Physical Chemistry

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Composition with Variation

Defining the Concept

Thermodynamics is an experimental science based on a small number of principles that are generalisations made from experience. It is concerned only with macroscopic or large-scale properties of matter and it makes no hypotheses about the small-scale or microscopic structure of matter. From the principles of thermodynamics one can derived general relations between such quantities as coefficients of expansion, compressibility, heat capacities, heat of transformation, and magnetic and dielectric coefficients, especially as these are affected by temperature. The principles of thermodynamics also tell us which of these relations must be determined experimentally in order to completely specify all the properties of the system.

Thermodynamics is complementary to kinetic theory and statistical thermodynamics. Thermodynamics provides relationships between physical properties of any system once certain measurements are made. Kinetic theory and statistical thermodynamics enable one to calculate the magnitudes of these properties for those systems whose energy states can be determined. There are three principal laws of thermodynamics. Each law leads to the definition of thermodynamic properties which help us to understand and predict the operation of a physical system. Here you can find some simple examples of these laws and properties for a variety of physical systems. Fortunately, many of the classical examples of thermodynamics involve gas dynamics. Unfortunately, the numbering system for the three laws of thermodynamics is a bit confusing.

The zeroth law of thermodynamics involves some simple definition of thermodynamic equilibrium. Thermodynamic equilibrium leads to the large-scale definition of temperature, as opposed to the small-scale definition related to the kinetic energy of the molecules. The first law of thermodynamics relates the various forms of kinetic and potential energy in a system to the work which a system can perform and to the transfer of heat. This law is sometimes taken as the definition of internal energy, and introduces an additional state variable, *enthalpy.*

The first law of thermodynamics allows for many possible states of a system to exist. But experience indicates that only certain states occur. This leads to the second law of thermodynamics and the definition of another state variable called entropy. The second law stipulates that the total entropy of a system plus its environment can not decrease; it can remain constant for a reversible process but must always increase for an irreversible process.

Functions of State

The sum total of the entropy change of any system and surrounding *(viz.,* $\Delta S_{sys} + \Delta S_{\mathrm{sur}}$) serves a criterion of spontaneity or feasibility of a process. If the total entropy change is positive, the process is feasible. If it is zero, the system remains in a state of equilibrium. However, in order to decide the feasibility of process knowledge of entropy change of the system as well as that of surrounding is essential. This is not convenient. Therefore consider entropy change in terms of other state functions, which can be determined more conveniently. Two such functions are Helmoholtz free energy (A) or Helmoholtz function and Gibbs free energy *(G)* are defined by

$$A = U - TS \qquad \text{...1.1}$$

$$G = H - TS \qquad \text{...1.2}$$

Since, *U, H, S,* depend only upon the state of a system (the temperature is included in the state), it is evident that the function

A and G also depend upon the state of the system. The exact nature of the function will be clear from their variation. If G_1, H_1 and S_1, represent the thermodynamic functions for the system in the initial state and G_2, H_2 and S_2 in the final state at constant temperature so hat change in Gibbs's free energy is

$$G_2 - G_1 = \Delta G = (H_2 - H_1) - T(S_2 - S_1)$$

or $\Delta G = \Delta H - T\Delta S$ ...1.3

Similarly $\Delta A = \Delta U - T\Delta S$ ...1.4

The variation of free energy change with variation of temperature and pressure may now be considered

$$G = H - TS \text{ since } H = V + PV$$

$$G = U + PV - TS$$

Upon differentiation this gives

$$dG = dU + PdV + VdP - TdS - SdT \qquad \text{...1.5}$$

From first law

$$dq = dU + PdV$$

And for a reversible process $dS = dq/T$ ...1.6

Combining equation 1.5 and 1.6 we get

$$dG = VdP - SdT \qquad \text{...1.7}$$

similarly $dA = -PdV - dT$ ...1.8

Entropy change for a given state is a definite quantity, independent of the fact whether the change is brought about reversibly or irreversibly. However, mathematically it is given by equation,

$$dS = \frac{dq_{rev}}{T} = \frac{dU + PdV}{T}$$

only if he the change is brought about reversibly. Suppose the small change of state is brought irreversibly. Now the heat absorbed by the system will be less ($\therefore\ q_{irr} < q_{rev}$), but the entropy change will have he same value. Hence for irreversible process

$$Tds > q_{rev}$$

We may thus write

$$TdS = dU + PdV \qquad \text{(For reversible process)}$$

$$TdS = dU + PdV \qquad \text{(For irreversible process)}$$

Combining the two

$$TdS = dU + PdV \qquad \text{...1.9}$$

Combining this with equation 1.5 we get

$$dG \leq VdP - SdT \qquad ...1.10$$

Therefore at constant temperature and pressure

$$dG \leq 0$$

Similarly dA $\leq$–PdV PdV and at constant volume

$$dA \leq 0$$

The criterion in terms of free energy change, *viz.*, $(dG)_{T,\,p}<0$ is the most useful criterion to decide between reversibility and irreversibility of a process.

Role of Gibbs Helmholtz

Gibbs Helmholtz equation relates the free energy change to the enthalpy change and the rate of change of free energy with temperature. Thus equation may be applied to any change at constant pressure.

Let G_1 represent the free energy of a system in its initial state at temperature T. Suppose the temperature rises to $T + dT$ where dT is infinitesimally small. Let the free energy at the new temperature be $G_1 + dG_1$

Now suppose that when the system is in its final state, its free energy is given by G_2 at the temperature T and by $G_2 + dG_2$ at the temperature $T + dT$. If pressure remains constant all along equation 1.7 is applicable, *i.e.,*

$$dG_1 = -S_1 dT \qquad ...1.11$$

$$dG_2 = S_2 dT \qquad ...1.12$$

where S_1, and S_2 are the entropies of the system in the initial and final states of the system, respectively. Subtracting Eq. 1.11 from Eq. 1.12.

$$d(G_2 - G_1) = -(S_2 - S_1)dT$$

or $$d\,(\Delta G) = -\,\Delta S dT$$

Substituting this value in Eq. 1.3 gives

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \qquad ...1.14$$

This equation is known as Gibbs-Helmholtz equation. It is applicable to all processes occurring at constant pressure. It relates electrical and chemical energy and find extensive application in electrochemical cells.

Some Characteristics

The thermodynamic properties, *U, H, S, A, G* are extensive properties because their value change with change in mass *(i.e.,* the number of mole) of the system. In the various thermodynamic equations, the change of state was considered to be due to change of temperature and pressure. This means there is no change in mass of the system and such systems are called *closed system.* However in the case of an *open system* containing two or more components, there can be change in the number of moles of various components as well. In that case, an extensive property, say, X, must be a function not only of temperature and the pressure but also of the number of moles of the various components present in the system.

Let T and P be the temperature and pressure, respectively, of a system and let n_1, n_2, n_3.... n_j be the respective numbers of moles of the constituents, 1, 2, 3, *...j.* Then, in view of what has beet said above, the property X must be a function of temperature, pressure and the number of moles of the various constituents, *i.e.,*

$$X = f(T, P, n_1, n_2, n_3, \ldots\ldots n_j)$$

where $n_1 + n_2 + n_3 + \ldots n_j$ = Total, number of moles = N (say).

For a small change in temperature, pressure and the number of moles of the components, the change in property dX will be given by the expression

$$\mathrm{dX} = \left(\frac{\partial X}{\partial T}\right)_{P,N} dT + \left(\frac{\partial X}{\partial P}\right)_{T,N} dP + \left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_2,\ldots.n_j} dn_1 \left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_1 n_2,\ldots.n_j} dn_2$$

$$+\left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_2,\ldots.n_j} dn_i + \left(\frac{\partial X}{\partial n_j}\right)_{T,P,n_1 n_2,\ldots.} dn_j \qquad 1.16$$

The quantity $\left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_1,n_2,\ldots\ldots n_j}$ is called the partial molar property of the concerned component.

This is more often represented as $\overline{X_i}$.

Thus, for the *i*th component in a system,.

partial molar internal energy=$\left(\partial U/\partial n_i\right)_{T,P,n_1,n_3....} = \overline{U_i}$

partial molar enthalpy = $\left(\partial H/\partial n_i\right)_{T,P,n_1,n_3....} = \overline{H_i}$

partial molar entropy = $\left(\partial S/\partial n_i\right)_{T,P,n_1,n_3....} = \overline{S_i}$

partial molar volume = $\left(\partial V/\partial n_i\right)_{T,P,n_1,n_2,....} = \overline{V_i}$

Partial Molar Free Energy, Concept of Chemical Potential

The most important partial molar quantity in Physical Chemistry is the partial molar free energy designated as chemical potential and represented as

$$\left(\partial G/\partial n_i\right)_{T,P,n_{1,2,.....n_j}} = \overline{G_i} = \mu_i \qquad ...1.17$$

The chemical potential of a given substance is, evidently, the change in free energy of the system that results on the addition of one mole of that particular substance at a constant temperature and pressure, to such a large quantity of the system that there is no appreciable change in the overall composition of the system.

For a small free energy change, Eq. 1.16 may be written as

$$\left(\partial G/\partial T\right)_{P,N} dT + \left(\partial G/\partial P\right)_{T,N} dP + \mu_1 dn_1 + \mu_2 dn_2 + ...\mu_j dn_j \qquad ...1.18$$

where μ_1, μ_2 ... and μ_j are chemical potentials of the components 1, 2,... and *j,* respectively.

If temperature and pressure remain constant, then

$$\left(dG\right)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + ...\mu_j dn_j \qquad ...1.19$$

If a system has a definite composition having n_v, n_2, ... n_j moles of the constituents 1, 2, ...*j,* respectively, then, on integrating Eq. 1.19 we have

$$\left(G\right)_{T,P,N} = n_1\mu_1 + n_2\mu_2 + ...n_j\mu_j \qquad ...1.20$$

From Eq. 1.20 Chemical Potential may be taken as the contribution per mole of each particular constituent of the mixture to the total free energy of the system under conditions of constant temperature and pressure.

It readily follows that for a total of 1 mole of a pure substance, G = μ, i.e., free energy is identical with chemical potential.

Role of Gibbs-Duhem

Eq. 1.20 shows that the free energy of a system, at constant temperature and pressure, can *b* expressed as a sum of $n\mu$ terms for the individual components of the system.

The total differential of G is written as

$$\begin{aligned} dG &= \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 ... \mu_j dn_j + n_j d\mu_j \\ &= \left(\mu_1 dn_1 + \mu_2 dn_2 + ...n_j dn_j\right) + \\ &\qquad \left(n_1 d\mu_1 + n_2 d\mu_2 + ...n_j d\mu_j\right) \qquad ...1.\ 21 \end{aligned}$$

But, according to Eq. 1.19, the first term on right hand side of Eq. 1.21 is equal to dG at constant temperature and pressure. It follows, therefore, that at constant temperature and pressure, for a system of a definite composition.

$$n_1 d\mu_1 + n_2 d\mu_2 + ...n_j d\mu_j = 0$$

or $$\Sigma n_i d\mu_i = 0 \qquad ...1.22$$

This simple relationship is known as The Gibbs-Duhem equation.

For a system having only two components *(e.g.,* a binary solution), the above equation reduces to

$$n_1 d\mu_1 + n_2 dn_2 = 0$$

or $$d\mu_1 = -\left(n_2 / n_1\right) d\mu_2 \qquad ....1.23$$

Eq. 1.23 shows that variation in chemical potential of one component affects the value for the other component as well. Thus, if $d\mu_1$ is positive, *i.e.,* if μ_1, increases, then $d\mu_2$ must be negative, *i.e.,* μ_2 must decrease and *vice versa.*

Some Important Results

In a special case when there is no change in the number of moles of the various constituents of a system, that is, when the system is closed one, then dn_1, dn_2, $...dn_j$ are all zero. In such a case Eq. 1.16 reduces to

$$dG = \left(\partial G / \partial T\right)_{P,N} dT + \left(\frac{\partial P}{\partial G}\right)_{T,N} dP \qquad ...1.24$$

For a closed system,

$$dG = VdP - SdTs$$

Hence, by equating coefficients of AT and dP in the above two equation, we get

$$\left(\partial G/\partial T\right)_{P,N} = -S \qquad ...1.25$$

and $$\left(\partial G/\partial P\right)_{T,N} = V \qquad ...1.26$$

These results are important as they help us in deriving expressions for the variation of chemical potential with temperature and pressure.

Chemical Potential and Changes

The variation of chemical potential of any constituent i of a system with temperature can be derived by differentiating Eq. 1.17 with respect to temperature and Eq. 1.25 with respect to n_i. The results are:

$$\frac{\partial^2 G}{\partial n_i \partial T} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} \qquad ...1.27$$

$$\frac{\partial^2 G}{\partial T \partial n_i} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_1....n_j} = -\overline{S_i} \qquad ...1.28$$

where $\overline{S_i}$, by definition, is the *partial molar entropy* of the component i

If follows from Eq. 1.27 and 1.28 that

$$\left(\partial \mu_i/\partial T\right)_{P,N} = -\overline{S_i} \qquad ...1.29$$

Eq. 1.29 gives the variation of chemical potential (μ_i) of any constituent i of the system with temperature.

Since the entropy of a substance is always positive hence, according to Eq. 1.29 the chemical potential would decrease with increase in temperature. This is illustrated in the figure given below for a substance in solid, liquid and gaseous states. It is evident that at the melting point (T_m), the chemical potentials of the solid and liquid phases are the same. Similarly, at the boiling point (T_b), the chemical potentials of liquid and gaseous phases are the same. These observations are extremely useful in the Phase rule studies.

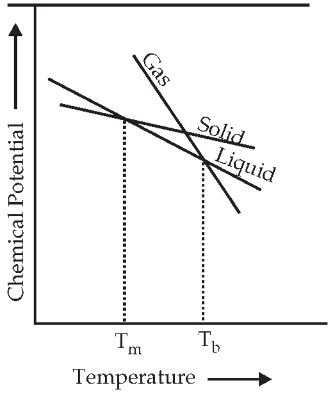


Fig. *Variation of Chemical Potential with Temperature*

Changes with Pressure

The variation of chemical potential of any constituent *i* of the system with pressure may be derived by differentiating Eq. 1.17 with respect to pressure and Eq. 1.26 with respect to N_i. The results are:

$$\frac{\partial^2 G}{\partial P \partial n_i} = \left(\frac{\partial \mu_1}{\partial P}\right)_{T,N} \qquad \text{...1.30}$$

and
$$\frac{\partial^2 G}{\partial n_i \partial P} = -\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_1 \ldots n_j} = -\overline{V_i} \qquad \text{...1.31}$$

where $\overline{V_i}$ by definition, is the *partial molar volume* of the component *i*.

If follows from Eqs. 1.30 and 1.31 that

$$\left(\partial \mu_i / \partial P\right)_{r,N} = -\overline{V_i} \qquad \text{...1.32}$$

Eq. 1.32 gives the variation of chemical potential (μ_i) of any constituent of the system with pressure.

