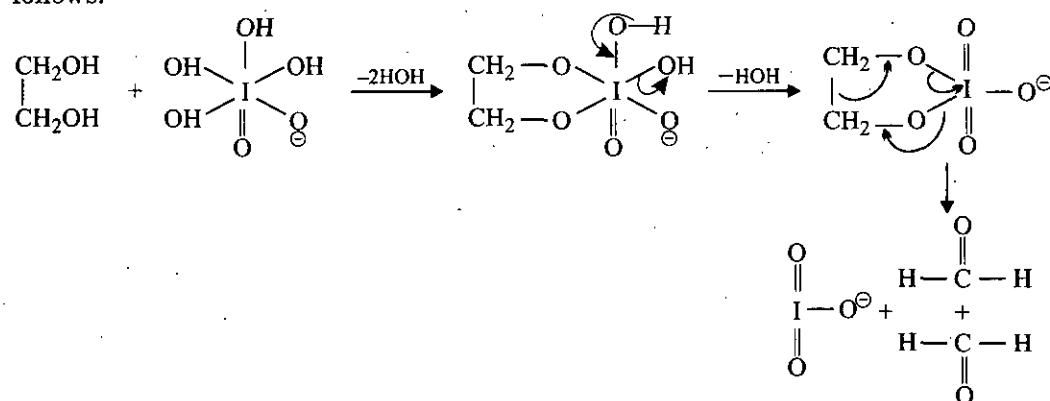
(a) When nitric acid or alkaline KMnO_4 is used as oxidising reagent. The following products are obtained.



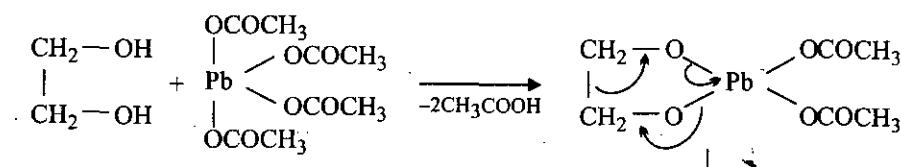
(b) **Oxidation with periodic acid :** When treated with aqueous HIO_4 , glycols undergo carbon-carbon bond fission to give aldehyde and/or ketones. This is a specific reaction of 1, 2-diols. The reaction proceeds through the formation of a cyclic ester of para periodic acid (H_5IO_6) which is formed by the reaction of water with meta periodic acid (HIO_4). Aqueous HIO_4 or H_5IO_6 is called **Malaprade reagent** and this reaction is referred to as **Malaprade reaction**.

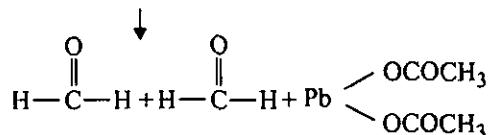
The active species of HIO_4 in aqueous solution is $\text{H}_4\text{IO}_6^{\ominus}$.

The mechanism of oxidative cleavage of vicinal glycols with aqueous HIO_4 is as follows:



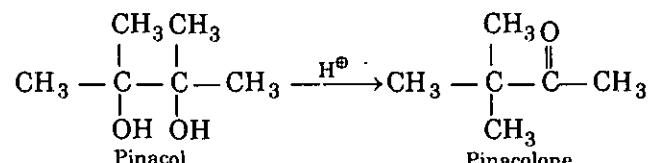
(c) **Oxidation with Lead tetracetate:** Similar to periodic acid, with $\text{Pb}(\text{OAc})_4$ also the oxidation of 1, 2-diols takes place via the formation of cyclic ester.





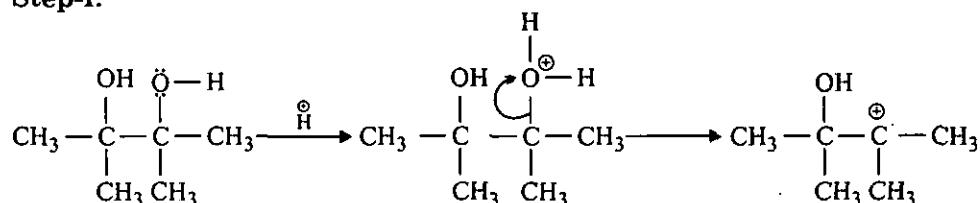
• 7.6. PINACOL-PINACOLONE REARRANGEMENT

Acid-Catalysed rearrangement of glycols is also called Pinacol-Pinacolone Rearrangement. 1, 2 Glycols on treatment with acid rearrange to form carbonyl compounds, the classical example being the acid catalysed rearrangement of pinacol to pinacolone.

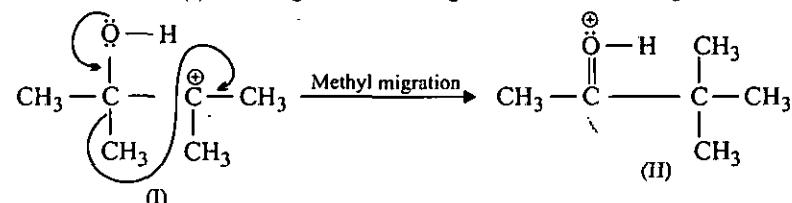


Mechanism:

Step-1:

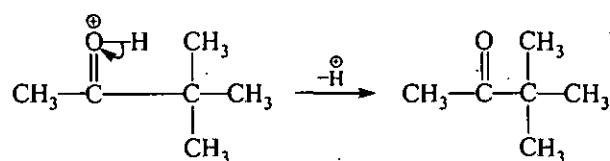


Step-II: Carbocation (I) undergoes rearrangement in this step.

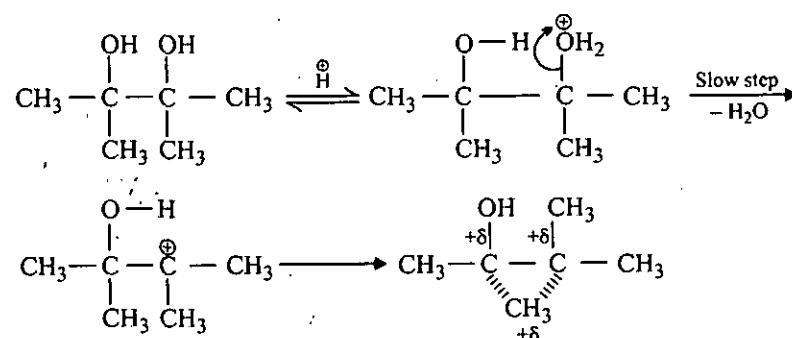


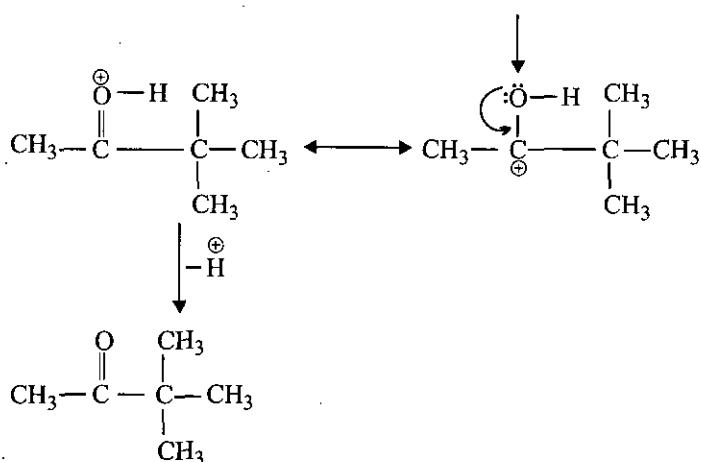
We know that carbocations rearrange by hydrogen or alkyl shift to get as stable as they can be but carbocation (I) is already tertiary and there is no ring strain, so why should it rearrange?

Due to migration of methyl group, positive charge moves on oxygen thus giving oxonium cation. In carbocation (I) carbon has incomplete octet but in cation (II) every atom has complete octet. Hence (II) is more stable than (I). Thus stability is the driving force for rearrangement.



This reaction is intramolecular rearrangement; thus actual mechanism can be written as follows:



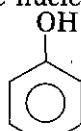


• 7.7. PHENOLS

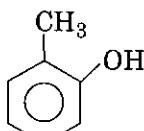
Introduction

The compounds in which $-\text{OH}$ group is directly attached to the benzene nucleus are called as *phenols*. These phenols may be monohydric, dihydric or trihydric depending upon the number of $-\text{OH}$ groups present.

(a) **Monohydric phenols** : These contain one $-\text{OH}$ group directly attached to the benzene nucleus. For example,

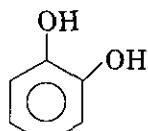


Phenol (carbolic acid)

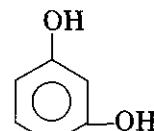


o-Cresol (*o*-Methyl phenol)

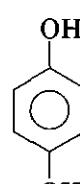
(b) **Dihydric phenols** : These contain two $-\text{OH}$ groups directly attached to the benzene nucleus. For example,



Catechol
(*o*-Dihydroxy benzene)

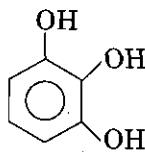


Resorcinol
(*m*-Dihydroxy benzene)

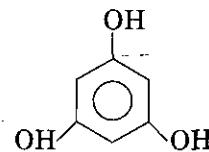


Hydroquinone or Quinol
(*p*-Dihydroxy benzene)

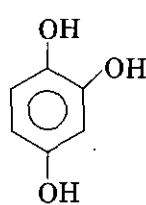
(c) **Trihydric phenols** : These contain three $-\text{OH}$ groups directly attached to the benzene nucleus.



Pyrogallol
(1, 2, 3-trihydroxy benzene)



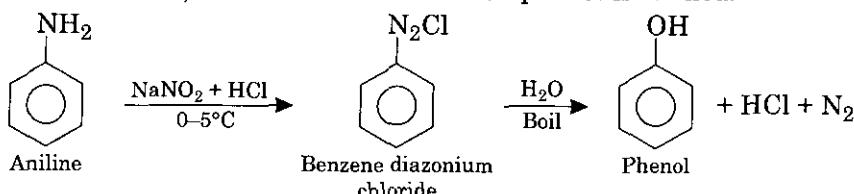
Phloroglucinol
(1, 3, 5-trihydroxy benzene)



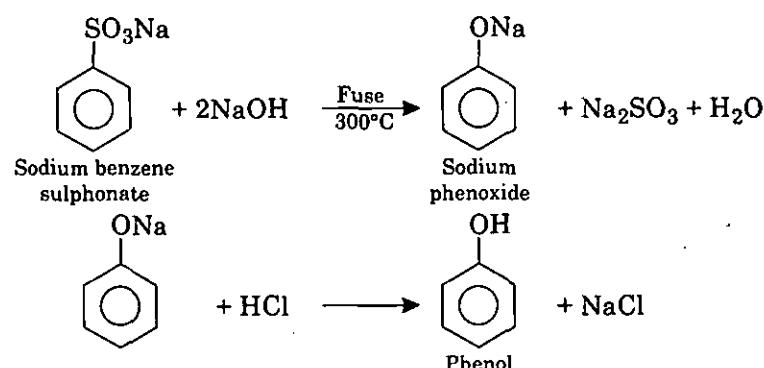
Hydroxy quinol
(1, 2, 4-trihydroxy benzene)

• 7.8. METHODS OF PREPARATIONS OF PHENOL

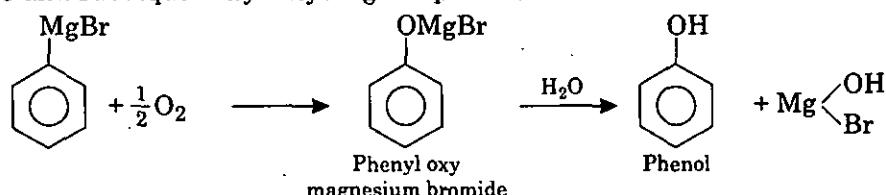
(i) **From aniline** : Benzene diazonium chloride obtained by the diazotination of aniline, is boiled with water then phenol is formed.



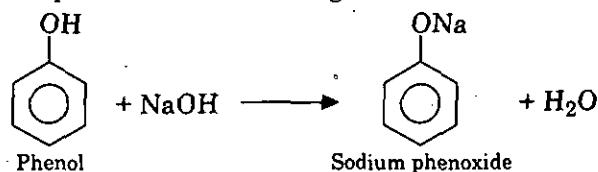
(ii) From benzene sulphonic acid : Sodium salt of the acid when fused with NaOH, gives sodium phenoxide which on treatment with mineral acid gives phenol.



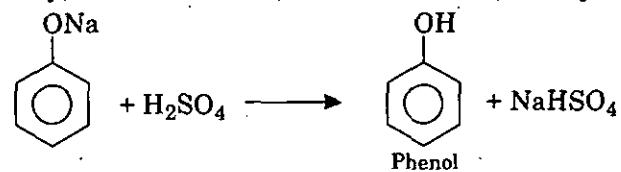
(iii) From Grignard's reagent : The oxidation of phenyl magnesium bromide and subsequent hydrolysis gives phenol.



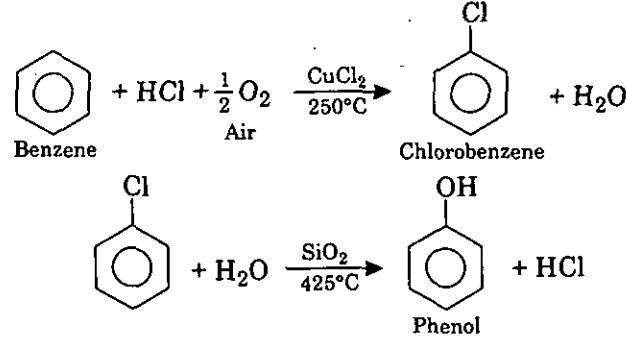
(iv) From middle oil fraction : The middle oil fraction contains compounds like phenols, naphthalene, pyridine etc. This fraction is first of all cooled when naphthalene crystallizes out first. The remaining fraction is now treated with NaOH which dissolves phenol and its homologues.



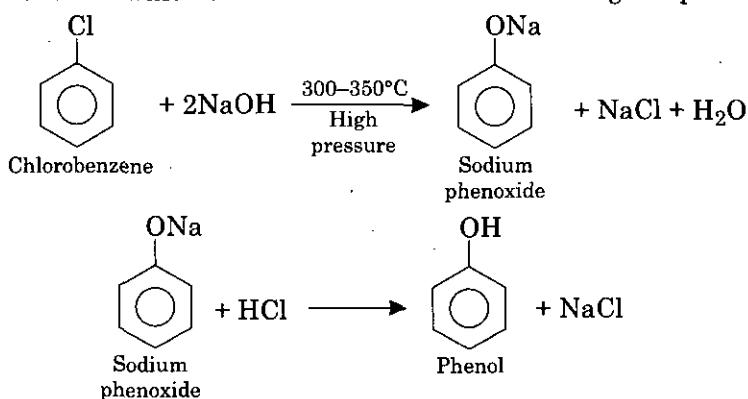
Now this solution is acidified with dil. H_2SO_4 which neutralizes the excess of NaOH and phenol separates out as a brown oily liquid. This is washed with water and fractionally distilled. The fraction distilling between 181–183°C is collected. It may still contain the impurity of *o*-cresol. Hence, it is cooled at 0°C, when phenol solidifies first.



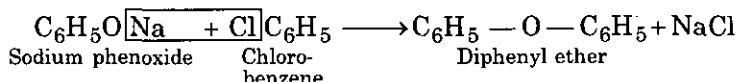
(v) Raschig process : This is the modern method for the preparation of phenol. In this method, vapours of benzene, air and HCl gas is passed over CuCl_2 catalyst heated to 250°C . The chlorobenzene so obtained is treated with steam at 425°C when phenol is obtained.



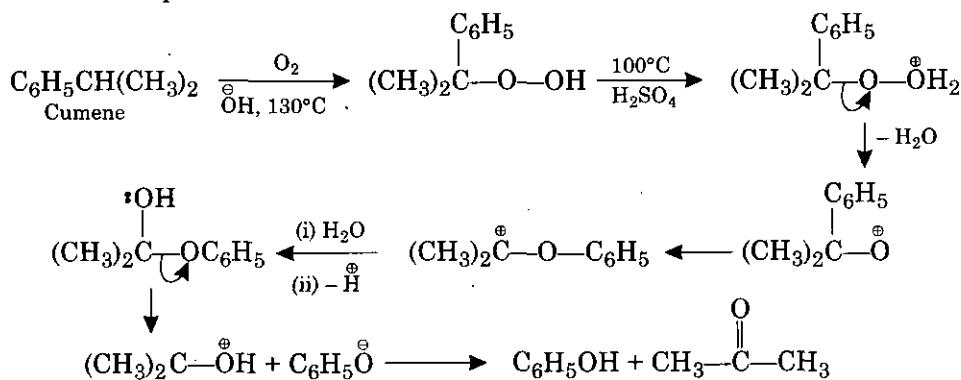
(vi) **Dow's process** : Chlorobenzene when treated with 10% caustic soda solution at 300–350°C and under high pressure in the presence of copper salt (catalyst), gives sodium phenoxide which on treatment with mineral acid gives phenol.



In the above reaction, some diphenyl ether is also formed, the formation of which can be checked by adding 10% diphenyl ether to the reaction mixture.



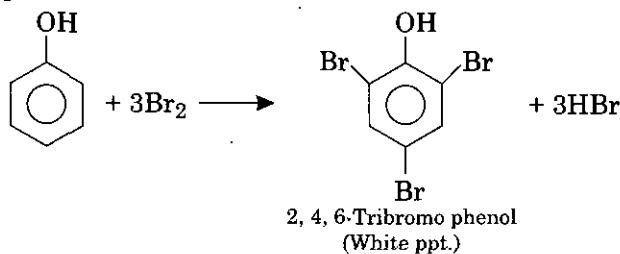
(vii) **From cumene** : This is the most important commercial method for the preparation of phenol and is known as cumene-phenol process. In this method, cumene (isopropyl benzene) is oxidised to the hydroperoxide, which is then decomposed by acid into acetone and phenol.



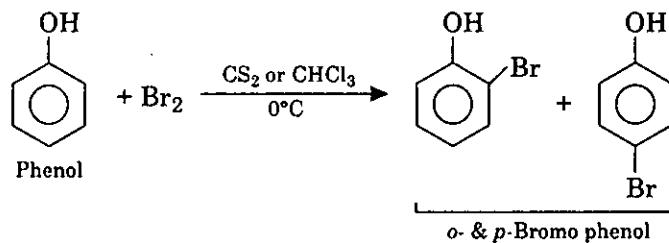
• 7.9. REACTIONS OF PHENOL

1. Electrophilic Substitution Reactions

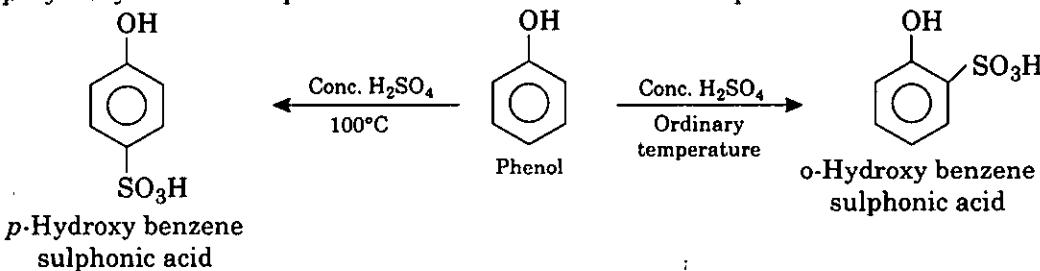
(i) **Halogenation** : Phenol can be readily halogenated due to the strong *o*- and *p*-directive influence of —OH group. With Br_2 water, it gives a white precipitate of 2, 4, 6 tribromo phenol.