Chemical Potential in Ideal Gases

For a system of ideal gases, a further development of Eq. 1.32 is also possible. In an ideal gas

$$PV = nRT \qquad \text{...1.32(a)}$$

Consider a system consisting of a number of ideal gases. Let n_1, n_2.... be the numbers of moles of various constituents present in the mixture. Then, in the ideal gas equation, n, the total number of moles, may be replaced by $(n_1 + n_2 + ...)$. Hence,

$$V = \frac{nRT}{P} = (n_1 + n_2 + ...)\frac{RT}{P} \qquad ...1.33$$

Differentiating Eq. 1.33 with respect to n_i, at constant temperature and pressure, we have

$$(\partial V/\partial n_i)_{T,P,n_1,n_2...} = \overline{V_i} = RT/P \qquad ...1.34$$

Substituting the value of $\overline{V_i}$ (= RT/P) in Eq. 1.32 we have

$$(\partial \mu_i/\partial P)_{T,N} = RT/P \qquad ...1.35$$

For a constant composition of the gas and at a constant temperature, Eq. 1.35 may also be expressed in the form

$$d\mu_i = (RT/P)dP = RT\, d \text{ In } P \qquad ...1.36$$

Let p_i be the partial pressure of the constituent i present in the mixture. Since each constituent behaves as an ideal gas, therefore,

$$p_i V = n_i RT \qquad ...1.37$$

It follows from Eq.1.37 and 1.32a that

$$p_i = (n_i/n)P \qquad ...1.38$$

Since n_1 and n_2 are constants, therefore, on taking logarithms and then differentiating, we get

$$d \ln p_i = d \ln P \qquad ...1.39$$

Substituting in Eq. 1.36, we have

$$d\mu_i = RT\, d \ln p_i \qquad ...1.40$$

On integrating Eq. 1.40 we get

$$\mu_i = \mu^o_{i(p)} + RT \ln p_i \qquad ...1.41$$

where $\mu^o_{i(p)}$ is the integration constant, the value of which depends upon the nature of the gas and on the temperature.

It is evident from Eq. 1.41 that the chemical potential of any constituent of a mixture of ideal gases is determined by its partial pressure in the mixture. If the partial pressure of the constituent i is unity, *i.e.,* $p_i = 1$, then

$$\mu_i = \mu^o_{i(p)} \qquad ...1.42$$

Thus, $\mu^o_{i(p)}$ gives the chemical potential of the gaseous constituent i when the *partial pressure* of the constituent is unity, at a constant temperature.

According to Eq. 1.37

$$p_i = (n_i/V)RT \qquad ...1.43$$

Now n_i/V represents molar concentration, *i.e.,* the number of moles per unit volume of the constituent i in the mixture. If this concentration is represented by c_i, then Eq. 1.43 gives

$$p_i = c_i RT \qquad ...1.44$$

Introducing this value of p_i in Eq. 1.41 we have

$$\mu_i = \mu_i^o(p) + RT + ln(c_i RT)$$

$$\mu_i = \mu^o_{i(p)} + \underbrace{RT\ln RT}_{\text{constant}} + RT\ln c_i$$

or

$$\mu_i = \mu^o_{i(c)} + RT\ln c_i \qquad ...1.45$$

where $\mu^o_{i(c)}$ is a constant depending upon the nature of the gas and the temperature. If $c_i = 1$, then

$$\mu_i = \mu^o_{i(c)}$$

Thus, $\mu^o_{i(c)}$ represents the chemical potential of the constituent i when the concentration of the constituent in the mixture is unity, at a constant temperature.

Lastly, since n_i/n represents the mole fraction (x_i) of the constituent i in the mixture, Eq. 1.38 may be represented as

$$p_i = x_i p \qquad ...1.46$$

Substituting this value of p_i in Eq. 1.41 we have

$$\mu_i = \mu^o_{i(p)} + RT + \ln(x_i P)$$

$$= \mu^o_{i(p)} + \underbrace{RT\ln P}_{\text{constant}} + RT\ln x_i$$

or $$\mu_i = \mu_{i(x)}^{o} + RT\ln x_i \qquad ...1.47$$

where the quantity $\mu_{i(x)}^{o}$ is also a constant which depends both on the temperature and the total pressure. If $x_i = 1$,

$$\mu_i = \mu_i^o(x)$$

Thus, $\mu_i^o(x)$ represents the chemical potential of the constituent when its mole fraction, at a constant temperature and pressure; is unity.

Concept of Clausius-Clapeyron

An equation of fundamental importance which finds extensive application in the one-component, two-phase systems, was derived by Clapeyron and independently by Clausius, from the Second law of thermodynamics and is generally known as the Clapeyron-Clausius equation. The two phases in equilibrium may be any of the following types:

(i) Solid and Liquid, S = *L,* at the melting point of the solid.

(ii) Liquid and Vapour, *L* = *V,* at the boiling point of the liquid.

(iii) Solid and Vapour, S = *V,* at the sublimation temperature of the solid.

(iv) One Crystalline Form and Another Crystalline Form, as for example, rhombic and monoclinic sulphur, $S_R = S_M$, at the transition temperature of the two allotropic forms.

Consider any two phases (say, liquid and vapour) of one and the same substance in equilibrium with each other at a given temperature and pressure. It is possible to transfer any definite amount of the substance from one phase to the other in a thermodynamically reversible manner, i.e., infinitesimally slowly, the system remaining in a state of equilibrium all along. For example, by supplying heat infinitesimally slowly to the system, it is possible to change any desired amount of the substance from the liquid to the vapour phase at the same temperature and pressure. Similarly, by withdrawing heat infinitesimally slowly from the system, it is possible to change any desired amount of the substance from the vapour to the liquid phase without any change in temperature and pressure. Since the system remains in a state of equilibrium, the free energy change of either process will be zero. We may conclude, therefore, that equal amount of a given substance must have exactly the same free energy in the two phases at equilibrium with each other.

Consider, in general, the change of a pure substance from phase A to another phase B in equilibrium with it at a given temperature and pressure. If G_A is the free energy per mole of the substance in the initial phase A and G_B is the free energy per mole in the final phase B, then, since

$$G_A = G_B$$

hence, there will be no free energy change, *i.e.,*

$$\Delta G = G_B - G_A = 0$$

If the temperature of such a system is raised, say from T to $T + dT$, the pressure will also have to change, say from P *to* $P + dP$, in order to maintain the equilibrium. The relationship between dT and dP can be derived from thermodynamics.

Let the free energy per mole of the substance in phase A at the new temperature and pressure be $G_A + dG_A$ and that in phase B be $G_B + dG_B$. Since the two phases are still in equilibrium, hence,

$$G_A + dG_A = G_B + dG_B \qquad \text{...1.48(a)}$$

According to thermodynamics,

$$dG = VdP - SdT \qquad \text{...1.48(b)}$$

This equation gives change of free energy when a system undergoes reversibly a change of temperature dT and a change of pressure dP.

Eq. 1.48(b) for phase A may be written as

$$dG_A = V_A dP - S_A dT$$

and for phase B, as

$$dG_B = V_B dP - S_B dT$$

Since $G_A = G_B$, hence, from Eq. 1.48

$$dG_A = dG_B$$

$$\therefore V_A\, dP - S_A dT = V_B dP - S_B dT$$

or

$$\frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A} \qquad \text{...1.49}$$

It may be noted that since V_A and V_B are the molar volumes of the pure substance in the two phases A and B, respectively, $V_B - V_A$ represents the change in volume when one mole of the substance passes from the initial phase A to the final phase B. It may be represented by ΔV. Similarly, $S_B - S_A$, being the change in entropy for the same process, may be put as ΔS. Hence

$$dP/dT = \Delta S/\Delta V \qquad \text{...1.50}$$

If q is the heat exchanged *reversibly* per mole of the substance during the phase transformation at temperature T, then the change of entropy (ΔS) in this process is given by

$$\Delta S = q/T$$

Hence $$\frac{dP}{dT} = \frac{q}{T\Delta V}$$

Thus,

$$\frac{dP}{dT} = \frac{q}{T(V_B - V_A)} \qquad \text{...1.51}$$

This is the Chapeyron-Clausis equation.

This equation, evidently, gives change in pressure dP which must accompany the change in temperature dT or *vice versa,* in the case of a system containing two phases of a pure substance in equilibrium with each other. Suppose the system consists of water in the two phases, *viz., liquid* and *vapour,* in equilibrium with each other at the temperature T, *i.e.,*

Water (liquid) = Water (vapour)

Then, q = Molar heat of vaporisation, ΔH_V

V_B = Volume of one mole of water in the vapour state, say, V_g

V_A = Volume of one mole of water in the liquid state, say, V_1

Eq. 1.51 therefore, takes the form

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_g - V_l)}$$

If the system consists of water at its freezing point, then, the two phases in equilibrium will be

Water (Solid) = Water (Liquid)
Ice

Eq. 1.51 may then be written as

$$\frac{dP}{dT} = \frac{\Delta H_f}{T\left(V_t - V_s\right)} \qquad \text{...1.52}$$

where ΔH_f is the molar heat of fusion if ice.

Integrated Form of Clapeyron-Clausius Equation for Liquid=Gas Equilibrium

The Clapeyron-Clausius equation as applied to liquid = vapour equilibrium, can be easily integrated. The molar volume of a substance in the vapour state is considerably greater than that in the liquid state. In the case of water, for example, the value of V_g at 100 C is 18   1670 = 30060 ml while that of V_t is only a little more than 18 ml. Thus, $V - V_t$ can be taken as V without introducing any serious error. The Clapeyron-Clausius equation 1.51, therefore, may be written as

$$\frac{dP}{dT} = \frac{\Delta H_v}{TV_g}$$

Assuming that the gas law is applicable, i.e., $PV = RT$ (per mole)

$$V_g = RT/P$$

Hence,

$$\frac{dP}{dT} = \frac{\Delta H_v}{T} \times \frac{P}{RT} = P\frac{\Delta H_v}{RT^2}$$

or $$\frac{1}{P} \times \frac{dP}{dT} = \frac{\Delta H_v}{RT^2}$$

or $$\frac{d(\ln P)}{dT} = \frac{\Delta H_v}{RT^2}$$

Assuming that ΔH_v remains constant over a small range of temperature, we have

$$\int d(\ln P) = \frac{\Delta H_v}{R}\int \frac{dT}{T^2} \qquad \text{...1.54}$$

$$\therefore \qquad \ln P = \frac{\Delta H_v}{R}\left(\frac{1}{T}\right) + C \qquad \text{...1.55}$$

where C is integration constant.

Eq. 1.55 is, evidently, the equation of a straight line. Hence, the plot of In P against $1/T$ should yield a straight line with *slope* $\Delta H_v / R$ and *intercept* = C. This enables evaluation of ΔH_v .

Eq. 1.53 can also be integrated between limits of pressure P_i and P_2 corresponding to temperature T_1 and T_2 Thus,

$$\int_{P_1}^{P_2} d(\ln P) = \frac{\Delta H_v}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$\therefore \qquad \mathrm{In}\frac{P_2}{P_1} = \frac{\Delta H_v}{R}\left[\frac{1}{T}\right]_{T_1}^{T2}$$

$$= \frac{\Delta H_v}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$\mathrm{In}\frac{P_2}{P_1} = \frac{\Delta H_v}{R}\left[\frac{T_2-T_1}{T_1T_2}\right] \qquad ...1.56$$

Applications of Clapeyron-Clausius Equation for Liquid = Vapour Equilibria

Eq. 1.56 can be used for calculating the molar heat of vaporisation, AH_v of a liquid if we know the vapour pressures at two temperature. Further if ΔH_v is known, vapour pressure at a desired temperature can be calculated from the knowledge of a single value of vapour pressure at a given temperature. It can also be used for calculating the effect of pressure on the boiling point of a liquid. A few examples are given below.

Calculation of Molar Heat of Vaporisation ΔH_v

The molar heat of vaporisation of liquid can be calculated if its vapour pressures at two different temperatures are known.

Example: Vapour pressures of water at 95 and 100 C are 634 and 760 mm, respectively. Calculate the molar heat of vaporisation, ΔH_v of water between 95 and 100 C.

Solution: Substituting the given data in Eq. 1.56, we have

$$\ln\frac{760\,\mathrm{mm}}{634\,\mathrm{mm}} = \frac{\Delta H_v}{8.314\,JK^{-1}\,\mathrm{mol}^{-1}}\left[\frac{373\,\mathrm{K}-368\,\mathrm{K}}{(368\,\mathrm{K})(373\,\mathrm{K})}\right]$$

$$\Delta H_v = 41363\ \mathrm{Jmol}^{-1}$$

Effect of Temperature on Vapour Pressure of a Liquid

If vapour pressure of a liquid at one temperature is known, that at another temperature can be calculated.

Example: The vapour pressure of water at 100 C is 760 mm. What will be the vapour pressure at 95 C? The heat of vaporisation of water in this temperature range is 41.27 kJ per mole.

Solution: Substituting the given data in Eq. 1.56, we have

$$\ln \frac{P_2}{760\,\text{mm}} = \frac{41.27 \times 10^3\,\text{J mol}^{-1}}{8.314\,\text{J K}^{-1}\,\text{mol}^{-1}} \left[\frac{368\,\text{K} - 373\,\text{K}}{(368\,\text{K})(373\,\text{K})} \right]$$

$$\therefore \qquad P_2 = 634.3\ \text{mm}$$

Effect of Pressure on Boiling Point

If the boiling point of a liquid at one pressure is known, that at another pressure can be calculated'.

Example: Ether boils at 33.5 C at one atmosphere pressure. At what temperature will it boil at a pressure of 750 mm, given that the heat of vaporisation of ether is 369.86 joules per gram.

Solution: Substituting the given data in Eq. 1.56, we have

$$\ln \frac{750\,\text{mm}}{760\,\text{mm}} = \frac{\left(369.86\,\text{J g}^{-1}\right)\left(74\,\text{g mol}^{-1}\right)}{8.314\,\text{J K}^{-1}\,\text{mol}^{-1}} \left[\frac{T_2 - 306.5\,\text{K}}{306.5\,K\left(T_2\right)} \right]$$

$$\therefore \qquad T_2 = 305.9\,\text{K} = 32.9\ \text{C}$$

The Clapeyron-Clausius Equation for Solid f Vapour Eqilibria

The Clapeyron-Clausius equation for solid f vapour equilibrium may be put as

$$\frac{dP}{dT} = \frac{\Delta H_s}{T\left(V_g - V_s\right)} \qquad \text{...1.57}$$

where ΔH_s stands for the *molar heat of sublimations* of the substance. Since the molar volume of a substance in the gaseous state is very much greater than that in the solid state, $V_g - V_s$ can be safely taken as V_g Eq.1.57 can thus be easily integrated, as before, to give the following expression:

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_s}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad ...1.58$$

Application of the Clapeyron-Clausius Equation for Solid = Liquid Equilibria

The Clapeyron-Clausius equation (1.52) for solid = liquid equilibrium cannot be integrated easily since V_s cannot be ignored in comparison with V_t. Also the laws of liquid state are not so simple as those for gaseous state. However, this equation can be used for calculating the effect of pressure on the melting point of a solid. Eq. 1.52 can also be used for calculating heats of fusion from vapour pressure data obtained at different temperatures.

Example: Calculate the value of dT/dP for the water = ice system at 0 C. ΔH_f for water is 6007.8 J mol^{-1} (1 J = 9.87 10^{-3}) dm^3 atm; molar volume of water = 18.00 cm^3; of ice 19.63 cm^3).

Solution: From the Clapeyron-Clausius equation (1.52),

$$\frac{dP}{dT} = \frac{\Delta H_f}{T_f\left(V_1 - V_2\right)}$$

$$V_t = 18.0\ cm^3\ mol^{-1} = 0.01800\ dm^3\ mol^{-1}$$

$$V_s = 19.63\ cm^3\ mol^{-1} = 0.01963\ dm^3\ mol^{-1}$$

$$1\ J = 9.87 \quad 10^{-3}\ atm\ (given)$$

$$\frac{dT}{dP} = \frac{T_f\left(V_1 - V_2\right)}{\Delta H_f}$$

$$= \frac{(273\,K)\left(0.01800\,dm^3\,mol^{-1} - 0.01963\,dm^3\,mol^{-1}\right)}{\left(6004.8\,J\,mol^{-1}\right)\left(9.87 \times 10^{-3}\,dm^3\,atm\,J^{-1}\right)}$$

$$= -\ 0.0075\ K\ atm^{-1}$$

Thus, the melting point of ice decreases by 0.0075 if pressure is increased.

2

Chemical Kinetics

Philosophy of Chemical Kinetics

Chemical kinetics constitutes an important topic in physical chemistry. It concerns itself with measurement of rates of reactions proceeding under given conditions of temperature, pressure and concentration. The study of this subject has been highly useful in determining the factor which influence rates of reactions as well in understanding mechanisms of a number of chemical reaction. The experimental data has led to the development of the modern theories of chemical reactivity of molecules. The studies have also been useful in working out conditions for getting maximum yields of several industrial products. A chemical reaction, as is well known, involves breaking of bonds in reacting molecules and formation of new bonds in product molecules. Since the number and nature of bonds are different in different substances, the rates of chemical reactions differ a lot from one another.