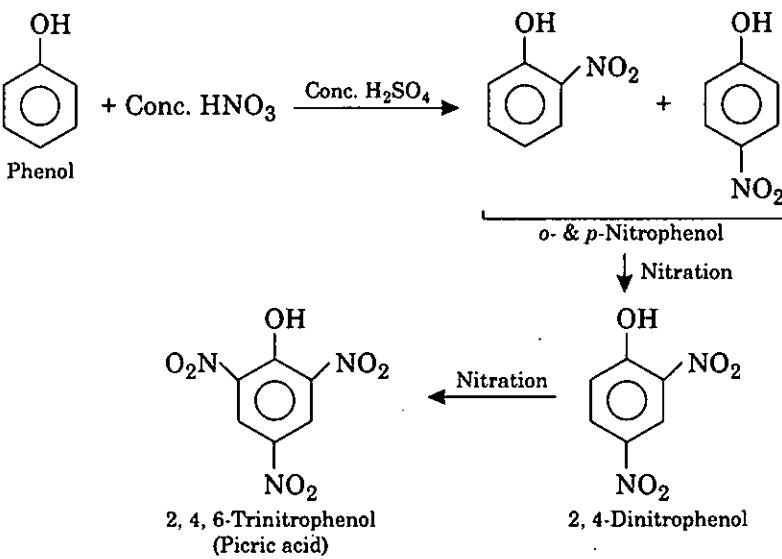
At low temperature and in presence of CS_2 or CHCl_3 , phenol on controlled halogenation gives mono halogen derivatives.



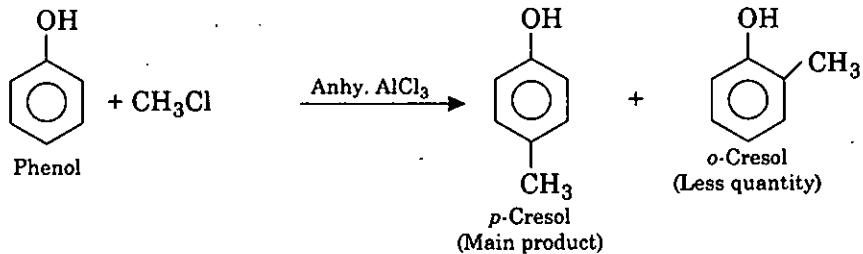
(ii) **Sulphonation** : Phenol can be readily sulphonated. On treatment with conc. H₂SO₄ at room temperature, o-hydroxy benzene sulphonic acid and at 100°C, p-hydroxy benzene sulphonic acid is obtained as the main product.



(iii) **Nitration** : On nitration with dil. HNO₃, o- and p-nitrophenol is obtained but on nitration with a mixture of conc. HNO₃ and conc. H₂SO₄, picric acid is obtained in small amount.



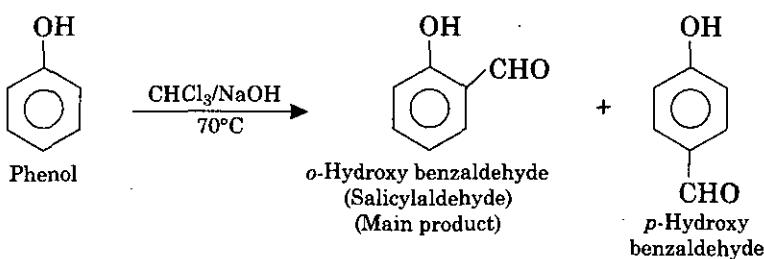
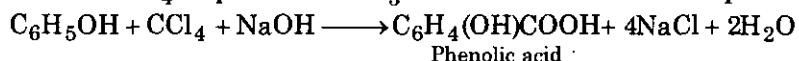
(iv) **Friedel Crafts reaction** : Phenol reacts with CH₃Cl in presence of anhydrous AlCl₃ to form p-cresol (main product) and o-cresol (less quantity).



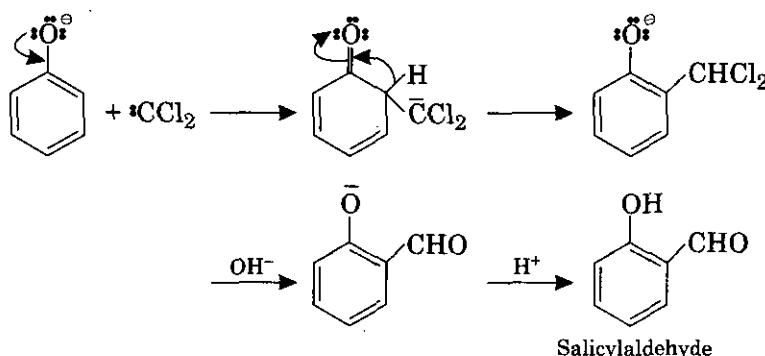
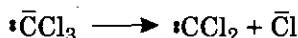
2. Riemer-Tiemann Reaction

Riemer-Tiemann reaction is a reaction for synthesising phenolic aldehydes and acids when heated with chloroform and alkali at 60°–70°C. On refluxing phenol and chloroform and sodium hydroxide, a formyl group (—CHO) is introduced into the benzene ring at o-position to —OH group. Small amounts of p-isomer is also obtained. The mixture can be separated by steam distillation, as only ortho isomer is steam volatile.

The use of CCl_4 in place of CHCl_3 leads to the formation of phenolic acid.



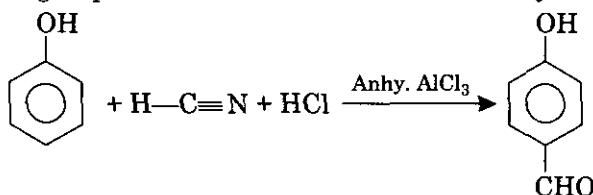
Mechanism : This reaction shows *electrophilic substitution* of the aromatic substrate and the electrophile *dichlorocarbene*; $\cdot\text{CCl}_2$ (carbon has only a sextet of electrons) formed by the action of strong alkali on chloroform.



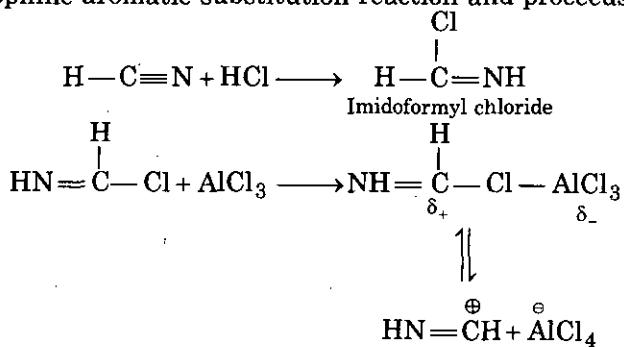
The *o*- and *p*-hydroxy benzoic acids are also obtained by similar reaction of alkali and CCl_4 .

3. Gattermann-Koch Reaction

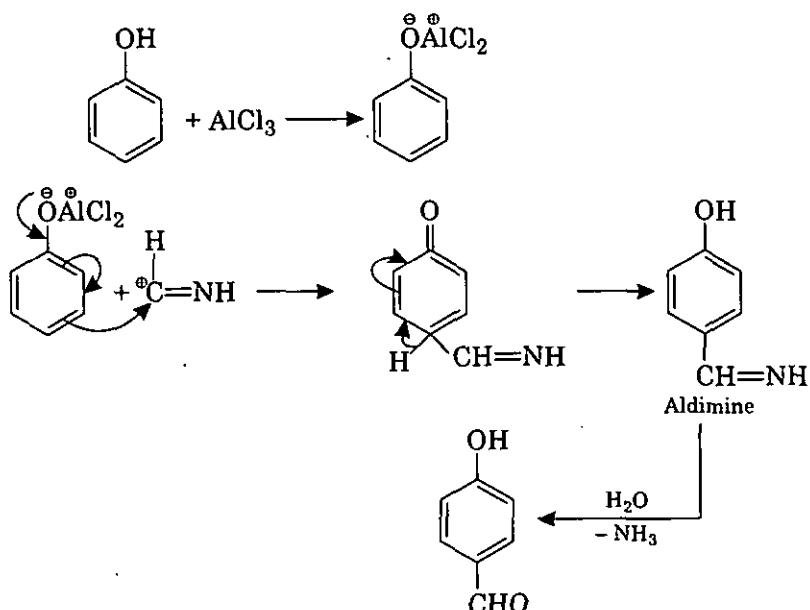
When phenol is treated with a mixture of hydrogen cyanide and hydrogen chloride in presence of anhydrous aluminium chloride, an aldehydic group is introduced in the *para* position to $-\text{OH}$ group. This is known as Gattermann's synthesis.