Thus, the reactions involving ions, such as precipitation reactions, are almost instantaneous. This is because in such reactions no bond are to be broken. The reactions involving organic molecule proceed slowly. This is because in such reactions a large number of bonds have to be broken in reactant molecules and a large number of bonds have to be formed in product molecules.

Thermodynamics predicts that at room temperature hydrogen and oxygen react to form water, all the reactants being essentially converted into the product. But when we actually carry out the experiment we find that the reaction takes place so slowly that unless we are willing to wait indefinitely, practically no water result. On the other hand, experiment shows that N_2O_4 decompose into NO_2 under atmospheric conditions almost instantaneously even though $-\Delta G$, which is a measure of the spontaneity of a reaction, is far less for the decomposition of N_2O_4 than that for the reaction between hydrogen and oxygen to form water. These two examples suggest that there is essentially no correlation between thermodynamics instability and rate of a chemical reaction. In fact, the rate of a reaction depends upon structure and energetic factors which are not uniquely specified by the thermodynamic quantities such as the free energy change. Hence, chemical kinetics is a technique complementary to thermodynamics for studying a given reaction.

You may be familiar with acid-base titration that use phenolphthalein as the endpoint indicator. You might not have noticed, however, what happens when a solution that contains phenolphthalein in the presence of excess base is allowed to stand for a few minutes. Although the solution initially has a pink colour, it gradually turns colourless as the phenolphthalein reacts with the OH⁻ ion in a strongly basic solution.

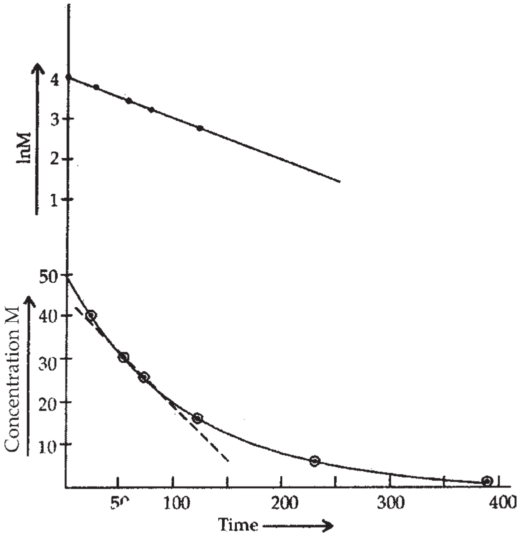


Fig. *Experimental data for the reaction between phenolphthalein and excess base.*

The following table shows what happens to the concentration of phenolphthalein in a solution that was initially 0.005 M in phenolphthalein and 0.61 M in OH^- ion. The phenolphthalein concentration decreases by a factor of 10 over a period of about four minutes.

Table

Time(s)	0	22	51	69	120	230	391
$\left[\begin{array}{l}\text{Phenolpthalein(M)}\\ \text{Moles lt}^{-1}\times 10^{-4}\end{array}\right.$	50	40	30	25	15	5	0.1
lnM	3.912	3.69	3.401	3.22	2.71	1.61	

Experiments such as the one that gave us the data in the above table are classified as measurements of chemical kinetics (from a Greek stem meaning "to move"). One of the goals of these experiments is to describe the rate of reaction — the rate at which the reactants are transformed into the products of the reaction.

The term *rate* is often used to describe the change in a quantity that occurs per unit of time. The rate of inflation, for example, is the change in the average cost of a collection of standard items per year. The rate at which an object travels through space is the distance travelled per unit of time, such as miles per hour or kilometres per second. In chemical kinetics, the distance travelled is the change in the concentration of one of the components of the reaction. The rate of a reaction is, therefore, the change in the concentration of one of the reactants $-\Delta(X)$ — that occurs during a given period of time $-\Delta t$.

$$\text{Rate of reaction} = \frac{\Delta X}{\Delta t}$$

Aspects of Reactions

The rate of the reaction between phenolphthalein and the OH^- ion isn't constant; it changes with time. Like most reactions, the rate of this reaction gradually decreases as the reactants are consumed. This means that the rate of reaction changes while it is being measured.

To minimise the error this introduces into our measurements, it seems advisable to measure the rate of reaction over a period of time that are short compared with the time it takes for the reaction to occur. We might try, for example, to measure the infinitesimally small change in concentration — d(X) — that occurs over an infinitesimally short period of time — *dt.* The ratio of these quantities is known as the instantaneous rate of reaction.

$$\text{Rate} = \frac{d(X)}{dt}$$

The instantaneous rate of reaction at any moment in time can be calculated from a graph of the concentration of the reactant (or product) versus time. The rate of reaction for the decomposition of phenolphthalein can be calculated from a graph of concentration versus time. The rate of reaction at any moment of time is equal to the slope of a tangent drawn at that moment.

The instantaneous rate of reaction can be measured at any time between the moment at which the reactants are mixed and the reaction reaches equilibrium. Extrapolating these data back to the instant at which the reagents are mixed gives the *initial instantaneous rate of reaction.*

Some Dimensions of Rate

An interesting result is obtained when the instantaneous rate of reaction is calculated at various points along the curve in the graph. The rate of reaction at every point on this curve is directly proportional to the concentration of phenolphthalein at that moment in time.

$$\text{Rate} = \text{k (phenolphthalein)}$$

Because this equation is an experimental law that describes the rate of the reaction, it is called the rate law for the reaction. The proportionality constant, *k,* is known as the rate constant.

Example: Calculate the rate constant for the reaction between phenolphthalein and the OH^- ion if the instantaneous rate of reaction is $2.5 \quad 10^{-5}$ mole per litre per second when the concentration of phenolphthalein is 0.0025.

***Solution*:** We start with the rate law for this reaction:

$$\text{Rate} = k \text{ (phenolphthalein)}$$

We then substitute the known rate of reaction and the known concentration of phenolphthalein into this equation to get rate constant

$$k = \text{Rate/phenolphthalein} = 2.5 \quad 10^{-5}/0.0025 = 0.01 \text{ s}^{-1}$$

***Example*:** Use the rate constant value from the above example for the reaction between phenolphthalein and the OH^- ion calculate the initial instantaneous rate of reaction for the experimental data.

***Solution*:** Substituting the rate constant for the reaction and the initial concentration of phenolphthalein rate of reaction can be calculated

Time (s)	0	22	51	69	120	230	391
Phenolpthalein (M) Moles lt^{-1} 10^{-4}	50	40	30	25	15	5	0.1
Rate 10^{-4}	0.5	0.4	0.3	0.25	0.15	0.05	0.001

Because the rate of reaction is the change in the concentration of phenolphthalein divided by the time over which the change occurs, it is reported in units of moles per litre per second. Because the number of moles of phenolphthalein per litre is the molarity of this solution, the rate can also be reported in terms of the change in molarity per second, *M/s.*

***Different Ways of Expressing the Rate of Reaction*:** There is usually more than one way to measure the rate of a reaction. We can study the decomposition of hydrogen iodide, for example, by measuring the rate at which either H_2 or I_2 is formed in the following reaction or the rate at which HI is consumed.

$$2\mathrm{HI}(g) \rightleftharpoons \mathrm{H}_2(g) + \mathrm{I}_2(g) \qquad ..(2.1)$$

Experimentally we find that the rate at which I_2 is formed is proportional to the square of the HI concentration at any moment in time.

$$\frac{d(I_2)}{dt} = k(HI)^2 \qquad ...(2.2)$$

What would happen if we studied the rate at which H_2 is formed? The balanced equation suggests that H_2 and I_2 must be formed at exactly the same rate.

$$\frac{d(H_2)}{dt} = \frac{d(I_2)}{dt}$$

What would happen, however, if we studied the rate at which HI is consumed in this reaction? Because HI is consumed, the change in its concentration must be a negative number. By convention, the rate of a reaction is always reported as a positive number. We therefore have to change the sign before reporting the rate of reaction for a reactant that is consumed in the reaction.

$$\frac{d(HI)}{dt} = K'(HI)^2 \qquad ...(2.3)$$

The negative sign does two things. Mathematically, it converts a negative change in the concentration of HI into a positive rate. Physically, it reminds us that the concentration of the reactant decreases with time.

What is the relationship between the rate of reaction obtained by monitoring the formation of H_2 or I_2 and the rate obtained by watching HI disappear? The stoichiometry of the reaction says that two HI molecules are consumed for every molecule of H_2 or I_2 produced. This means that the rate of decomposition of HI is twice as fast as the rate at which H_2 and I_2 are formed. We can translate this relationship into a mathematical equation as follows:

$$-\frac{d(HI)}{dt} = 2\left[\frac{d(H_2)}{dt}\right] = 2\left[\frac{d(I_2)}{dt}\right] \qquad ...(2.4)$$

As a result, the rate constant obtained from studying the rate at which H_2 and I_2 are formed in this reaction *(k)* is not the same as the rate constant obtained by monitoring the rate at which HI is consumed *(k′)*

***Example*:** Calculate the rate at which HI disappears in the following reaction at the moment when I_2 is being formed at a rate of 1.8 10^{-6} moles per litre per second:

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

Solution: The balanced equation for the reaction shows that 2 moles of HI disappear for every mole of I_2 formed. Thus, HI is consumed in this reaction twice as fast as I_2 is formed:

$$-\frac{d[HI]}{dt} = 2\frac{d[I_2]}{dt} = 2 \times 1.8 \times 10^{-6} = 3.6\,\text{moles}\,\text{lt}^{-1}\,\text{s}^{-1}$$

A Comparative Study

In the 1930s, Sir Christopher Ingold and co-workers at the University of London studied the kinetics of substitution reactions such as the following:

$$\mathrm{CH_3Br}(aq) + \mathrm{OH^-}(aq)\ f\quad \mathrm{CH_3OH}(aq) + \mathrm{Br^-}(aq)$$

They found that the rate of this reaction is proportional to the concentrations of both reactants.

$$\text{Rate} = k(CH_3Br)(OH^-) \qquad \text{...(2.5)}$$

When they ran a similar reaction on a slightly different starting material, they got similar products.

$$\mathrm{(CH_3)_3CBr(aq) + OH(aq)}\ f\quad \mathrm{(CH_3)_3COH(aq) + Br^{-}(aq)}$$

But now the rate of reaction was proportional to the concentration of only one of the reactants.

$$\text{Rate} = \mathrm{k[(CH_3)_3CBr]} \qquad \text{...(2.6)}$$

***These Results Illustrate an Important Point*:** The rate law for a reaction cannot be predicted from the stoichiometry of the reaction; it must be determined experimentally. Sometimes, the rate law is consistent with what we expect from the stoichiometry of the reaction.

$2\ \mathrm{HI(g)}\ f\quad \mathrm{H^2(g)} + I^2(g)\quad \text{Rate} = k[\mathrm{HI}]^2$

Often, however, it is not.

$\mathrm{2N_2O_5\ (g) \rightarrow 4NO_2(g)} + O_2(g)\quad \text{Rate} = \mathrm{k[N_2O_5]}$

Order and Molecularity

Some reactions occur in a single step. The reaction in which a chlorine atom is transferred from $\mathrm{ClNO_2}$ to NO to form $\mathrm{NO_2}$ and ClNO is a good example of a one-step reaction.

$\mathrm{ClNO_2(g)} + NO(g)\ f\quad \mathrm{NO_2(g) + ClNO(g)}$

Other reactions occur by a series of individual steps. $\mathrm{N_2O_5}$, for example, decomposes to $\mathrm{NO_2}$ and $\mathrm{O_2}$ by a three-step mechanism.

Step 1: $\mathrm{N_2O_5}\ f\quad \mathrm{NO_2 + NO_3}$

Step 2: $\mathrm{NO_2 + NO_3}\ f\quad \mathrm{NO_2 + NO + O_2}$

Step 3: $\mathrm{NO + NO_3}\ f\quad \mathrm{2\ NO_2}$

The steps in a reaction are classified in terms of molecularity, which describes the number of molecules consumed. When a single molecule is consumed, the step is called unimolecular. When two molecules are consumed, it is bimolecular.

Example: Determine the molecularity of each step in the reaction by which N_2O_5 decomposes to NO_2 and O_2.

Solution: All we have to do is count the number of molecules consumed in each step in this reaction to decide that the first step is unimolecular and the other two steps are bimolecular

Step 1: $N_2O_5\ f\ NO_2 + NO_3$

Step 2: $NO_2 + NO_3\ f\ NO_2 + NO + O_2$

Step 3: $NO + NO_3\ f\ NO_2$

Reactions can also be classified in terms of their order. The decomposition of N_2O_5 is a first-order reaction because the rate of reaction depends on the concentration of N_2O_5 raised to the first power.

$$\text{Rate} = k\,[N_2O_5]$$

The decomposition of HI is a second-order reaction because the rate of reaction depends on the concentration of HI raised to the second power.

$$\text{Rate} = \text{k}\ [HI]^2$$

When the rate of a reaction depends on more than one reagent, we classify the reaction in terms of the order of each reagent.

Order of the reaction between NO and O_2 to form NO_2 has the following rate law:

$$\text{Rate} = k\,[NO]^2[O_2]$$

This reaction is first-order in O_2, second-order in NO, and third-order overall.

The difference between the molecularity and the order of a reaction is important. The molecularity of a reaction, or a step within a reaction, describes what happens on the molecular level. The order of a reaction describes what happens on the macroscopic scale. We determine the order of a reaction by watching the products of a reaction appear or the reactants disappear. The molecularity of the reaction is something we deduce to explain these experimental results.

Role of Collision Theory Model

The collision theory model of chemical reactions can be used to explain the observed rate laws for both one-step and multi-step reactions. This model assumes that the rate of any step in a reaction depends on the frequency of collisions between the particles involved in that step.

The figure below provides a basis for understanding the implications of the collision theory model for simple, one-step reactions, such as the following:

$ClNO_2$(g) + NO*(g) f* NO_2(g) + ClNO(g)

The kinetic molecular theory assumes that the number of collisions per second in a gas depends on the number of particles per litre. The rate at which NO_2 and ClNO are formed in this reaction should, therefore, be directly proportional to the concentrations of both $ClNO_2$ and NO.

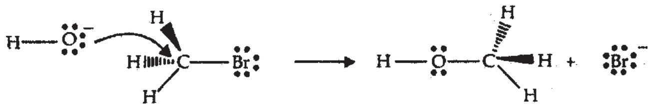
$$\text{Rate} = k\,[ClNO_2][NO]$$

The collision theory model suggests that the rate of any step in a reaction is proportional to the concentrations of the reagents consumed in that step. The rate law for a one-step reaction should, therefore, agree with the stoichiometry of the reaction.

The following reaction, for example, occurs in a single step.

CH_3Br(aq) + OH^-*(aq) f* CH_3OH(aq) + Br^- *(aq)*

When these molecules collide in the proper orientation, a pair of non-bonding electrons on the OH^- ion can be donated to the carbon atom at the centre of the CH_3Br molecule, as shown in the figure below:

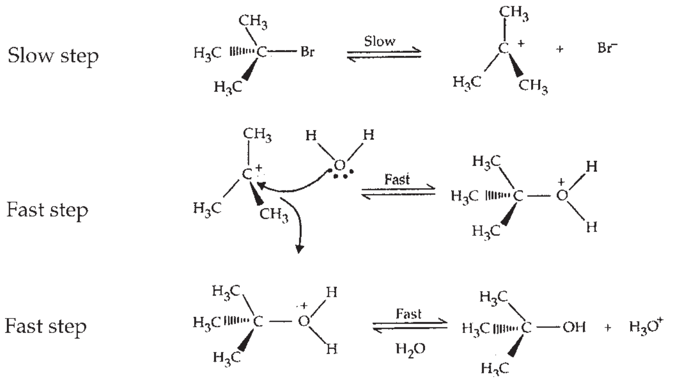


When this happens, a carbon-oxygen bond forms at the same time that the carbon-bromine bond is broken. The net result of this reaction is the substitution of an OH^- ion for a Br^- ion. Because the reaction occurs in a single step, which involves collisions between the two reactants, the rate of this reaction is proportional to the concentration of both reactants.

$$\text{Rate} = k[CH_3Br][OH^-]$$

Not all reactions occur in a single step. The following reaction occurs in three steps, as shown in the figure below.

$$(CH_3)_3CBr(aq) + OH^-(aq) \rightleftharpoons (CH_3)_3COH(aq) + Br^-(aq)$$



The overall rate of reaction is, therefore, more or less equal to the rate of the first step. The first step is, therefore, called the rate-limiting step in this reaction because it literally limits the rate at which the products of the reaction can be formed. Because only one reagent is involved in the rate-limiting step, the overall rate of reaction is proportional to the concentration of only this reagent.

$$\text{Rate} = k[(CH_3)_3CBr]$$

The rate law for this reaction, therefore, differs from what we would predict from the stoichiometry of the reaction. Although the reaction consumes both $(CH_3)_3CBr$ and OH^-, the rate of the reaction is only proportional to the concentration of $(CH_3)_3CBr$.

The rate, laws for chemical reactions can be explained by the following general rules.

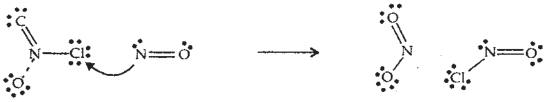
- The rate of any step in a reaction is directly proportional to the concentrations of the reagents consumed in that step.
- The overall rate law for a reaction is determined by the sequence of steps, or the mechanism, by which the reactants are converted into the products of the reaction.
- The overall rate law for a reaction is dominated by the rate law for the slowest step in the reaction.

***The Activation Energy of Chemical Reactions*:** Only a small fraction of the collisions between reactant molecules convert the reactants into the products of the reaction. This can be understood by turning, once again, to the reaction between $ClNO_2$ and NO.

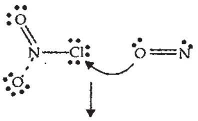
$$ClNO_2(g) + NO(g) \; f \; NO_2(g) + ClNO(g)$$

In the course of this reaction, a chlorine atom is transferred from one nitrogen atom to another. In order for the reaction to occur, the nitrogen atom in NO must collide with the chlorine atom in $ClNO_2$.

Orientation 1

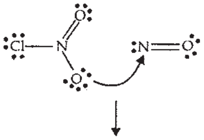


Orientation 2



No reaction

Orientation 3



No reaction

Every chemical reaction results in the breaking of some bonds (needing energy) or making of new ones (releasing energy). Obviously some bonds have to be broken before new ones can be made. Activation energy is involved in breaking some of the original bonds. For a reaction to take place, particles must collide with energies equal to or greater than the activation energy for the reaction. Only a small proportion of molecules have energies equal to or greater than the activation energy, as is shown in the following figure, the hatched part. Since different reactions have different proportion of molecules having activation energy, hence rates of reaction will be different.

The overall standard free energy for the reaction between $ClNO_2$ and NO is favourable.

$$ClNO_2(g) + NO(g) \;\; f \;\; NO_2(g) + ClNO(g)$$

$$\Delta G = -23.6 \text{ KJ/mol}$$

But, before the reactants can be converted into products, the free energy of the system must overcome the activation energy for the reaction. The vertical axis in this diagram represents the free energy of a pair of molecules as a chlorine atom is transferred from one to the other. The horizontal axis represents the sequence of infinitesimally small changes that must occur to convert the reactants into the products of this reaction.

To understand why reactions have an activation energy, consider what has to happen in order for $ClNO_2$ to react with NO.

First, and foremost, these two molecules have to collide, thereby organising the system. Not only do they have to be brought together, they have to be held in exactly the right orientation relative to each other to ensure that reaction can occur. Both of these factors raise the free energy of the system by lowering the entropy. Some energy also must be invested to begin breaking the Cl–NO_2 bond so that the Cl–NO bond can form.

NO and $ClNO_2$ molecules that collide in the correct orientation, with enough kinetic energy to climb the activation energy barrier, can react to form NO_2 and ClNO. As the temperature of the system increases, the number of molecules that carry enough energy to react when they collide also increases. The rate of reaction therefore increases with temperature. As a rule, the rate of a reaction doubles for every 10 C increase in the temperature of the system.

The symbol used to represent the activation energy is written with a capital *"E_a"*. This is unfortunate, because it leads students to believe the activation energy is the change in the internal energy of the system, which is not quite true. E_a measures the change in the potential energy of a pair of molecules that is required to begin the process of converting a pair of reactant molecules into a pair of product molecules.

Reaction won't occur if the oxygen end of the NO molecule collides with the chlorine atom on $ClNO_2$ Orientation 2. Nor will it occur if one of the oxygen atom on $ClNO_2$ collides with nitrogen atom on NO (Orientation 3).

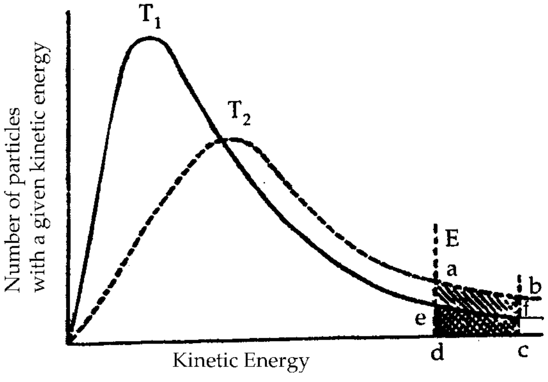
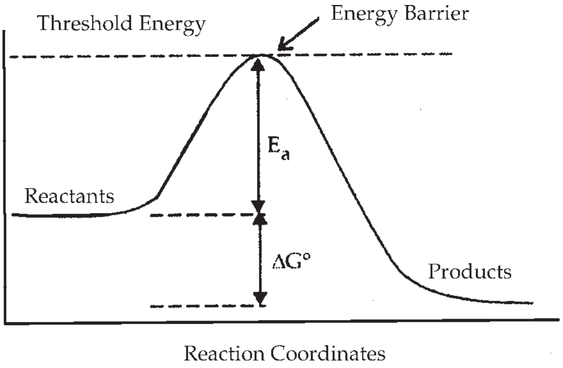


***Fig.** Energy distribution in molecules at two different temperatures.*

Another factor that influences whether reaction will occur is the energy the molecules carry when they collide. In any system, the molecules present will have a very wide range of energies. For gases, Maxwell-Boltzmann distribution can represent this, as shown in the figure above. This is important because the kinetic energy of molecules carry when they collide is the principal source of the energy that must be invested in a reaction to get it started. Even if the molecules are oriented properly each collision would not lead to a reaction unless the molecules collide with a certain minimum energy called the activation energy of the reaction. Activation energy is the minimum energy required before a reaction can occur. This can be shown on a energy profile for the reaction. For a simple overall exothermic reaction, the energy profile is shown in the following figure. If the molecules collide with less energy than the activation energy, nothing important happens. They bounce apart. One can think of the activation energy as a barrier to the reaction. Only those collisions which have energies equal to or greater than the activation energy result in a reaction.



Rates of Chemical Reactions: Catalysts

Aqueous solutions of hydrogen peroxide are stable until we add a small quantity of the I^- ion, a piece of platinum metal, a few drops of blood, or a freshly cut slice of turnip, at which point the hydrogen peroxide rapidly decomposes.

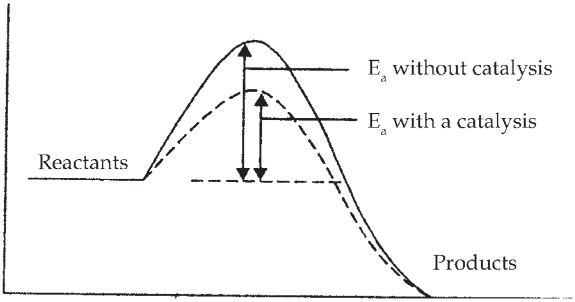
$$2H_2O_2(aq)\ f\ \ 2H_2O(aq) + O_2(g)$$

This reaction, therefore, provides the basis for understanding the effect of a catalyst on the rate of a chemical reaction. Four criteria must be satisfied in order for something to be classified as catalyst.

- Catalysts increase the rate of reaction.
- Catalysts are not consumed by the reaction.
- A small quantity of catalyst should be able to affect the rate of reaction for a large amount of reactant.
- Catalysts do not change the equilibrium constant for the reaction.

The first criterion provides the basis for defining a catalyst as something that increases the rate of a reaction. The second reflects the fact that anything consumed in the reaction is a reactant, not a catalyst. The third criterion is a consequence of the second, because catalysts are not consumed in the reaction, they can catalyse the reaction over and over again. The fourth criterion results from the fact that catalysts speed up the rates of the forward and reverse reactions equally, so the equilibrium constant for the reaction remains the same.

Catalysts increase the rates of reactions by providing a new mechanism that has a smaller activation energy. A larger proportion of the collisions that occur between reactants now have enough energy to overcome the activation energy for the reaction. As a result, the rate of reaction increases.



Reaction Coordinate

To illustrate how a catalyst can decrease the activation energy for a reaction by providing another pathway for the reaction, let's look at the mechanism for the decomposition of hydrogen peroxide catalysed by the I^- ion. In the presence of this ion, the decomposition of H_2O_2 doesn't have to occur in a single step. It can occur in two steps, both of which are easier and therefore faster. In the first step, the I^- ion is oxidised by H_2O_2 to form the hypoiodite ion, OI^-.

$$H_2O_2\ (aq) + I^-\ (aq) \rightarrow H_2O\ (aq) + OI^-\ (aq) \qquad ...(2.7)$$

In the second step, the OI^- ion is reduced to I^- by H_2O_2.

$$OI^-\ (aq) + H_2O_2\ (aq) \rightarrow H_2O\ (aq) + O_2(g) + I^-\ (aq)$$

Because there is no net change in the concentration of the I^- ion as a result of these reactions, the I^- ion satisfies the criteria for a catalyst. Because H_2O_2 and I^- are both involved in the first step in this reaction, and the first step in this reaction is the rate-limiting step, the overall rate of reaction is first-order in both reagents.

***Determining the Activation Energy of a Reaction*:** The rate of a reaction depends on the temperature at which it is run. As the temperature increases, the molecules move faster and therefore collide more frequently. The molecules also carry more kinetic energy. Thus, the proportion of collisions that can overcome the activation energy for the reaction increases with temperature.

The only way to explain the relationship between temperature and the rate of a reaction is to assume that the rate constant depends on the temperature at which the reaction is run. In 1889, Svante Arrhenius showed that the relationship between temperature and the rate constant for a reaction obeyed the following equation.

$$k = Ae^{-E_a/RT} \qquad ...(2.8)$$

In this equation, k is the rate constant for the reaction, A is a proportionality constant that varies from one reaction to another, E_a is the activation energy for the reaction, R is the ideal gas constant in joules per mole kelvin, and T is the temperature in kelvin.

The Arrhenius equation can be used to determine the activation energy for a reaction. We start by taking the natural logarithm on both sides of the equation.

$$\text{In } k = \ln \text{A} - \frac{E_a}{RT} \qquad ...(2.9)$$

According to this equation, a plot of ln *k* versus 1/T should give a straight line with a slope of $-E_a/R$. The Arrhenius equation can also be used to calculate what happens to the rate of a reaction when a catalyst lowers the activation energy.

Rate Expressions and Mixing

***Integration of Rate Expression for First-Order Reactions*:** The differential rate expression for the first-order reaction, A → P is given by

$$r = -\frac{d[A]}{dt} = \frac{d[P]}{dt} = k[A] \qquad ...(2.10)$$

Separating the variables, *i.e.,* bringing concentration terms on one side and the time on the other side, we get

$$-d[A]/[A] = k_1 dt$$

Replacing [A] by c_A for the sake of notational convenience, we have

$$-dc_A/c_A = k_1 dt$$

Before performing the actual integration, let us first ascertain the limits of integration. Let the initial concentration at initial time $t = 0$ be c_0. Subsequently, at any other time, *t,* the concentration will be *c.* On integration, we obtain

$$\int_{c_0}^{c} -dc_A / c_A = k_1 \int_0^t dt$$

$$[-\ln c]_{c_0}^{c} = k_1 [t]_0^t$$

$$-\ln(c/c_0) = k_1 t$$

$$c = c_0 e^{-k_1 t} \qquad ...(2.11)$$

From Eq. 2.11 we can also write

$$k_1 = \frac{1}{t} \ln \frac{c_0}{c} \qquad ...(2.12)$$

Eq. 2.12 gives the expression for *the first-order rate constant,* k_v Eq. 2.12 is usually written in another form. If initial concentration of the reactant is *a* and *x* moles of it react in time *I,* then the concentration of the reactant left behind at time *t* will be *(a – x).* In such a case, $c_0 \propto a$ and $c \propto (a - x)$. Hence, Eq. 2.9 takes the form

$$K_1 = \frac{1}{t}\ln\frac{a}{a-x} \qquad \text{...(2.12(a))}$$

Eq. 2.12 shows that the concentration of a first-order reaction decreases exponentially with time.

***Example*:** Show diagrammatically how the rate of a first-order reaction varies with concentration of reactant.

Solution: For a first-order reaction, $r = k_1[A]$.

Hence the plot of rate versus [A] is a straight line passing through the origin, as shown in the following figure.

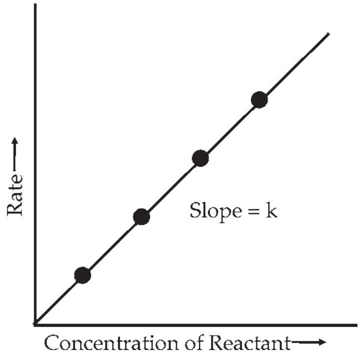


Fig. *The plot of rate versus reactant concentration for a first-order reaction*

The student should bear in mind that though Eq. 2.12 a is easy to remember and use in simple numerical problems, it has to be expressed in appropriate form in certain decomposition reactions before the rate constants of those reactions can be determined. This is illustrated in various examples given below.

***Example*:** Nitrous oxide, N_2O, decomposes into N_2 and O_2, the reactants and the products being all gaseous, (This is an example of a homogeneous gaseous reaction). If the reaction is first-order, develop expression for the rate constant as a function of time, initial pressure and the total pressure.

Solution: $N_2O\ (g) \rightarrow N_2(g) + 1/2O_2\ (g)$

Let the initial pressure of N_2O be P_i. If x is the decrease in pressure after time t then

$$P_{N_2O} = P_i - x; \quad P_{N_2} = x\,P_{O_2} = x/2$$

According to Dalton's law of partial pressures, the total pressure of the system at time *t* is given by

$$P = P_{N_2O} + P_{N_2} + P_{O_2}$$

$$= (P_i - x) + x + x/2 = P_i + x/2$$

Hence

$$x = 2(P - P_i)$$

$$P_{N_2O} = P_i - x = P_1 - 2(P_i - P) = 3P_i - 2P$$

Evidently, in the first-order rate equation (Eq. 2.12) applied here, $a \propto P_i$ Hence,

$$k_1 = \frac{1}{t} \ln \frac{P_i}{3P_i - 2P}$$

Example: The gas-phase thermal decomposition of one mole of di-tert-butyl peroxide, in a constant volume apparatus, yields two moles of acetone and one mole of ethane. If lite reaction obeys first-order kinetics, develop expression the rate-constant as a function of time, initial pressure and total pressure.