If para position is blocked, then $-\text{CHO}$ group goes to *ortho* position. This reaction is an *electrophilic aromatic substitution* reaction and proceeds as follows :

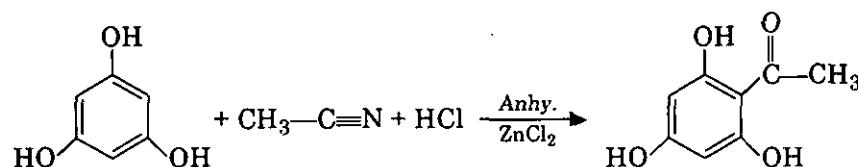


Mechanism

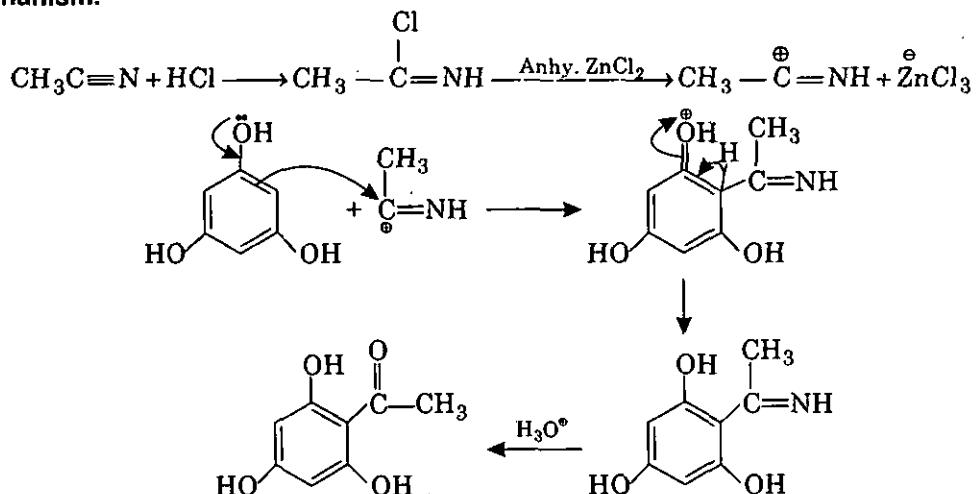


4. Houben-Hoesch Reaction

This reaction is an extension of Gattermann's synthesis and involves acylation of highly reactive polyhydric phenols. When a polyhydric phenol is treated with an alkyl cyanide and hydrogen chloride gas in presence of anhydrous AlCl₃ or ZnCl₂, ketimine hydrochloride is formed. This on hydrolysis with hot water gives acyl derivative of phenol. Acyl group is generally introduced at *ortho* position with respect to —OH group.

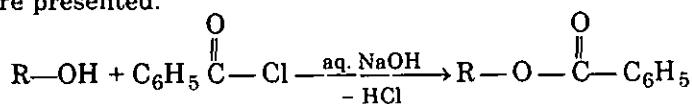


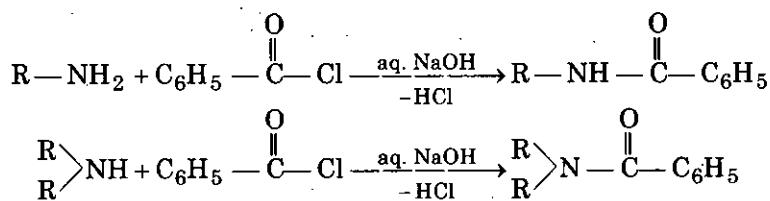
Mechanism.



5. Schotten-Baumann Reaction

Benzoylation of alcohols and primary or secondary amine by benzoyl chloride in aqueous basic medium is known as Schotten-Baumann reaction. Here both these examples are presented.





• SUMMARY

- The compounds having one or more —OH group in saturated or unsaturated alkyl groups are called alcohols. These are mono-, di-, tri- or poly hydridic.
- Monohydric alcohols are primary ($\text{R}-\text{CH}_2-\text{OH}$), secondary ($\text{R}_2\text{CH}-\text{OH}$) and tertiary ($\text{R}_3\text{C}-\text{OH}$) alcohols.
- The reactions of alcohols depends upon —OH group and nature of alkyl group.
- Diols give different products on oxidation, depending nature of oxidising agent.
- Phenols are the compounds in which —OH groups is/are directly attached with arene ring.
- In electrophilic substitution reaction of phenol —OH group is *ortho* and *para* directive.
- Phenolic aldehydes are prepared by Riemer-Tiemann or Gattermann-Koch reaction.

• STUDENT ACTIVITY

1. Write atleast four methods for the preparation of primary alcohols.

2. Explain the esterification of alcohol.

3. What is Lucas test ?

4. Discuss the oxidation of alcohols or diols.

5. What is Pincol-Pinaclone reaction ?

6. Describe any four methods for the preparation of phenol.

7. Describe the electrophilic substitution reactions of phenol.

- 8. What do you know about Riemer-Tiemann reaction ?**

- TEST YOURSELF

Answer the following questions :

1. What are the alcohols ? Classify them.
 2. Classify the primary alcohols.
 3. Write any five methods for the preparation of alcohols.
 4. How do you prepare alcohols from Grignard reagent ?
 5. Why does alcohol react with alkali metals ?
 6. Write a note on esterification of alcohols.
 7. Discuss the Lucas test for the identification of prim-, sec- and ter- alcohols.
 8. What happens when prim-, sec.- and ter.-alcohols oxidised ?
 9. What is PCC reagent ? How do this reagent used for the oxidation of primary alcohol ?
 10. What is Oppeneauer oxidation reaction ?
 11. Describe the oxidation of diols using different oxidants.
 12. What is Pinacol-Pinacolone reaction ? Describe its mechanism.
 13. What are the phenols ? Classify them.
 14. Write any five methods for the preparation of phenol.
 15. Describe electrophilic substitution reactions of phenol.
 16. Write short note on the following name reactions :
 - (i) Riemer-Tiemann reaction
 - (ii) Gattermann-Koch reaction
 - (iii) Houben-Hoesch reaction
 - (iv) Schotten-Baumann reaction.
 17. Which one of the following will give tertiary alcohol by reacting with $\text{Cl}_2 \text{Al}_3\text{MgI}_2$?

- (a) HCHO (b) CH_3CHO (c) CH_3COCH_3 (d) $\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{CH}_2$

18. An alcohol of molecular formula $\text{C}_4\text{H}_{10}\text{O}$ on oxidation gives $\text{C}_4\text{H}_8\text{O}_2$. The alcohol is most likely :
 (a) Primary alcohol (b) Secondary alcohol
 (c) Tertiary alcohol (d) All the above

19. Phenol on heating with CCl_4 and alcoholic KOH gives salicylic acid. The reaction is known as :
 (a) Friedel Crafts reaction (b) Schmidt reaction
 (c) Riemer-Tiemann reaction (d) Kolbe's reaction

20. The general formula of primary alcohol is :
 (a) $\text{R}-\text{CH}_2\text{OH}$ (b) R_2-CHOH (c) R_3-COH (d) $\text{R}_2\text{C}=\text{O}$

ANSWERS

17. (c) 18. (a) 19. (c) 20. (a) 21. (c) 22. (d) 23. (b) 24. (a) 25. (a)
 26. (a) 27. (b) 28. nucleophilic 29. acidic 30. anhydrous AlCl₃ 31. ester
 32. glycols 33. reduction 34. CH₂Cl₂ 35. acidic



8

ALDEHYDES AND KETONES (Aliphatic and Aromatic)

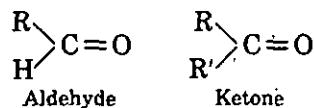
(Formaldehyde, Acetaldehyde, Acetone and Benzaldehyde)

LEARNING OBJECTIVES

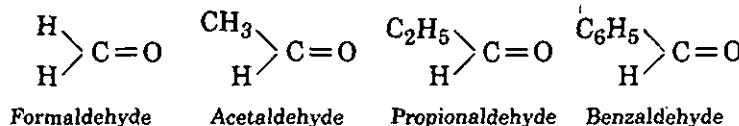
- Introduction
- Preparations
- Reactions
- Summary
- Student Activity
- Test Yourself

• 8.1. INTRODUCTION

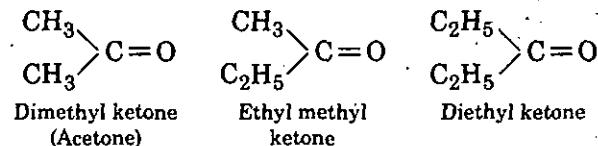
Both aldehydes and ketones have the general formula $C_nH_{2n}O$. Both types of compounds contain the carbonyl ($>C=O$) group. In aldehydes, one valency of this group is united with one hydrogen atom and the other is united with an alkyl group (except formaldehyde). In ketones, both the valencies are united with alkyl groups. For examples,



(a) Aldehydes



(b) Ketones

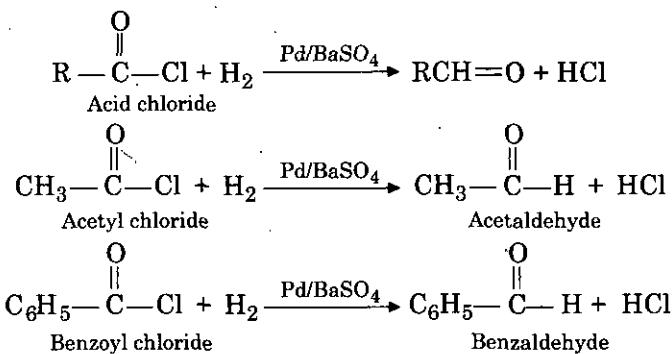


Aldehydes are the first oxidation products of primary alcohols and their functional group is aldehydic group, $-C\begin{smallmatrix} O \\ // \\ H \end{smallmatrix}$ which can occur at the end of the carbon chain.

Ketones are the first oxidation products of secondary alcohols and their functional group is ketonic group $\begin{smallmatrix} O \\ || \\ C \end{smallmatrix} - (>C=O)$ which being bivalent cannot occur at the end of the C-chain.