***Solution*:** Stoichiometrically, we have

$(CH_3)_3C - O - C(CH_3)_3 \rightarrow 2(CH_3)_2C = O + C_2H_6$

Let the initial pressure of the peroxide be P_r. If *x* is the decrease in pressure after time *t,* then the pressure of the peroxide at time *t* is $(P_i - x)$, that of acetone is 2*x* and that of ethane is *x.* Hence, from Dalton's law of partial pressures, the total pressure is given by

$$P = (P_i - x) + 2x + x = P_i + 2x$$

or $$x = (P - P_i)/2$$

The pressure of peroxide = $P_i - x = P_i - \dfrac{P - P_i}{2} = (3P_i - P)/2$

Hence, $k_1 = \dfrac{1}{t} \ln \dfrac{a}{a - x} = \dfrac{1}{t} \ln \dfrac{P_i}{(3P_i - P)/2}$

$$= \frac{1}{t} \ln \frac{2P_i}{(3P_i - P)}$$

***Example*:** From the following data show that the decomposition of hydrogen peroxide in aqueous solution is a first-order reaction. What is the value of the rate constant?

Time in minutes	0	10	20	30	40
N	5.0	20.0	15.7	12.5	9.6

where N is volume in ml of potassium permanganate required to decompose a definite volume of hydrogen peroxide solution.

Solution: The equation for a first-order reaction is

$$k_1 = \frac{1}{x}\ln\frac{a}{a-x}$$

The volume of $KMnO_4$ used, evidently, corresponds to the undecomposed hydrogen peroxide. Hence, the volume of $KMnO_4$ used at zero time corresponds to the initial concentration *a* and the volume used after time *t*, corresponds to (a – *x)* at that time. Inserting these values in the above equation, we get

When $t = 10$ min, $\frac{1}{10}\ln\frac{25}{20.0} = 0.022287\ \text{min}^{-1} = 0.0003140\ \text{s}^{-1}$

When $t = 20$ min, $k_1 = \frac{1}{20}\ln\frac{25}{15.7} = 0.023230\ \text{min}^{-1} = 0.0003871\ \text{s}^{-1}$

When $t = 30$ min, $k_1 = \frac{1}{30}\ln\frac{25}{12.5} = 0.023690\ \text{min}^{-1} = 0.0003848\ \text{s}^{-1}$

When $t = 40$ min, $k_1 = \frac{1}{40}\ln\frac{25}{9.6} = 0.023897\ \text{min}^{-1} = 0.0003983\ \text{s}^{-1}$

The constancy of k_1 shows that the decomposition of H_2O_2 in aqueous solution is a first-order reaction.

The average value of the rate constant is $0.0003879\ \text{s}^{-1}$

Example: From the following data for the decomposition of ammonium nitrite in aqueous solution, show that the reaction is first-order.

Time (minutes)	10	15	20	15	∞
Volume of N_2 (c.c.)	6.25	9.0	11.40	13.65	35.05

Solution: For this reaction,

$$k_1 = \frac{1}{t}\ln\frac{V_\infty}{V_\infty - V_r}$$

$$V_\infty = 35.05 = a$$

The values of k_1, at different times are obtained is below:

Time	$V_\infty - V_t$	$\frac{1}{t}\ln\frac{V_\infty}{V_\infty - V_t} = k_t$
10 min	$35.05 - 6.25 = 28.80$	$\frac{1}{10}\ln\frac{35.05}{28.80} = 0.01976\,\text{min}^{-1}$
15 min	$35.05 - 9.00 = 26.05$	$\frac{1}{15}\ln\frac{35.05}{26.05} = 0.01976\,\text{min}^{-1}$
20 min	$35.05 - 11.40 = 23.65$	$\frac{1}{20}\ln\frac{35.05}{23.65} = 0.01964\,\text{min}^{-1}$
25 min	$35.05 - 13.65 = 21.40$	$\frac{1}{25}\ln\frac{35.05}{21.40} = 0.01971\,\text{min}^{-1}$

A constant value of k_1 shows that the reaction is first-order.

Examples: 5 ml of ethyl acetate was added to a flask containing 100 ml of 0.1 M HCl placed in a thermostat maintained at 30 C. 5 ml of the reaction mixture was withdrawn at different intervals of time and after chilling, titrated against a standard alkali. The following data were obtained:

Time (minutes)	0	75	119	183	∞
ml of alkali used	9.62	12.10	13.10	14.75	21.05

From the above data show that the hydrolysis of ethyl acetate is a first-order reaction.

***Solution*:** The hydrolysis of ethyl acetate will be first-order reaction if the above data conform to the equation

$$k_1 = \frac{1}{t}\ln\frac{V_\infty - V_0}{V_\infty - V_t}$$

where V_0 V_t and V_∞ represent the volumes of alkali used at the commencement of the reaction, after time *t* and at the end of the reaction, respectively. Hence,

$$V_\infty - V_o = 21.05 - 962 = 11.43$$

The values of k_1 at different times are obtained as follows:

Time	$V_\infty - V_t$	$\frac{1}{t}\ln\frac{V_\infty - V_0}{V_\infty - V_t} = k_1$

75 min	21.05 – 12.10 = 8.95	$\frac{1}{75}\ln\frac{11.43}{8.95} = 0.03159\,\text{min}^{-1}$
119 min	21.05 – 13.10 = 7.95	$\frac{1}{119}\ln\frac{11.43}{7.95} = 0.003264\,\text{min}^{-1}$
183 min	21.05 – 14.75 = 6.30	$\frac{1}{183}\ln\frac{11.43}{6.30} = 0.003254\,\text{min}^{-1}$

A constant value of k_1 shows that the hydrolysis of ethyl acetate is a first-order reaction.

Example: The optical rotations of sucrose in 0.5 M HCl at 35 C at various time intervals are given below. Show that the reaction is first-order:

Time (minutes)	0	10	20	30	40	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	–11.1

Solution: The inversion of sucrose will be a first-order reaction if the above data conform to the equation

$$k_1 = \frac{1}{t}\ln\frac{r_0 - r_\infty}{r_t - r_\infty}$$

where r_0 r_t and r_∞ represent optical rotations at the commencement of the reaction, after time and at the completion of the reaction, respectively.

In this case $a_0 = r_0 - r_\infty = +32.4 - (-11.1) = +43.5$

The value of k_1 at different times are calculated as follows:

Time	r_t	$r_t - r_\infty$	$\frac{1}{t}\ln\frac{r_\infty - r_0}{r_\infty - r_t} = k_1$
10 min	+28.8	39.9	$\frac{1}{10}\ln\frac{43.5}{39.9} = 0.008625\,\text{min}^{-1}$
20 min	+ 25.5	*36.6*	$\frac{1}{20}\ln\frac{43.5}{36.6} = 0.008625\,\text{min}^{-1}$
30 min	+22.4	*33.5*	$\frac{1}{30}\ln\frac{43.5}{33.5} = 0.008694\,\text{min}^{-1}$
40 min	+ 19.6	30.7	$\frac{1}{40}\ln\frac{43.5}{30.7} = 0.008717\,\text{min}^{-1}$

The constant of k_1 indicates that the inversion of sucrose is a first-order reaction.

Example: During decomposition of N_2O_5 dissolved in carbon tetrachloride at 35 C, the following results were obtained. Show that the reaction is first-order.

Time (min)	0	40	80	100	160	240	∞
Volume of oxygen collected at constant pressure (c.c.)	0	15.6	27.6	7.7	45.8	58.3	84.6

Solution: The rate equation for the first-order reaction is

$$k_1 = \frac{1}{t} \ln \frac{a}{a-x} \qquad \text{...(cf. Eq. 2.12 } a\text{)}$$

The initial concentration of N_2O_5 in the solution = 84.6 – 0 = 84.6, *i.e.*, a = 84.6

The values of $(a - x)$ at different intervals of time are:

Time (min), t	40	80	120	160	240
a – x	69.0	57.0	46.9	36.8	26.3

Incorporating the values of t, a and $(a - x)$ in Eq. 2.12 *a* the values of k_1 at different time intervals come out to be as follows:

Time (min)	40	80	120	160	240
k_1 *per min*	5.03 10^{-3}	4.94 10^{-3}	4.92 10^{-3}	5.20 10^{-3}	4.87 10^{-3}

Since k_1 is fairly constant, the reaction is first-order

Example: The following data are obtained for the hydrolysis of benzene diazonium chloride: $C_6H_5N = N - Cl + H_2O \rightarrow C_6H_5OH + HCl + N_2(g)$:

Time (min)	0	2	8	16	24	50	∞
Pressure (p) of N_2 at constant volume (arbitrary units)	0	1.6	6.2	11.2	15.5	24.4	34.0

Assuming first-order kinetics, calculate the rate constant.

Solution: In this case, evidently, $a \infty (p_\infty - p_0) \propto 34.0$ and $(a - x) \propto (p_\infty - p_t)$

Time (min), t	2	8	16	24	50
(a – x)	32.4	27.8	22.8	18.5	9.6

$$k_1 = \frac{1}{t} \ln \frac{a}{a-x} \qquad \text{...(cf. Eq. 2.12}a\text{)}$$

Incorporating the various values of t, a and $a - x$, in Eq. 2.12 a, we get the following values of k_1 at different intervals of time:

Time (min)	2	8	16	24	50
k_v per min	2.41 10^{-2}	2.52 10^{-2}	2.50 10^{-2}	2.53 10^{-2}	2.53 10^{-2}

The average value of rate constant thus comes out to be 2.498 10^{-2} min^{-1}.

Integration of Rate Expression for Second-order Reactions

***Case (i) When the Reactants are Different*:** Consider a second-order reaction

$$A + B \rightarrow P$$

where the initial concentration of A is a mol dm^{-3} and that of B is b mol dm^{-3}. After a time t, x mol dm^{-3} of A and x mol dm^{-3} of B react to form x mol dm^{-3} of the product. Thus, the reactant concentrations at time t are $(a - x)$ and $(b - x)$, respectively. The differential rate expression for the second-order reaction is evidently,

$$r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[P]}{dt} = k_2 [A][B]$$

This can be written as

$$r = dx/dt = k_2(a - x)\,(b - x) \qquad \text{...(2.13)}$$

where k_2 is the *second-order rate constant.* Separating the variables, we have

$$\frac{dx}{(a-x)(b-x)} = k_2\,dt \qquad \text{...(2.14)}$$

Resolving into partial fractions (assuming that $a > b$) we have

$$\frac{1}{(a-x)(b-x)} = \frac{1}{a-b}\left[\frac{1}{b-x} - \frac{1}{a-x}\right] \qquad \text{...(2.15)}$$

Using this result we can integrate Eq. 2.15 as follows:

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{a-b}\left[\int \frac{dx}{b-x} - \int \frac{dx}{a-x}\right] = k_2 \int dt \qquad \text{...(2.16)}$$

We have taken the factor *l/(a – b)* outside the integral sign because this quantity is a constant.

Carrying out the integration, we have

$$\frac{1}{a-b}\left[-\ln(b-x)-\{-\ln(a-x)\}\right] = k_2 t+C$$

or $$\frac{1}{a-b}\ln\left[\frac{a-x}{b-x}\right] = k_2 t+C \qquad \text{...(2.17)}$$

where C is the constant of integration. To determine it, we recall that at $t = 0$, $x = 0$. Hence, from Eq. 2.17

$$C = \frac{1}{a-b}\ln\left(\frac{a}{b}\right) \qquad \text{...(2.18)}$$

Substituting this value of C in Eq. 2.17 we have

$$\frac{1}{a-b}\ln\left(\frac{a-x}{b-x}\right) = k_2 t+\frac{1}{a-b}\ln\left(\frac{a}{b}\right)$$

Rearranging and solving for k_2, we get

$$k_2 = \frac{1}{(a-b)t}\left[\ln\left(\frac{a-x}{b-x}\right)-\ln\left(\frac{a}{b}\right)\right]$$

$$k_2 = \frac{1}{(a-b)t}\ln\frac{b(a-x)}{a(b-x)} \qquad \text{...(2.19)}$$

Eq. 2.19 is the required integrated expression for the rate constant of a second-order reaction. Here we have assumed that *a>b.* If we had assumed that *b > a,* then the reader can easily verify that

$$k_2 = \frac{1}{(b-a)^t}\ln\frac{a(b-x)}{b(a-x)} \qquad \text{...(2.20)}$$

It can be easily seen that neither Eq. 2.19 nor Eq. 2.20 applicable when the concentrations of both the reactants are the same, *i.e.,* when *a = b.* If we write Eq. 2.19 in the form

$$\frac{1}{(b-a)}\ln\frac{b(a-x)}{a(b-x)} = k_2^t \qquad \text{...(2.21)}$$

we see that it is the equation of a straight line, passing through the origin *(viz., y = mx),* where

$$y \equiv \frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)}; m \equiv k_2; x = t$$

The plot of the left-hand side of Eq. 2.21 versus t gives a straight line whose slope is equal to the rate constant, k_2.

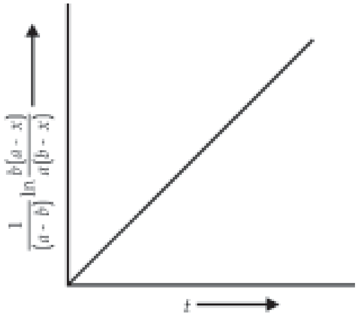


Fig. *Evaluation of rate constant for a second-order reaction*

Case (ii) When both the Reactants are the same: In effect it means that two molecules of the same reactant are involved in chemical reaction. The second-order reaction in this case would be represented as

$$2A \rightarrow P$$

and the rate of the reaction would be expressed as

$$r = dx/dt = k_2(a-x)^2 \qquad \text{...(2.22)}$$

where, as before a is the initial concentration of A, x is the concentration of the product formed after time t and $(a - x)$ is the concentration of A remaining at time t.

Separating the variables and integrating, we have

$$\int \frac{dx}{(a-x)^2} = k_2 dt \qquad \text{...(2.23)}$$

$$\left(-\frac{1}{a-x}\right)(-1) = k_2 t + C$$

$$\text{or} \quad \frac{1}{a-x} = k_2 t + C \qquad \text{...(2.24)}$$

To determine the integration constant C, we recall that at $t = 0$, $x = 0$ so that $C = 1/a$. Hence,

$$\frac{1}{a-x} = k_2 t + \frac{1}{a}$$

Transposing and solving for k_2, we get

$$k_2 = \frac{1}{t}\left[\frac{1}{a-x} - \frac{1}{a}\right] \qquad ...(2.25)$$

or $$k_2 = \frac{1}{t}\left(\frac{x}{a(a-x)}\right) \qquad ...(2.26)$$

which is the required integrated expression for the rate constant of a second-order reaction in which two molecules of the same reactant are involved in the reaction.

The classic example of the above type of the second-order reaction is the gaseous decomposition of hydrogen iodide.

$$2HI\ (g) \rightarrow H_2\ (g) + I_2\ (s)$$

The rate expression for this reaction is

$$r = -d[HI]/dt = k_2[HI]^2$$

The rate constants of second-order reactions in which the two reactants, although different, have the same initial concentration, are also determined with the help of Eq. 2.26.

Example: The reaction between triethylamine and methyl iodide in nitrobenzene solvent

$$(C_2H_5)_3N + CH_3I \xrightarrow{C_6H_5NO_2} (C_2H_5)_3[NCH_3]^+ I^-$$

was studied kinetically at 25 C. The following data were obtained:

t (s)	***x (mol dm^{-3})***
1,200	0.00876
1,800	0.01066
2,400	0.01208
3,600	0.01392
5,400	0.01538

Here x is the concentration in mol dm^{-3} of $(C_2H_5)_3N$ or CH_3I reacted at time t. The initial concentrations of both the reactants were 0.0198 mol dm^{-3} each. Assuming that the reaction is second-order, calculate the rate constant.

Solution: According to the data given above, a = 0.0198 mol dm^{-3} and at t = 1200 s, x = 0.00876 mol dm^{-3}. Hence, from Eq. 2.26,

$$\therefore \qquad k_2 = \frac{1 \times 0.00876\,\text{mol}\,\text{dm}^{-3}}{1200\,\text{s} \times 0.0198\,\text{mol}\,\text{dm}^{-3}\,(0.0198 - 0.00876)\,\text{mol}\,\text{dm}^{-3}}$$

$$= 0.0334\ \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$$

We can similarly calculate k_2 for the other given values of t and x and tabulate the result as follows:

t (s)	***x (mol dm^{-1})***	***k_2 (dm^3 mol^{-1} s^{-1})***
1,200	0.00876	0.0334
1,800	0.01066	0.0327
2,400	0.01208	0.0329
3,600	0.01392	0.0332
5,400	0.01538	0.0325

As can be seen the k_2 values are fairly constant. The average value of k_2 is 0.0329 dm^3 mol^{-1} s^{-1}.

Example: The following results were obtained for the saponification of ethyl acetate

$\left(CH_3COOC_2H_5 + NaOH \rightarrow CH_3COOH + C_2H_5OH\right)$ using equal concentrations of ester and alkali:

t (minutes)	0	4.89	10.07	23.66	∞
ml of acid used	47.65	38.92	32.63	22.58	11.84

Show that the reaction is second-order.

Solution: The equation for the second-order reactions, using equivalent concentrations of the reactants, is

$$k_2 = \frac{1}{t}\left(\frac{x}{a(a-x)}\right) \qquad \text{...(cf Eq. 2.26)}$$

In the saponification of ethyl acetate, the volume of the acid used corresponds to the amount of unused sodium hydroxide. Therefore, the volume of acid used at zero time, *i.e.,* at the commencement of the reaction, corresponds to the initial concentration *a* and the volume used after time *t* corresponds to *(a − x)* at that time.

In the present case, $a = 47.65$

The value of k_2 is calculated as follows:

t	$a - x$	x	$\frac{1}{t}\left(\frac{x}{a(a-x)}\right) = k_2\left(\text{dm}^3\ \text{mol}^{-1}\ \text{min}\right)$
4.89	38.92	8.73	$\frac{1}{4.89} \times \frac{8.73}{7.65 \times 38.92} = 0.000962$
10.07	32.62	15.03	$\frac{1}{10.07} \times \frac{15.03}{47.65 \times 32.62} = 0.000960$
23.66	22.58	25.07	$\frac{1}{23.66} \times \frac{25.07}{47.65 \times 22.58} = 0.000983$

A fairly constant value of k_2 indicates that the reaction is second-order.

For the second order reaction A + 3B → P, where P stands for products in differential rate equation is

$$\frac{dx}{dt} = k_2(a-x)(b-3x)$$

which on integration gives

$$k_2 t = \frac{1}{(3a-b)} \ln\left[\frac{b(a-x)}{a(b-3x)}\right]$$

Integration of Rate Expression for Third-order Reactions

Let us consider a third-order reaction of the type

$3A \rightarrow P$

Let *a* be the initial concentration of A and *x* the amount of A that has reacted at time *t* so that the amount of A remaining at time *t* is *a* − *x*. The differential rate equation is

$$r = \frac{dx}{dt} = k_3(a-x)^3 \qquad \text{...(2.27)}$$

where *k* is the *third-order rate constant*. Separating the variables and integrating, we get

$$\int \frac{dx}{(a-x)^3} = \int k_3\, dt = k_3 \int dt$$

or
$$\frac{1}{2(a-x)^3} = k_3 t + C \qquad \text{...(2.28)}$$

To determine the integration constant C, we know that at $t = 0$, $x = 0$ so that

$$C = 1/2\ a^2 \qquad \text{...(2.29)}$$

Substituting in Eq. 2.28 transposing and solving for k_y we get

$$k_3 = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right] \qquad \text{...(2.30)}$$

$$k_3 = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right] \qquad \text{...(2.31)}$$

Integration of Rate Expression for Zero-order Reactions

Examples are known of reactions in which the reaction rate is not affected by changes in concentrations of one or more reactants. These are called zero-order reactions. In such reactions the rate may be determined by some other limiting factor such as the amount of catalyst used in a catalytic reaction or the intensity of light absorbed in a photochemical reaction. Mathematically, for a zero-order reaction A → P,

$$r = \frac{d[A]}{dt} = k_0 \qquad \text{...(2.32)}$$

where k_Q is the rate-constant. Rearranging,

$$-d[A] = k_0 dt \qquad \text{...(2.33)}$$

If at $t = 0$, the initial concentration is $[A]_0$ and the concentration at $t = t$ is [A], then, integration yields

$$-\int_{[A]_0}^{[A]} d[A] = k_0 \int_{t=0}^{t=t} dt$$

So that

$$k_o t = [A]_0 - [A] \qquad \text{...(2.34)}$$

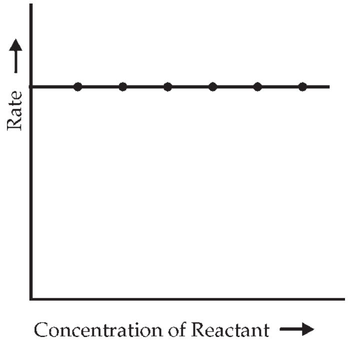


Fig. *The plot of rate versus concentration for a zero-order reaction*

The reaction rate does not vary with concentration of reactant.

Reaction and Half-lifetime

In order to characterise the rate at which a chemical reaction may proceed it is customary to introduce a convenient parameter called the half-lifetime of the reaction. It is defined as *the time required for the reaction to be half completed* and is denoted by the symbol, $t_{1/2}$ It can be related to the corresponding rate constant.

$t_{1/2}$ *for a First-Order Reaction.*

It follows from Eq. 2.12a that at $x = a/2$, $t = t_{1/2}$

Hence,

$$K_1 = \frac{1}{t_1/2} \ln \frac{a}{a-(a/2)}$$

$$= \frac{1}{t_1/2} \ln 2 = \frac{0.693}{t_{1/2}}$$

Thus, $t_{1/2} = 0.693/k_1$ ...(2.35)

From Eq. 2.35 we find that $t_{1/2}$ of *a first-order reaction is independent of the concentration of the reactant.* This is illustrated in the following figure.

Example: The rate-constant for a first-order reaction is $1.54 \quad 10^{-3}\ s^{-1}$. Calculate its half-lifetime.

Solution: Substituting the data directly in Eq. 2.35 we have

$$t_{1/2} = \frac{0.693}{1.54 \times 10^{-3} s^{-1}} = 450\text{s}$$

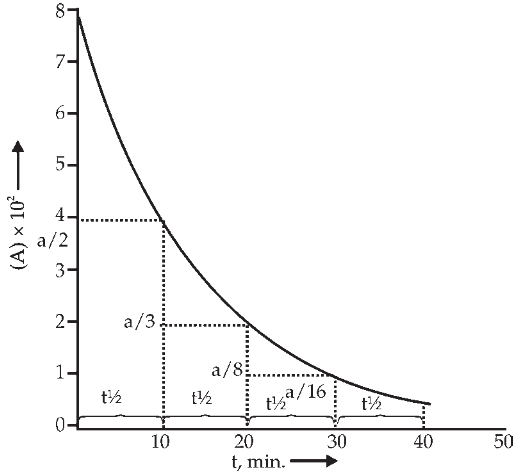


Fig. *Graph showing that $t_{1/2}$ of a first-order reaction is independent of the reactant concentration.*

Example: The half-life of the homogeneous gaseous reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$, which obeys first-order kinetics, is 8.0 minutes. How long will it take for the concentration of SO_2Cl_2 to be reduced to 1 per cent of the initial value?

Solution: From Eq. 2.35 by rearranging, we get

$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{8.0\,\text{min}} = 0.087\,\text{min}^{-1}$$

For a first-order reaction

or $$k_1 = \frac{1}{t}\text{In}\frac{a}{a-x}$$

$$= \frac{1}{k_1}\text{In}\frac{a}{a-x} = \frac{1}{0.087}\text{In}\left(\frac{100}{1}\right) = 52.93\,\text{min}$$

$t_{1/2}$ *for a Second-Order Reaction*

From Eq. 2.26, we see that al $x = a/2$, $t = t_{1/2}$ Hence,

$$k_2 = \frac{1}{t_1/2}\left[\frac{a/2}{a\left(a-\frac{a}{2}\right)}\right] = \frac{1}{t_1/2}\times\frac{a/2}{a(a/2)} = \frac{1}{at_1/2}$$

Thus, $$t_{1/2} = 1/(k_2a) \qquad \text{...(2.36)}$$

From Eq. 2.36 we find that $t_{1/2}$ of *a second-order reaction is inversely proportional to the initial concentration of the reactant* and thus it does not remain constant as the reaction proceeds.

Example: The rate-constant for a second-order reaction is 3.33 10^{-2} dm^3 mol^{-1} s^{-1}. If the initial concentration of the reactant is 0.05 mol dmr^{-3}, calculate its half-life.

Solution: Substituting in Eq. 2.36 we have

$$t_{1/2} = \frac{1}{\left(3.33\times10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}\right)\left(5\times10^{-2}\,\mathrm{mol\,dm^{-3}}\right)}$$

$$= 600\ \mathrm{s} = 10\ \mathrm{min}$$

Example: Derive an expression for the half-life of an nth-order reaction where n ≥ 2.

Solution: An nth-order reaction may be represented as

$$\mathrm{nA} \rightarrow \mathrm{Products}$$

The differential rate equation is

$$-d[A]/dt = k_n[A]^n \qquad \text{...(i)}$$

where k_n is the nth-order rate constant

Separating the variables and integrating, we obtain

$$\int -\frac{d[A]}{[A]^n} = k_n\int dt \qquad \text{...(ii)}$$

or

$$t = \frac{1}{k_n(n-1)[A]^{n-1}} + C \qquad \text{...(iii)}$$

where C is the constant of integration which we have to determine.

Let [A] = *a* and $[A]_o = a_0$, the initial concentration. Then, Eq. *(iii)* can be written as

$$t = \frac{1}{k_n(n-1)[A]^{n-1}} + C \qquad \text{...(iv)}$$

At $t = 0$, $a = a_a$, so that

$$C = \frac{1}{k_n(n-1)\,a_0^{n-1}} \qquad \text{...(v)}$$

Substituting for C in Eq. *(iv),* we get

$$t = \frac{1}{k_n(n-1)}\left[\frac{1}{a^{n-1}} - \frac{1}{a_0^{n-1}}\right] \qquad \text{...(vi)}$$

When $t = t_{1/2}$, $a - a_o/2$ so that from Eq. (iv),

$$t_{1/2} = \frac{1}{k_n(n-1)}\left[\frac{1}{(a_0/2)^{n-1}} - \frac{1}{a_0^{n-1}}\right] \qquad \text{...(vii)}$$

or

$$t_{1/2} = \frac{2^{n-1}-1}{k_n(n-1)\,a_0^{n-1}} \qquad \text{...(viii)}$$

which is the desired expression. This *expression shows that for an nth-order reaction,* $t_{1/2} \propto (1/a_0)^{n-1}$.

$t_{1/2}$ for an nth-Order Reaction

In general, for an nth-order reaction nA → Products, having

$$r = \frac{d[A]}{dt} = k_n[A]^n$$

it has been shown in above example that

$$t_{1/2} = \frac{2^{n-1}-1}{k_n(n-1)\,a_0^{n-1}} \qquad \text{...(2.37)}$$

where a_0 is the initial concentration of A and k_n is the nth-order rate constant. From Eq. 2.37 we see that

$$t_{1/2} \propto \frac{1}{a_0^{n-1}} \qquad \text{...(2.38)}$$

It is easy to see from Eq. 2.38 that for a first-order reaction ($n = 1$), $t_{1/2}$ is independent of a_0, for a second-order reaction ($n = 2$), $t_{1/2} \propto 1/a_0$, for a third-order reaction ($n = 3$), $t_{1/2} \propto (1/a_0)^2$, and so on. These conclusions we have arrived at earlier, too.

Example: The $t_{1/2}$ of a reaction is halved as the initial concentration of the reaction is doubled. What is the order of the reaction ?

Solution: From Eq. 2.38 $t_{1/2} \propto 1/a_0^{n-1}$

In the present case,

$$\frac{1}{2}t_{1/2} \propto \frac{1}{(2a_0)^{n-1}}$$

Hence, $$\frac{t_{1/2}}{1/2_{t_{1/2}}} = \frac{1/\left(a_0^{n-1}\right)}{1/\left(2a_0\right)^{n-1}}$$

or $$2 = 2^{n-1}$$

or $$2^1 = 2^{n-1}, \text{ so that}$$

$$n = 2$$

The reaction is second-order.

Example: The $t_{1/2}$ of a reaction is doubled as the initial concentration of the reaction doubled. What is the order of the reaction?

Solution: Proceeding as in the last example,

$$\frac{t_{1/2}}{2t_{1/2}} = \frac{1/\left(a_0\right)^{n-1}}{1/\left(2a_0\right)^{n-1}}$$

or $$1/2 = 2^{n-1}$$

or $$(2)^{-1} = -1, \text{ so that}$$

$$n = 0$$

The reaction is zero-order.

Units of Rate Constant

The units of rate constant for a given reaction can be determined by starting with the appropriate rate equation for the reaction, as is shown in the following examples.

Example: Staring from the full rate equation, determine the units of the rate constant k for (a) a zero-order reaction (b) a first-order reaction (c) a second-order reaction (d) a third-order reaction and (e) a half-order reaction. Assume that concentrations are expressed in molar units and time in seconds.

Solution: *(a)* $-d[A]/dt = k_0$

$$\text{Units of } k_0 = \text{units of } [A]/\textit{units} \text{ of } t = \frac{\text{mol dm}^{-3}}{s} = \text{mol dm}^{-3}\, s^{-1}$$

It should be noted that units of $d[A]$, the change in concentration, are the same as those of [A]. Similarly, the units of *dt* are the same as those of *t.*

(b) $-d[A]/dt = k_1[A]$ or $\quad K_1 = -\frac{1}{[A]} \times \frac{d[A]}{dt}$

$$\therefore \quad \text{Units of } k_1 = \frac{\text{mol dm}^{-3}}{s} \times \frac{\text{mol dm}^{-3}}{s} = s^{-1}$$

(c) (*i*) $-d[A]/dt = k_2[A]^2$ or $\quad k_2 = -\frac{1}{[A]} \times \frac{d[A]}{dt}$

$$\therefore \text{ Units of } k_2 = \frac{1}{\text{mol dm}^{-3}} \times \frac{\text{mol dm}^{-3}}{s} = \text{dm}^3 \text{ mol}^{-1} s^{-1}$$

(ii) $-d[A]/dt = k_2[A][B]$ or $k2 = -\frac{1}{[A][B]} \times \frac{d[A]}{dt}$

$$\therefore \text{ Units of k2} = \frac{1}{\left(\text{mol dm}^{-3}\right)^2} \times \frac{\text{mol dm}^{-3}}{s} = \text{dm}^3 \text{ mol}^{-1} s^{-1}$$

Notice that the units of it depend upon the total order of the reaction and not on the way order is composed with respect to the different reactants.

(d) $-d[A]/dt = k_3[A]^3$ or $\quad k_3 = \frac{1}{[A]^3} \times \frac{d[A]}{dt}$

$$\therefore \quad \text{Units of k}_3 = \frac{1}{\left(\text{mol dm}^{-3}\right)^3} \times \frac{\text{mol dm}^{-3}}{s} = \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

(e) $-d[A]/dt = k_{1/2}\,[A]_{1/2}$ or $\quad k_{1/2} = \frac{1}{[A]^{1/2}} \times \frac{d[A]}{dt}$

$$\therefore \text{ Units of k}_{1/2} = \frac{1}{\left(\text{mol dm}^{-3}\right)^{1/2}} \times \frac{\text{mol dm}^{-3}}{s}$$

$$= \text{mol}^{1/2} \text{ dm}^{-3/2} s^{-1}$$

In general, for an *nth-order reaction,* the units of k_n are $(\text{dm}^3)^{n-1}$ mol^{1-n} s^{-1}.