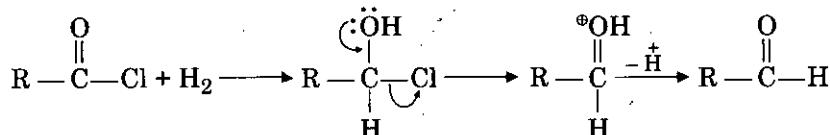
• 8.2. PREPARATIONS

(1) From acid chlorides : When acid chloride is reduced with H_2 in the presence of palladium suspended in $BaSO_4$, aldehydes are formed (Rosenmund's reduction).

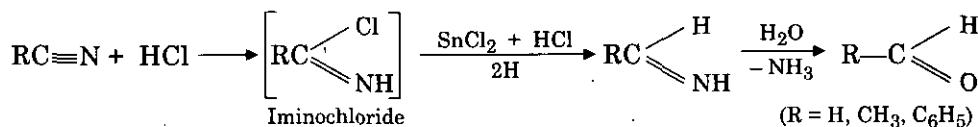


The function of BaSO_4 is to poison the catalytic activity of Pd and thus prevents further reduction of aldehyde into alcohol. (*Only aldehydes can be prepared, while ketones cannot be prepared by this method.*)

The following mechanism seems to occur :



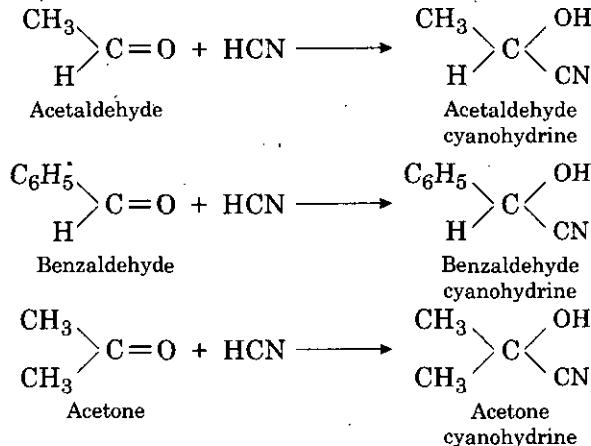
(2) From nitriles : When alkyl cyanide is reduced by anhydrous stannous chloride and HCl in absolute ether, aldehydes and ketones are produced (**Stephen's reaction**).



• 8.3. REACTIONS

1. Nucleophilic Addition Reactions

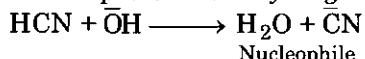
(a) Addition of HCN : Hydrogencyanide adds to the carbonyl group to form cyanohydrin.



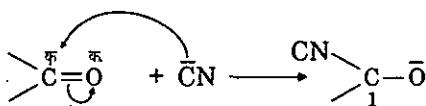
Mechanism

It involves nucleophilic attack of carbonyl carbon by the cyanide ion followed by attachment of hydrogen to carboxylic oxygen, as illustrated below :

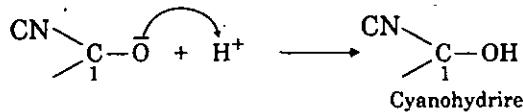
Step 1. The base removes a proton from hydrogen cyanide to produce cyanide ion.



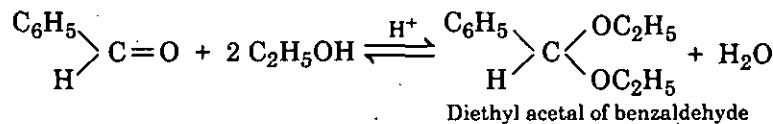
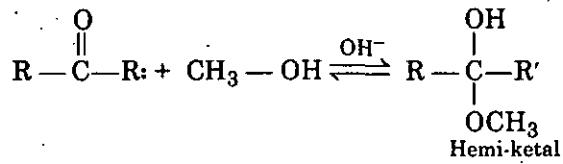
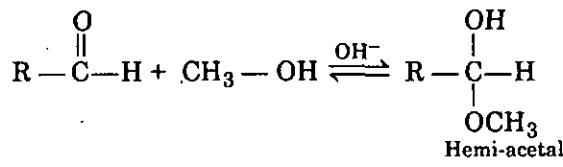
Step 2. The cyanide ion attacks the carboxyl carbon to form an anion.



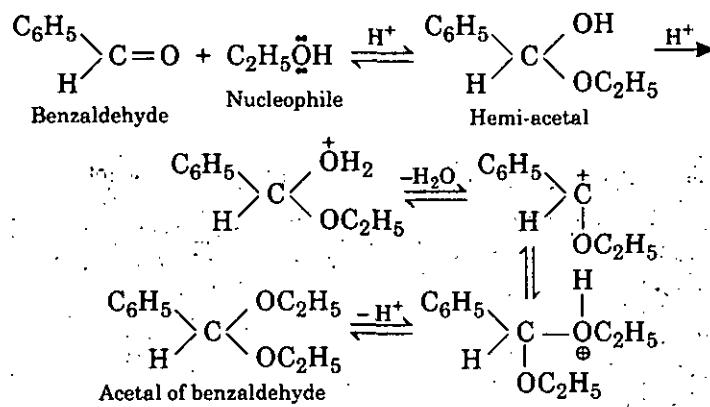
Step 3. The proton from the solvent usually water combines with the anion to give cyanohydrate.



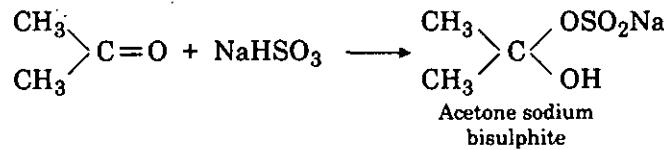
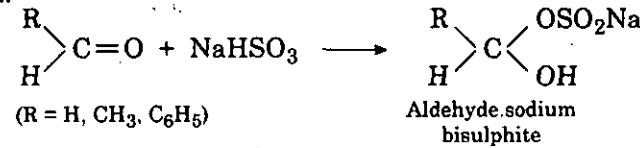
(b) Addition of alcohols: Alcohols add to the carbonyl group of aldehydes to form hemi-acetals and then form acetals in presence of an anhydrous acid.



Mechanism



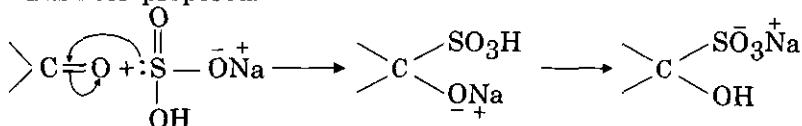
(c) Addition of sodium bisulphite: When aldehydes or ketones are treated with a saturated solution of sodium bisulphite, a crystalline white precipitate of addition product is formed.



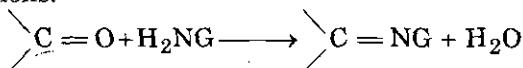
All ketones do not show this reaction. Only those ketones produce crystalline products in which at least one methyl group is attached to the carbonyl group.

Mechanism :

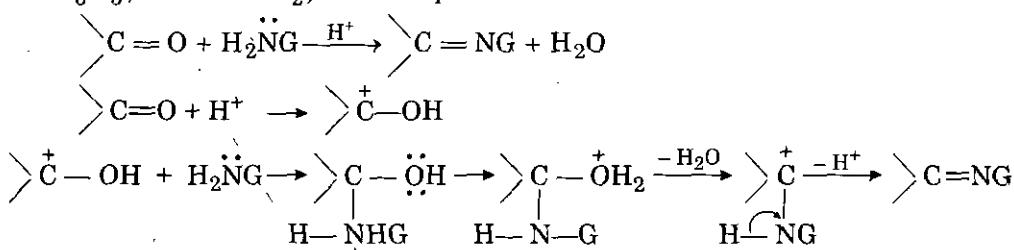
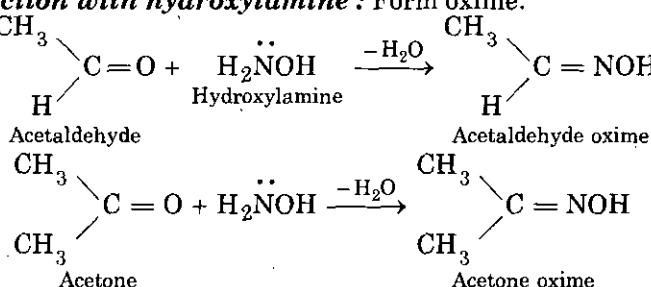
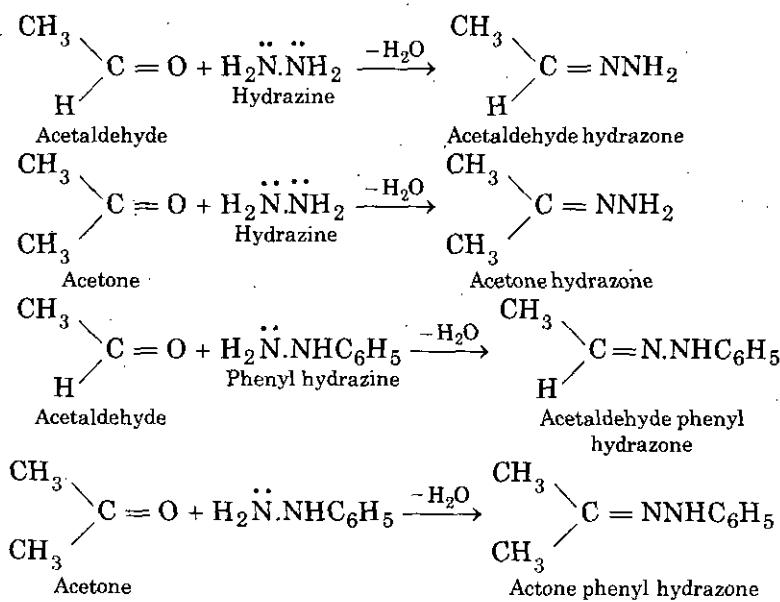
The mechanism is not well established. However, from kinetic studies the following mechanism has been proposed.