Order of a Reaction: Fixing Ways

The order of a reaction is never known before hand, though majority of reactions are first-order or second-order. The following methods are commonly used for determining the order of a reaction:

***The Use of Differential Rate Expressions*:** According to this method, which was devised by van't Hoff, the rate of an *n*th-order reaction is given by

$$r = k_n c^n \qquad ...(2.39)$$

Taking logs, we have

$$\ln r = \ln k_n + n \ln c \qquad ...(2.40)$$

Thus, if the double-logarithmic plot of rate versus concentration gives a straight line, then the slope gives the value of n and the intercept gives ln k.

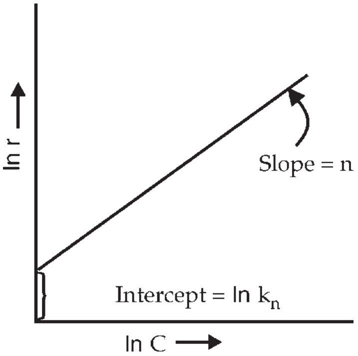


Fig. *ln r versus ln c for an nth-order reaction.*

Also, if r_1 and r_2 are the rates at two different reactant concentrations c_1 and c_2 then

$$\frac{r_1}{r_2} = \frac{-dc_1/dt}{-dc_2/dt}$$

$$= \frac{k_n c_1^n}{k_n c_2^n}$$

Taking logs,

$$\ln\frac{r_1}{r_2} = n\ln\frac{c_1}{c_2}, \text{ whence}$$

$$n = \frac{\ln(r_1/r_2)}{\ln(c_1/c_2)} \qquad ...(2.41)$$

The Use of Integral Rate Expressions**:** We have already demonstrated this method in solving problems for reactions of various orders. This method can be used either analytically or graphically. In the analytical method, we assume a certain order for the reaction and calculate the rate constants from the given data. The constancy of the *k*-values obtained suggests that the assumed order is correct. If the *k*-values obtained are not constant, we assume a different order for the reaction and again calculate the *k*-values using the new rate expression and see if *k* is constant.

In the graphical method, if the plot of ln c versus *t* is a straight line the reaction is first-order. Similarly, the integrated expression for the second-order reaction can be utilised graphically to ascertain if the reaction is second-order, and so on.

The Half Life Method**:** We have shown above that, provided all reactants are present in the same molar concentrations, the half-life, $t_{1/2}$, of *n*th-order reaction is given by Eq. 2.38.

If two experiments are carried out at different initial molar concentrations, then

$$\frac{\left(t_{1/2}\right)_1}{\left(t_{1/2}\right)_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking logs,

$$\ln\frac{\left(t_{1/2}\right)_1}{\left(t_{1/2}\right)_2} = (n-1)\ln\frac{a_2}{a_1}$$

or

$$n = 1+\frac{\ln\left(t_{1/2}\right)_1/\ln\left(t_{1/2}\right)_2}{\ln\left(a_2/a_1\right)}$$

This method was suggested by Ostwald. The determination of half lives of a reaction at two different initial concentration may lead to the determination of *n*.

Isolation Method**:** Sometimes the kinetics of a reaction are studied in successive experiments by keeping the concentrations of all but one reactant in large excess so that the result gives the order with respect to the reactant whose concentration is changing significantly. Thus, the synthesis of HI from H_2 and I_2 is pseudo first-order with respect to H_2 in the presence of large excess of

I_2 and also pseudo first-order with respect to I_2 in the presence of large excess of H_2. Hence, overall it is a second-order reaction.

Reaction Rates and Temperature

It is a common experience that increase of temperature, has a marked effect on the rate of a chemical reaction. *The ratio of the rate constants of a reaction at two temperatures differing by* 10 C is *known as the* temperature coefficient *of the reaction.* The temperatures usually selected for this purpose are 25 and 35 C. Thus,

$$\text{Temperature coefficient} = \frac{\text{Rate constant at } 35°C}{\text{Rate constant at } 25°C} = \frac{k_{35}}{k_{25}}$$

The value of the temperature coefficient for most of the reactions is close to 2 and in some cases it approaches even 3. For example, the temperature coefficient for the dissociation of hydrogen iodide,

$$2HI\ f\ \ H_2 + I_2$$

is 1.8 while that for the reaction of methyl iodide with sodium ethoxide

$$CH_3I + C_2H_5ONa \rightarrow CH_3OC_2H_5 + NaI$$

is 2.9.

This means that in many reactions the rate constant becomes as high as twofold or even threefold as the temperature rises by 10 C.

Why such a small rise of temperature speeds up a reaction to such a large extent can be explained on the basis of the collision theory. According to this theory, for chemical reactions to occur, there must be collisions between the reactant molecules. However, most of the collisions taking place between the molecules are ineffective. The important postulate of the collision theory is that only those collisions result in chemical reactions in which the colliding molecules are associated with a certain minimum energy called the *threshold energy*. When molecules having low energies collide, nothing happens to the molecules except some alteration in their speed or direction of motion. But, when molecules associated with high energies collide, there is loosening or breaking of bonds, resulting in chemical reaction.

There is a definite distribution of velocities and kinetic energies amongst the various molecules of a gas. The distribution of kinetic energies at two different temperatures is shown in figure 1 molecules having energies more than the threshold energy E are represented by the shaded portion under the curves.

As the temperature increases from T_1 to T_2, the energy distribution undergoes a change. There is a general shift in the distribution of energies as shown in the figure. Now there are more molecules on the high side of kinetic energy. The number of molecules whose energies are equal to or greater than the threshold energy at temperature T_1 is represented by the shaded area *efcd* and at temperature T_2 by the shaded area *abcd.* As can be seen, the shaded area *abcd* is nearly *twice* the shaded area *efcd.* This means that the number of molecules having energy equal to or greater than the threshold energy (whose collisions result in chemical reaction) becomes nearly double even with a small increase of temperature from T_1 to T_2. Consequently, *the rate of reaction which depends upon the number of effective collisions, becomes almost double with a small increase of temperature.*

Measurement of Activation Energy

It is a common laboratory observation that:

A mixture of oxygen and hydrogen (1 : 2 by volume) may remain as such at room temperature apparently without reacting. However, the moment an electric spark is passed through the mixture, the reaction proceeds instantaneously, almost explosively. Similarly, a mixture of methane and oxygen remains intact without reacting noticeably until a lighted matchstick is introduced into the mixture. *Why is it so* ?

Even when the concentrations of reactants involved in two reactions are the same, one reaction may be very fast and the other very slow. Thus, under similar conditions of temperature and pressure, the oxidation of nitric oxide [$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$] is much faster than the oxidation of carbon monoxide [$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$]. *Why is it so?*

We may answer these questions on the basis of the collision theory by involving the concept of activation energy.

There is a certain minimum energy *(threshold energy)* which the colliding molecules must acquire before they are capable of reacting. Most of the molecules, however, have much less kinetic energy than the threshold energy. The excess energy that the reactant molecules having energy less than the threshold energy must acquire in order to react to yield products is known as activation energy. Thus

Activation Energy = Threshold energy – Energy actually possessed by molecules.

According to this concept, non-active molecules (having energy less than the threshold energy) can be *'activated'* by absorption of extra energy. This extra energy is, evidently, the *activation energy.*

***Concept of Energy Barrier*:** The reactant molecules have to acquire a certain amount of energy before they can react in collisions to yield products. In other words there is an energy barrier placed between reactants and products. This barrier has to be crossed before reactants can yield products. This barrier determines the magnitude of threshold energy which reactant molecules must acquire before they can yield products.

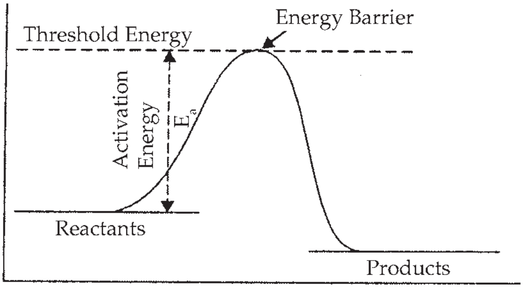


Fig. *The concept of energy barrier in chemical reactions.*

As is evident from the above figure, E_a is the activation energy of the reactants. They must absorb this much of energy before they can react and change into products. The energy of the products is shown to be less than that of the reactants. This indicates that the reaction is *exothermic.*

We can now easily answer the questions posed above. A reaction (if feasible) will occur only if the required activation energy is supplied to the molecules. This is the reason that although the reaction between hydrogen and oxygen is highly feasible from the point of view of thermodynamics at the room temperature, yet it takes place at a noticeable rate only if the required activation energy in the form of electric spark or heat is supplied to the reactants.

Futher, different reactions require different amounts of activation energy. A reaction which requires a higher activation energy is slow at ordinary temperature. Consider the two:

$$NO(g) + 1/2\ O_2(g) \rightarrow NO_2(g) \qquad (\textit{Fast})$$

$$CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g) \qquad (\textit{Slow})$$

reactions, referred to above. The first reaction is *fast* at ordinary temperature because it requires a comparatively *lower activation energy.* The second reaction is *slow* because it requires a comparatively *lusher activation energy.*

It is thus evident that whether a given reaction is slow or fast at a given temperature depends upon the activation energy of the reaction. *A reaction which has lower activation energy will proceed at a faster rate at a given temperature. Thus, differences in activation energies are largely responsible for observed inferences in rates of different reactions.*

Effect of Catalyst: *A catalyst is a substance that can increase the velocity of a reaction but which itself remains unchanged in amount and chemical composition at the end of the reaction.* The process of increasing the rate of a reaction through the use of a catalyst is known as *catalysis.* The action of a catalyst can be explained by using the concept of energy barrier and activation energy. *When a catalyst is added, a new reaction path with a lower energy barrier is provided*(dotted curve in following fig.). Since the energy barrier is reduced in magnitude, a larger number of molecules of the reactants can get over it. Thus increases the rate of the reaction.

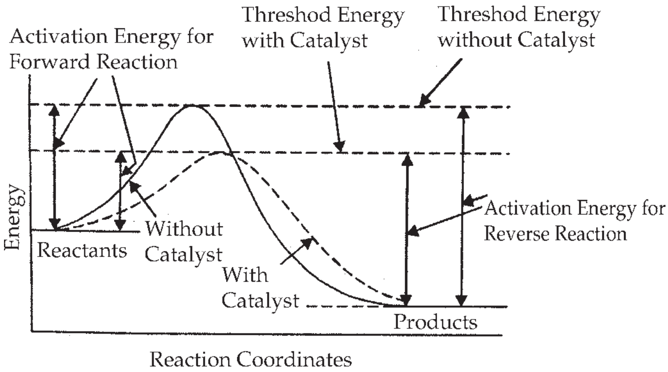


Fig. *Effect of catalyst on the rate of reaction.*

As is evident from the above figure, by the addition of a catalyst, the activation energy for the reverse reaction is lowered by exactly the same amount as for the forward reaction. This explains why a catalyst for a reaction has an equal effect on the reverse reaction as well. In other words, a catalyst speeds up both the backward and the backward reactions by the same amount. Thus, if a catalyst doubles the rate of the forward reaction, it also doubles the rate of the reverse reaction. A catalyst, therefore, does not alter the position of equilibrium in a reversible reaction. It simply hastens the approach of the equilibrium by speeding up both the forward and the backward reactions.

Calculation of Energy of Activation (The Arrhenius Equation): Arrhenius proposed the following *empirical equation* for calculating the energy of activation of a reaction having rate constant k at temperature T:

$$k = A e^{-E_a/RT}$$

where E_a is called the *Arrhenius activation energy and A is called the Arrhenius pre-exponential factor*. Since the exponential factor is dimensionless, the pre-exponential factor A has the same units as the rate constant k. The units of k for *a first-order reaction* are s^{-1}, *which is the unit of frequency.* Hence, A is also called the *frequency factor*. E_a and A are called the *Arrhenius parameters*. Taking logs of Eq. 2.38 we have

$$\ln k = -E_a/(RT) + \ln A$$

From Eq. 2.9, it is evident that a plot of ln k versus the reciprocal of absolute temperature (1/T) gives a straight line, (Fig. below) slope = $-E_a/R$ and intercept = ln A.

Differentiating Eq. 2.9 with respect to temperature, we get

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2} \qquad \text{...(2.42)}$$

Integrating Eq. 2.42 between T_1 and T_2 when the corresponding rate constants are k_1 and k_2, respectively and assuming that E_a is constant over this temperature-range, we obtain

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \qquad \text{...(2.43)}$$

This is the integrated Arrhenius equation.

Thus, knowing the rate constants at two different temperatures, the energy of activation E_a can be readily determined.

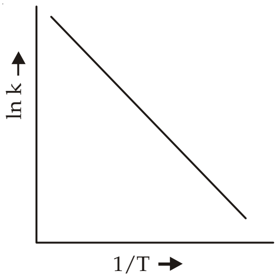


Fig. *The Arrhenius plot of ln k versus 1 /T for a reaction.*

Example: The activation energy of a non-catalysed reaction at 37 C is 83.68 kJ mol^{-1} and the activation energy of the same reaction catalysed by an enzyme is 25.10 kJ mol^{-1}. Calculate the ratio of the rate constants of the enzyme- catalysed and the non-catalysed reactions.

Solution: According to the Arrhenius equation, $k = Ae^{-E_a/RT}$

Let k_e and k_n be the rate constants of the enzyme-catalysed and non-catalysed reactions, respectively. Assuming that the Arrhenius pre-exponential factor A is the same in both cases, we have

$$\frac{k_e}{k_n} = \frac{e^{-E_a/RT}(\text{enzyme}-\text{catalysed})}{e^{-E_a/RT}(\text{non}-\text{catalysed})}$$

$$= \exp\left(\frac{83.68\,\text{kJ mol}^{-1} - 25.10\,\text{kJ mol}^{-1}}{\text{RT}}\right)$$

$$= \exp\left(\frac{58.58\,\text{kJ mol}^{-1}}{8.314 \times 10^{-3}\,\text{kJ k}^{-1}\text{mol}^{-1} \times 310\,\text{K}}\right) = \text{e}^{22.728}$$

$$\ln\frac{k_e}{k_n} = 22.728$$

$$\frac{k}{k_n} = 7.424 \quad 10^{9}$$

Thus the enzyme-catalysed reaction is about 10 billion times faster than the non-catalysed reaction.

Example: Can the activation energy of a reaction be zero or negative?

Solution: From the Arrhenius relation $k = A e^{-E_a/RT}$, we see that if E_a, is zero, then, $k = A$. *i.e., every collision between molecules leads to the chemical reaction which is not true.* Hence, E, cannot be zero. If on the other hand, E_a is negative, then the exponential factor can be written as e^x where $x = E\ /RT$.

If $x << 1$, then,

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + ...$$

$$= 1 + x \text{ (neglecting higher power of } x)$$

$$= 1 + E_a / RT$$

Hence, $k = A\ (1 + E/RT)$, *i.e.,* $k > A$, which is absurd.

Hence, E_a cannot be negative either.

Example: What value of the rate constant is predicted by the Arrhenius equation if

$T \rightarrow \infty$? Is this value physically reasonable?

Solution: From the relation $k = A e^{-E_a/Rt}$, we see that if $T \rightarrow \infty$, $k \rightarrow A$ so that $E_a = 0$. This implies that there is no activation energy for the reaction. Hence, the result is not *physically reasonable.*

Reaction Rates: the Concepts

There are two important theories of reaction rates. These are the *collision theory* developed by Arrhenius and van't Hoff and the modern *transition state theory,* also called the *activated complex theory,* developed by Eyring, Polanyi and Evans in 1935.

The Collision Theory of Bimolecular Gaseous Reactions. This is the earliest theory of reaction rates. Since reaction between two species takes place only when they are in contact, it is reasonable to suppose that the reactant species must collide before they react. Since our knowledge of molecular collisions is more complete for the gaseous phase than for the liquid phase (in the latter case we speak of encounters rather than collisions), we will restrict our discussion to bimolecular reactions in the gaseous phase.