**(2) Nucleophilic Addition Reactions Involving Loss of Water Molecule**

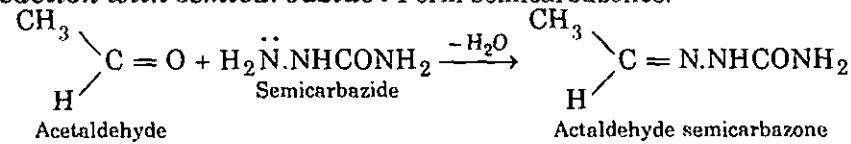
A number of substances with $-\text{NH}_2$ group condense with carbonyl compounds to form $\text{C}=\text{N}$ compounds along with water. These reactions usually occur in weakly acidic solutions.



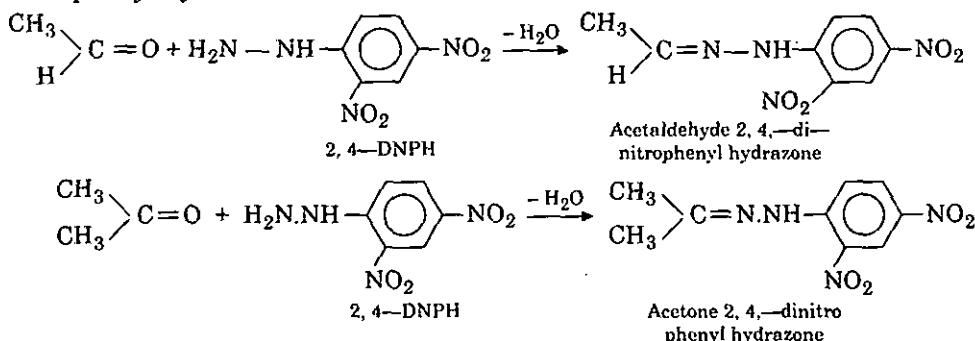
Mechanism : The general mechanism with H_2NG (where G is $-\text{OH}$, $-\text{NH}_2$, $-\text{NHC}_6\text{H}_5$, $-\text{NHCONH}_2$) can be explained as follows :

**(i) Reaction with hydroxylamine :** Form oxime.**(ii) Reaction with hydrazine and phenyl hydrazine :** Form hydrazone and phenyl hydrazone.

(iii) Reaction with semicarbazide : Form semicarbazones.



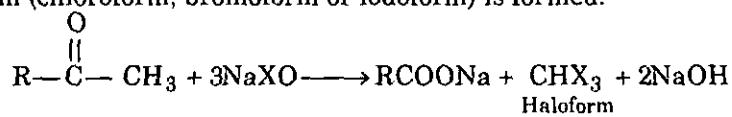
(iv) Reaction with 2, 4-dinitrophenyl hydrazine (2, 4-DNPH) : Form 2, 4-dinitrophenyl hydrazone.



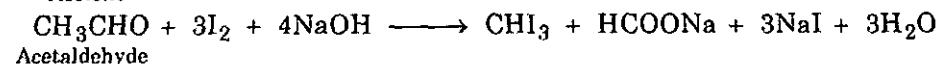
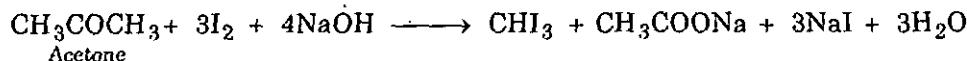
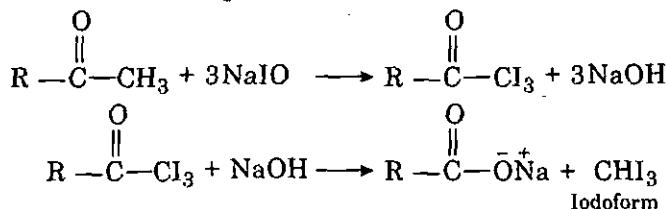
Similarly we can show the reactions with formaldehyde (HCHO) and benzaldehyde ($\text{C}_6\text{H}_5\text{.CHO}$).

3. Some Specific Reactions

(I) Iodoform Test : Methyl ketone (ethyl alcohol and acetaldehyde) give an important oxidation reaction known as haloform reaction. When such compounds are treated with hypohalite (alkaline solution of halogen), they are oxidised to acids and haloform (chloroform, bromoform or iodoform) is formed.

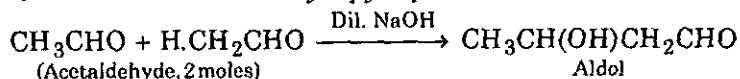


This is a characteristic test of $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$ group. For this purpose, sodium hypoiodite solution (mixture of I_2 and NaOH or Na_2CO_3) is used which produces a yellow solid i.e., iodoform, CHI_3 . This is known as iodoform test.

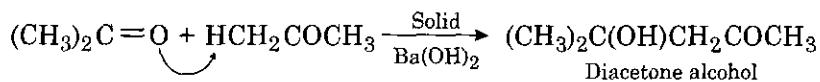


Acetone gives this test in the presence of NH_4OH , while acetaldehyde and ethyl alcohol do not.

(II) Aldol Condensation : Acetaldehyde in presence of dilute NaOH , K_2CO_3 or HCl , undergoes condensation to form a syrupy liquid known as *aldol*.



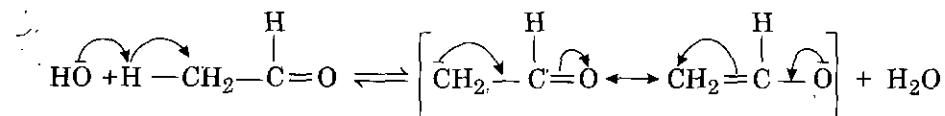
Acetone, in presence of $\text{Ba}(\text{OH})_2$, gives diacetone alcohol (aldol condensation).



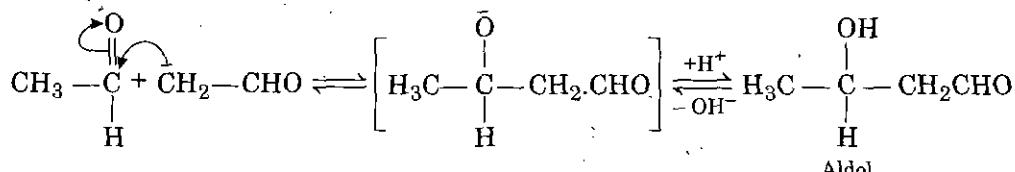
[Aldol condensation is possible only when the carbonyl compound contains at least one α -hydrogen atom].

Mechanism :

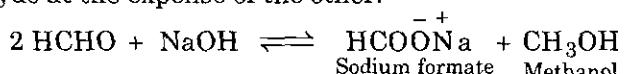
One molecule of aldehyde loses a proton under the influence of OH⁻ ion to form a carbanion. It is resonance stabilised.



The carbanion is a nucleophile, so it adds to a molecule of aldehyde at the carbonyl carbon, yielding aldol anion. This anion takes a proton from water yielding aldol and releasing the base OH^- ion.

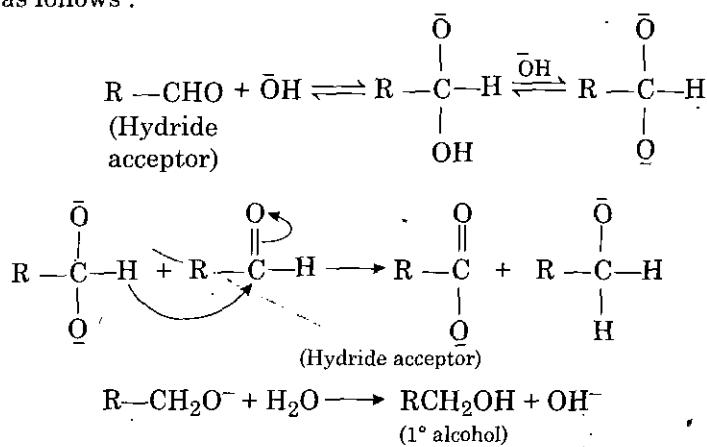


(III) Cannizzaro's Reaction : Aldehydes (except HCHO) from resinous mass when warmed with concentrated NaOH solution. Aldehydes which have no alpha hydrogen, e.g., HCHO, C_6H_5CHO etc. undergo disproportionation in presence of strong base to form equal amounts of the corresponding alcohol and carboxylic acid. This reaction is known as *Cannizzaro's reaction*, and involves the reduction of one molecule of an aldehyde at the expense of the other.

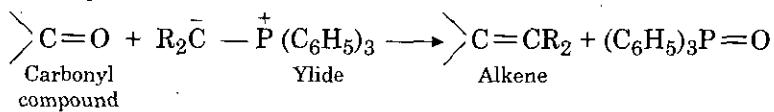


Mechanism :

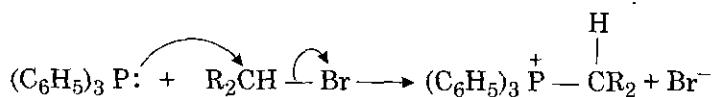
It is given as follows :

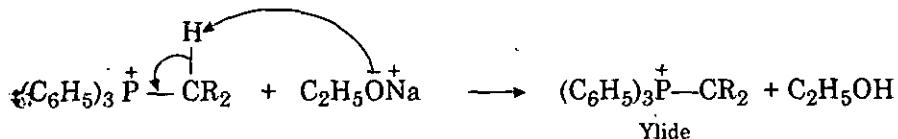


(IV) Wittig Reaction : Wittig reaction involves the treatment of aldehydes and ketones with phosphorus ylide to form alkenes.



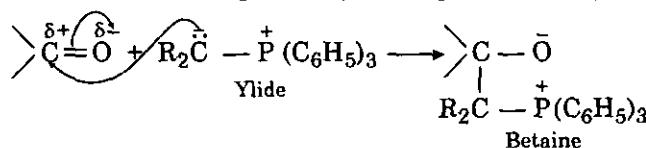
An ylide is a molecule possessing adjacent opposite charges. Phosphorus ylides are prepared from primary alkyl halides and triphenyl phosphine.



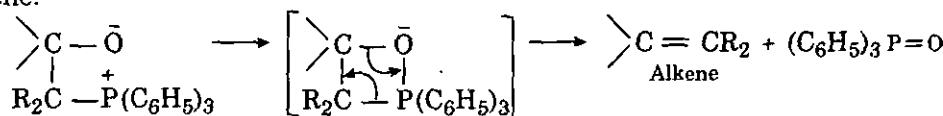


Mechanism :

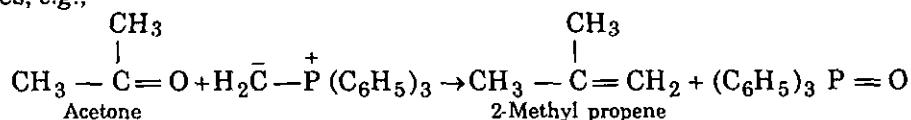
Step 1. The negative carbon of the ylide attacks the carbonyl carbon to form a **betaine**, which is a molecule having non-adjacent opposite charges.



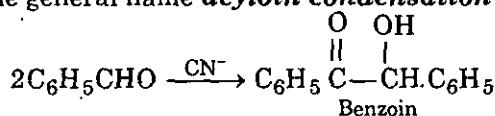
Step 2. The betaine undergoes elimination of triphenyl phosphine oxide to form an alkene.



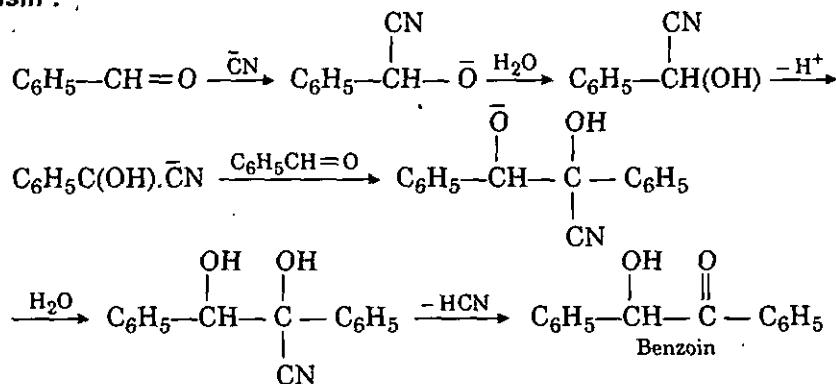
Wittig reaction forms an excellent method of preparing alkenes from aldehydes and ketones, e.g.,



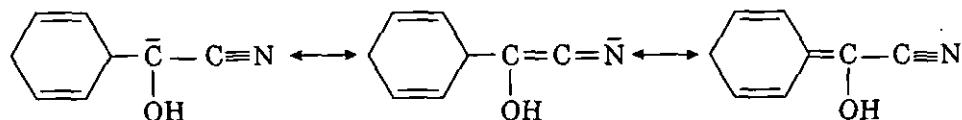
(V) Benzoin Condensation : When aromatic aldehydes are refluxed with alcoholic solution of potassium cyanide they undergo self condensation and form α -hydroxy ketone. When benzaldehyde is the aromatic aldehyde the product formed is called **benzoin** and the reaction is known as **benzoin condensation**. For aromatic aldehydes, the general name **acyloin condensation** is applicable.



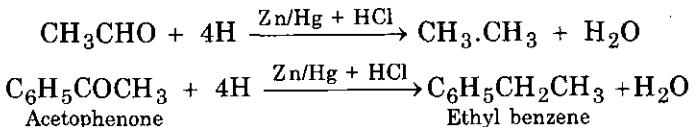
Mechanism :



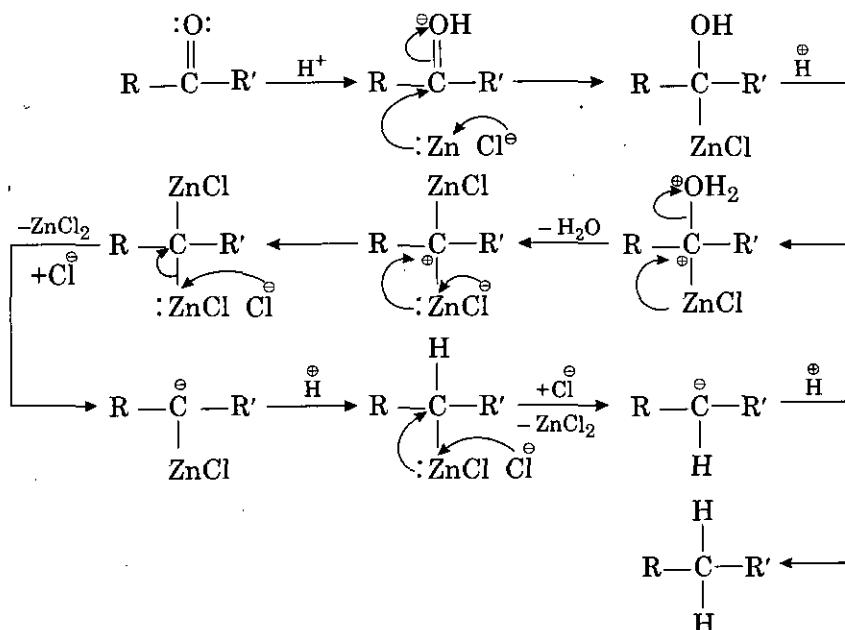
It is observed that the carbanion intermediate is resonance stabilised and is obtained preferentially, in the above sequence, from the cyanohydrine intermediate.



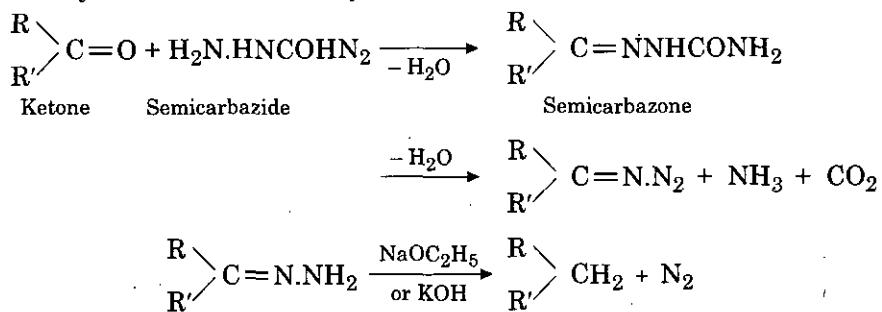
(VI) Clemmensen Reduction : When a carbonyl group in an organic compound is reduced into methylene group by means of zinc amalgam and concentrated acid, the process is called **Clemmensen reduction**. Thus, aldehydes and ketones are reduced to give the corresponding hydrocarbons.



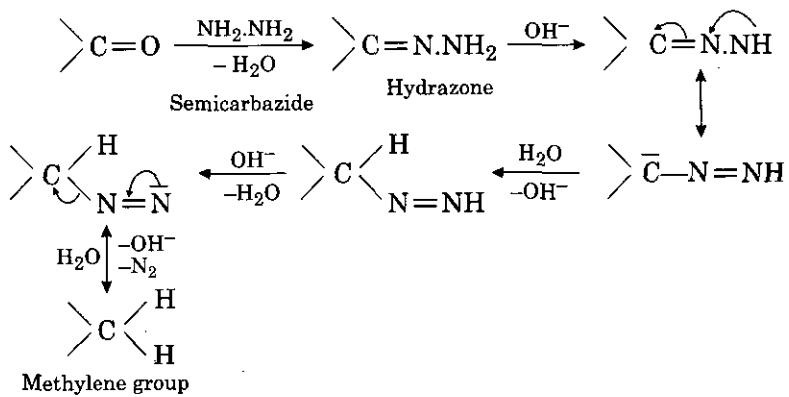
Mechanism



(VII) Wolf-Kishner Reduction : The conversion of the carbonyl group of aldehydes and ketones to methylene group by heating the semicarbazone, hydrazone or azine (or carbonyl compound) in the presence of an alkaline catalyst such as sodium ethoxide or hydroxide is called *Wolf-Kishner reduction*.



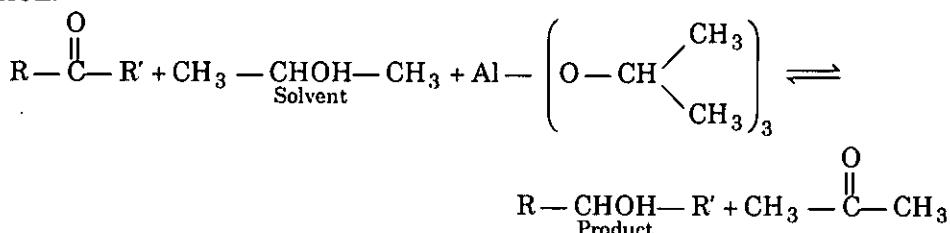
The mechanism is as follows:



(VIII) Meerwein-Ponndorf-Verley (MPV) Reduction : This is a common method for the reduction of carbonyl compounds particularly of unsaturated aldehydes and ketones. This reagent attacks only carbonyl compounds.

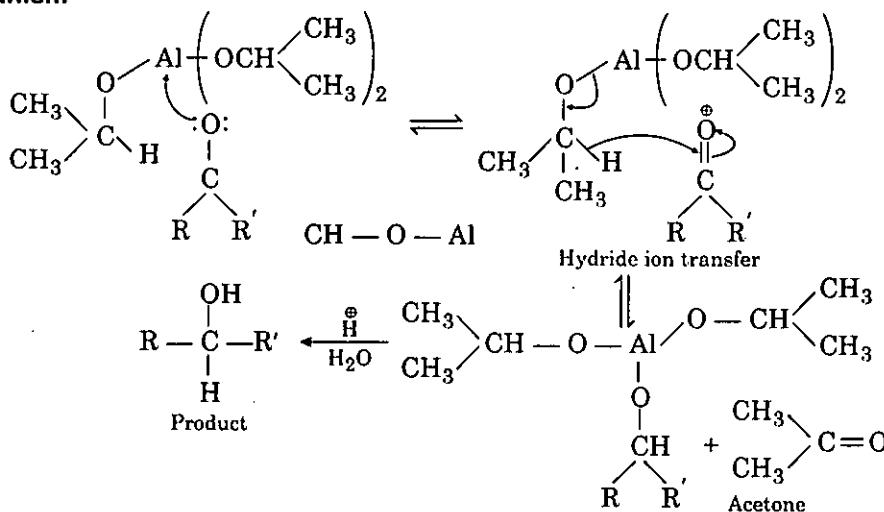
When ketone is dissolved in a solution of isopropyl alcohol containing aluminium isopropoxide, the ketone is reduced to corresponding alcohol. An equimolar amount of

isopropyl alcohol is changed into acetone. This method which is very selective in that it reduces only carbonyl compounds is known as **Meerwein-Ponndorf-Verley reduction**.



In this reduction, metal salt of secondary alcohols (generally, aluminium isopropoxide) can transfer hydride to carbonyl group of aldehyde and ketone. Since metal alkoxides undergo fast hydrogen-metal exchange reaction, an alcohol may be used as the source of hydrogen in presence of catalytic amount of aluminium isopropoxide. Isopropanol and aluminium isopropoxide are mostly used. If acetone is continuously removed, the reaction can be forced to high conversion.

Mechanism



• SUMMARY

- Aldehydes and ketons have carbonyl group $\left(\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array} \right)$
- These compounds may be prepared from acid chlorides and nitriles.
- These compounds show nucleophilic addition reactions.
- Iodoform test is used for the identification of $-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3$ group. In this test I_2 and NaOH is used.
- Aldol condensation is carried out by the aldehydes and ketones having $\alpha-\text{H}$ atom(s) e.g., CH_3CHO , CH_3COCH_3 etc.
- Cannizzaro's reaction is carried out by the aldehydes which do not contain $\alpha-\text{H}$ atom e.g., HCHO , $\text{C}_6\text{H}_5\text{CHO}$ etc. In this reaction both oxidation and reduction takes place of aldehyde.
- In Wittig reaction ylide is used which changes carbonyl compound into alkene.
- Benzoin condensation takes place by benzaldehyde in the presence of alc. KOH.
- By Clemmensen reduction carbonyl compound is reduced to hydrocarbon.
- In Wolf-Kishner reduction semicarbazide is used which reduces ketone into alkene.
- By MPV reduction one ketone changes to other ketone using aluminium iso propoxide in the presence of sec. alcohol as a solvent.

• STUDENT ACTIVITY

1. Describe two methods of preparation of aldehyde and ketone.

2. Describe the addition reaction of aldehyde or ketone with HCN and NaHSO_3 .

3. Discuss the nucleophilic substitution reaction of aldehyde or ketone in which water molecule is eliminated.

4. Explain aldol condensation or Cannizzaro's reaction.

5. What is Wittig reaction ? Explain its mechanism.

6. How do you prepare benzoin from benzaldehyde ?

7. Discuss Clemmensen or Wolf Kishner reduction.

• TEST YOURSELF

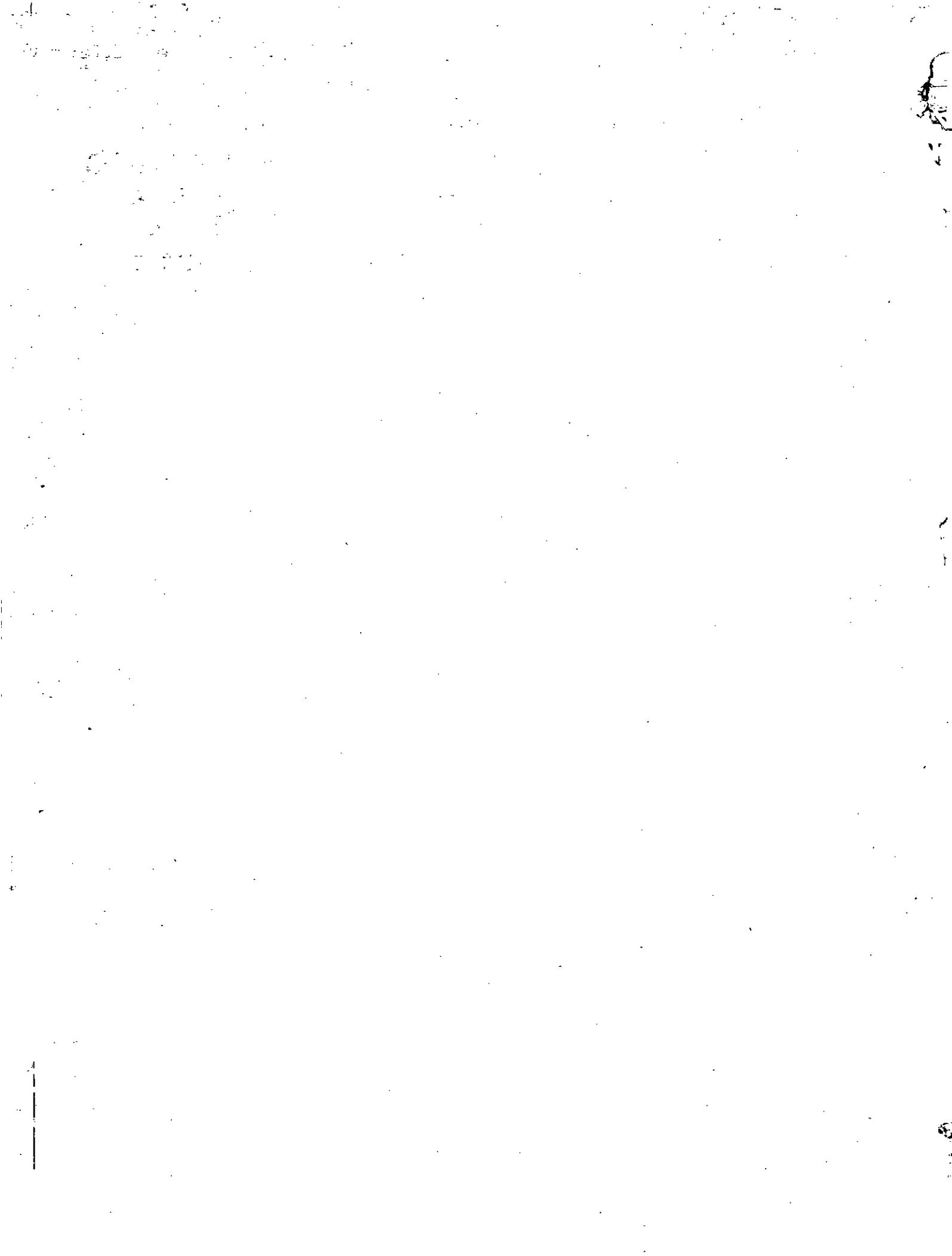
1. What are the aldehydes and ketones ?
2. How do you prepare aldehydes from acid chloride ?
3. What are cyanohydrine ? How do you prepare them ?
4. What is the use of NaHSO_3 in aldehydes or ketones ?
5. Discuss the reaction of alcohol on aldehyde or ketone.
6. What do you know about nucleophilic addition reactions of aldehydes and ketones you? Give two examples.
7. Describe nucleophilic addition reactions in which water molecule is eliminated. Give three examples.
8. What is the condition for aldol condensation ? Describe aldol condensation with mechanism.
9. What is iodoform test ? Give its equations.
10. What happens when benzaldehyde shows Cannizzaro's reaction.
11. Describe Wittig's reaction?
12. Discuss the benzoin condensation along with its mechanism.
13. How does Clemmensen reduction reaction take place ? Give the examples of acetaldehyde and acetone.
14. What is the difference between Clemmensen reduction and Wolf Kishner reduction ?
15. What is MPV reaction ?
16. Acetone undergoes reduction with hydrazine in the presence of NaOH to give propane. This reaction is known as :

(a) Clemmensen reduction	(b) Wolf Kishner reduction
(c) Aldol condensation	(d) None of these

ANSWERS

16. (b) 17. (d) 18. (b) 19. (a) 20. (c) 21. (b)
 22. (c) 23. (b) 24. (d) 25. (b) 26. (b)
 27. (d) 28. (c) 29. (b) 30. (b) 31. Aldol
 condensation
 32. Resenmund 33. Cannizzaro 34. Carbonyl
 group 35. KCN





c. PCM-203

स्वामी विवेकानन्द सुभर्ति विश्वविद्यालय

संस्था के लिए ज्ञान का अधिकारी बनना हमारा उद्देश्य

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