From the kinetic theory of gases, the number of bimolecular collisions per second per cm^{-3} among molecules of one species is given by

$$Z = 2n^2\sigma^2\ (8\pi kT/\mu)^{1/2} \qquad ....(2.44)$$

For a reaction involving two different gases A and B, the rate of bimolecular collisions between unlike molecules is given by

$$Z_{AB} = n_A n_B \left(\sigma_{av}\right)^2 \left(8\pi kT/\mu\right)^{1/2} \qquad \text{....(2.45)}$$

where n_A and n_B are numbers of A and B molecules, respectively: σ_{av} is the average collision diameter defined as $(\sigma_A + \sigma_B)/2$ and μ is the reduced mass, defined as $\mu = (m_A m_B)/(m_A + m_B)$. The collision number Z_{AB} is given, in terms of molar masses M_A and M_B of the two gases, by the expression.

$$Z_{AB} = n_A n_B \left(\sigma_{av}\right)^2 \left[\frac{\left(M_A + M_B\right) 8\pi RT}{M_A M_B}\right]^{1/2} \qquad \text{...(2.46)}$$

In a special case when the reacting species A and B are the same, $\sigma_{av} = \sigma$ and $n_A = n_B$ and if we also take account of the indistinguishability of the colliding molecules by dividing by 2, then, Eq. 2.45 reduces to Eq. 2.44.

Let us calculate Z_{AB} for the reaction between H_2 and I_2 at 700 K and 1 atm pressure, the quantities of the two gases being 1 mole each, Accordingly, $n_{H_2} = n_{I_2} \approx 10^{19}$ molecules cm^{-3}; $\sigma_{H_2} = 2.2\,\text{Å}$, $\sigma_{I_2} = 4.6\,\text{Å}$, so that $\sigma_{av} = 3.4$ Å. Hence, according to Eq. 2.46,

$$Z_{AB} = \left(10^{19}\right)^2 \left(3.4 \times 10^{-8}\right)^2 \left[\frac{(2+254) 8 \times 3.14 \times 8.314 \times 10^7 \times 700}{2 \times 254}\right]^{1/2}$$

$$= 10^{38} \quad 1.16 \quad 10^{-15} \quad 8.58 \quad 10^{5} \approx 10^{29} \text{ collisions } s^{-1}\ cm^{-3}$$

Since there are approximately 10^{29} collisions s^{-1} for 10^{19} molecules of each species, each molecule makes about 10^{10} collisions s^{-1} with the molecules of the other species. If each collision were to lead to a chemical reaction, then the whole reaction would be expected to be complete in about 10^{-10} s. However, this predicted rate of the reaction is in complete disagreement with the experimental rate. Hence, we conclude that all collisions do not result in chemical reaction.

In order for a reaction to occur, the energy of collision must equal or exceed some critical value called the *threshold energy*. The effective energy is, of course, not the total kinetic energy of the two colliding molecules but is, instead, the kinetic energy corresponding to the component of the relative velocity of the two molecules along the line of their centres at the moment of collision. It is this energy with which the two molecules are pressed together.

The detailed analysis of the dynamics of bimolecular collisions leads to the result that the number of collisions s^{-1} cm^{-3} between molecules A and B, when the relative kinetic energy E along the line of centres is greater than the threshold energy, is given by

$$Z_{AB} = Z_{AB}\, e^{-E/RT} \qquad \text{...(2.47)}$$

Assuming that Z_{AB} gives the rate of relative collisions between A and B, we can write

$$-dn_A/dt = Z_{AB} \qquad \text{...(2.48)}$$

$$= n_A n_B (\sigma_{av})^2 \left[\frac{(M_A + M_B)8\pi RT}{M_A M_B}\right]^{1/2} e^{-Ea/RT}$$

molecules cm^{-3} s^{-1}...(2.49)

Let us now proceed to obtain the theoretical expression for the rate constant. If the concentration of A is expressed in mol dm^{-3}, then

$$[A] = 10^3\, n_A/N_A = [B] \qquad \text{...(2.50)}$$

where N_A is Avogadro number. Hence, the rate law expression

$$-d[A]/dt = k_z[A][B] \qquad \text{...(2.51)}$$

can be written as

$$-\frac{10^3\, dn_A}{N_A dt} = k_2 \frac{10^6}{(N_A)^2} n_A n_B \qquad \text{...(2.52)}$$

Hence,
$$k_2 = \frac{N_A}{10^3\, n_A n_B} \times \frac{dn_A}{dt} \qquad \text{...(2.53)}$$

Using Eq. 2.46 for $-dn_A/dt$, we have

$$k_2 = \frac{N_A(\sigma_{av})^2}{10^3}\left[\frac{(M_A + M_B)8\pi RT}{M_A M_B}\right] e^{-E/RT}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \ \text{...(2.54)}$$

Comparing Eq. 2.54 with the Arrhenius equation $k_2 = A\, c^{-Ea/RT}$, we find that the Arrhenius pre-exponential factor is given by

$$A = \frac{N_A(\sigma_{av})^2}{10^3}\left[\frac{(M_A + M_B)8\pi RT}{M_A M_B}\right]^{1/2} \qquad \text{...(2.55)}$$

The activation energy E_a in the Arrhenius equation is thus identified the relative kinetic energy E along the line of centres of the two colliding molecules which is required to cause a reaction between them.

Let us calculate A and k_2 for the $H_2 - I_2$ reaction at 700 K. E_a has been found to be 167.4 kJ mol^{-1}. Substituting the various values in Eq. 2.55, A comes out to be = 6.0 10^{11} dm^3 mol^{-1}s$-^1$. Hence, from Arrhenius equation

$$k_2 = 6.0 \quad 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \exp(-167400 \text{ I}/8.314 \text{ J} \quad 700 \text{ K})$$

$$= 0.22 \text{ dm}^3 \text{ mol}^{-1} \ s^{-1}$$

which compares favourably with the experimental value of 0.064 dm^3 mol^{-1} s^{-1}, keeping in view the uncertainty in the values of the activation energy and the average collision diameter.

The orientational requirement can be taken into account by introducing the so called stearic factor P for the bimolecular rate constant. Accordingly

$$k_2 = \text{PAe}^{-\text{Ea}/\text{RT}} \qquad \text{...(2.56)}$$

Since the value of A depends on the value chosen for the cross-section, and the values are base on taking the values for non-reactive collision cross section. Hence, orientation requirement can be taken into account by replacing the collision cross section a^2 in equation (2.50) by the reactive cross section σ^{*2}. A more conventional procedure takes the view that the cross section for reaction can be expressed in terms of the collisional cross section and stearic factor P such that σ^{*2}.

= $P\sigma^2$ then the expression for the rate coefficient becomes

$$k_2 = \left[\sigma_{av}^2 N_A (8\pi RT/\mu)^{1/2}\right]\left[\exp(-E_a/RT)\right] \qquad \text{...(2.57)}$$

$$= \left[\sigma^{*2} N_A (8\pi RT/\mu)^{1/2}\right]\left[\exp(-E_a/RT)\right]$$

$$= 2.753 \quad 10^{29} \; P(\sigma_{av})^2 \left[T\frac{(M_A + M_B)}{M_A M_B}\right]\left[\exp(-E_a/RT)\right]$$

...(2.58)

In this equation the molar mass is in units of g mol^{-1} and units of A are dm^3 mol^{-1} s^{-1}. This displays very clearly the three contributing to the value of k_2.

The theory would be all very well if we could calculate the stearic factor P. In some cases we can. However, many reactions are much more complicated and we can not hope to estimate P in a simple way. What we want is a more powerful theory of P, which let us avoid simply having to guess its value.

***Reactions in Solution*:** Molecular motion in liquids is diffusional in place of free flight but the concept of activation energy and stearic requirements survive. Molecules have to jostle their way through the solvent and so the encounter frequency is drastically less than in a gas. Since a molecule migrates only slowly into the region of a possible reaction partner, it also migrates only slowly away from it.

In other words, the members of the encounter pair linger in each other's vicinity for a much longer time and so their chance of undergoing reaction is greatly enhance. Further more, the activation energy of reaction is a much more complicated quantity in solution than in gases, for the encounter pair is surrounded by solvent and its energy is determined by all the interactions. The following table compares some calculated values of A with experimental values obtained form Arrhenius plots of lnk against I/T:

Table: *Activation energies, pre-exponential factors for gas phase reactions*

Reaction	**A/dm^3 mol^{-1} σ^{-1}**		***E_a/kJ mol^{-1}***	***$P = \sigma^{*2}/\sigma_2$***
	Expt.	***Theory***		
$2NOCl \rightarrow 2NO + Cl_2$	9.4 10^{9}	5.9 10^{10}	102.0	0.16
$2NO_2 \rightarrow 2NO + O_2$	2.0 10^{9}	4.0 10^{10}	111.0	5 10^{-2}
$2ClO \rightarrow Cl_2 + O_2$	6.3 10^{7}	2.5 10^{10}	0.0	2.5 10^{-3}
$K + Br_2 \rightarrow KBr + Br$	1.0 10^{12}	2.1 10^{11}	0.0	4.8
$H_2 + C_2H_4 \rightarrow C_2H_6$	1.24 10^{6}	7.3 10^{11}	180	1.7 10^{-6}

In the first reaction pre-exponential factor shows good agreement between theory and experiment but there are major discrepancies. Some pre-exponential actors are orders of magnitude smaller than the calculated values. This suggest that collision with sufficient energy is not the only criterion for reaction and that some other factors such as the relative orientation of the colliding species has to be taken into account.

The collision theory is applicable to simple gaseous reactions. For reactions between complicated molecules, the observed rate is found to be much smaller than the theoretically predicated rate, sometimes by a factor of 10^5 or reactions involving fairly complicated molecules. The discrepancy is explained by the fact that the colliding molecule is treated as a hard sphere having no internal energy. Again, the spherical model ignores the dependence of the effectiveness of a collision on the relative orientation of the colliding molecules. Also, the activation energy has been treated as though it were related entirely to translational motion, ignoring the effect of rotational and vibrational motion. For these reasons the collision theory is applicable only to reactions between very simple gaseous molecules.

Take the case of reaction

$H_2 + C_2H_4 \rightarrow C_2H_6$

At 628 K experimental pre-exponential factor has the value of $1.24 \quad 10^6$ $dm^3\ mol^{-1}\ s^{-1}$. From equation 2.54

$$A = \frac{N_A(\sigma_{av})^2}{10^3}\left[\frac{(M_{H_2} + M_{C_2}H_4)8\pi RT}{M_{H_2}M_{C_2H_4}}\right]^{1/2}$$

$M_A(H_2) = 2.016 \qquad MB(C_2H_4) = 28.05$

$$\left[\frac{(MH_2 + M_{C_2H_4})8\pi RT}{M_{H_2}M_{C_2H_4}}\right]^{1/2} = \left[\frac{(2.016 + 28.05)8 \times 3.146 \times 8.314 \times 10^7 \times 628}{2.016 \times 28.05}\right]^{1/2}$$

$$= 835.06 \quad 10^3 \text{ m s}^{-1}$$

$$\sigma_{av} = \frac{1}{2}(0.27\,\text{nm} + 0.64\,\text{nm}) = 0.46 \times 10^{-9}\ \text{m}$$

$$\sigma^2_{av} = 0.211 \quad 10^{-18}\text{m}^2$$

$$A = (0.211 \quad 10^{-18} \quad 6.022 \quad 10^{23}\ \text{mol}^{-1})\ (835.06 \quad 10^3\ \text{ms}^{-1}/1000$$

$$= 1.064 \quad 10^8\ \text{m}^3\ \text{mol s}^{-1} = 1.064 \quad 10^{11}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

Expt A = $1.24 \quad 10^6$ $dm^3\ mol^{-1}\ s^{-1}$

The two values of A differ by a factor of 10^5.

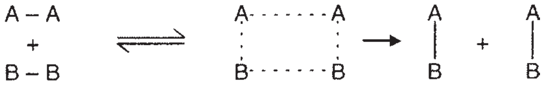
Bimolecular Reactions: Complexities

The collision theory of reaction rates dealt with earlier gives a useful, even if a crude, picture of reaction rates and permits us to calculate the rates of reactions between simple molecules when the activation energies are known. However, this theory leaves much to be desired. It does not furnish a method of calculating activation energies theoretically. It provides no information on the details of reactive collisions. It also does not account for the role that the internal energy might play in the reaction.

As a result of the development of quantum mechanics, another theoretical approach to chemical reaction rates has been developed which gives a deeper understanding of the reaction process. It is known as the *Absolute Reaction Rate Theory or the Transition State Theory* or, more commonly, as the *Activated Complex Theory (ACT),* developed by H. Eyring and M. Polanyi in 1935. According to ACT, the bimolecular reaction between two molecules A_2 and B_2 passes through the formation of the so-called activated complex which then decomposes to yield the product AB, as illustrated below:

$$A_2 + B_2 \rightleftharpoons (A_2B_2)^{\#} \longrightarrow 2AB$$

or



Let us delve into the details of what happens when A_2 and B_2 molecules approach each other from a large distance. Initially, there occurs a weak van der Waals interaction between them as a result of the London dispersion forces. When, however, the molecules approach each other still more closely, due to inter-electronic and internuclear interactions, the van der Waals attraction changes into the van der Waals repulsion which eventually becomes so predominant that the molecules may fly apart after a collision. If, on the other hand, the two molecules have enough kinetic energy, they may approach each other so closely as to permit another kind of interaction in which the mutual perturbation is strong enough to form a new bond between the four atoms. This single system is called an activated complex or the *transient state.* The molecules A_2 and B_2 must receive an additional amount of energy, called the activation energy, to convert them into the energy-rich activated complex.

Though somewhat ill-defined, the activated complex can be treated as a distinct chemical species in equilibrium with the reactants which then decompose into products. It is amenable to thermodynamic treatment, like any ordinary molecule. It is, however, a special molecule in which one vibrational degree of freedom has been converted to a translational degree of freedom along the reaction coordinate. The reaction coordinate in the abscissa of the figure given below could be the bond length which changes in going from the reactants to the products. In other words, the reaction coordinate is a measure of the progress of a reaction. It must be remembered that the activated complex is not merely an intermediate in the process of breaking or forming of chemical bonds. It is unstable because it is situated at the maximum of the potential energy barrier separating the products from the reactants. The difference between the energy of the activated complex and the energy of the reactants is the activation energy, E_a.

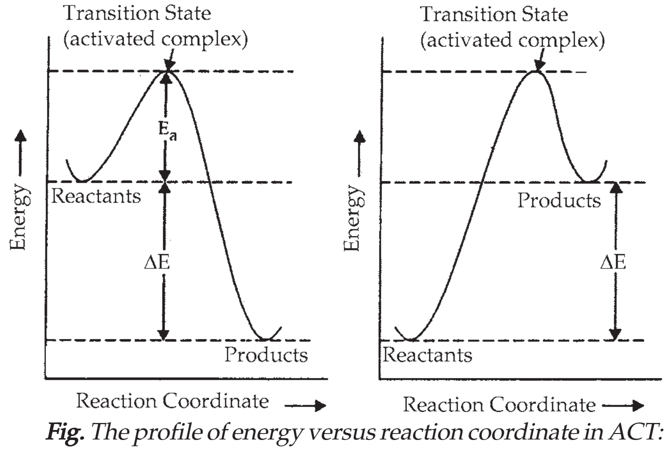


Fig. *The profile of energy versus reaction coordinate in ACT: (a) Exothermic reaction; (b) Endothermic reaction.*

Both the forward and the reverse reactions proceed through the same activated complex. Thus, if a bond is in the process of being broken in the activated complex for the forward reaction, the bond is in the process of being formed in the activated complex for the reverse reaction.

Collision vs Complex Theory

Activated complex theory is basically treated as a statistical mechanics problem. For a simple reaction between two atoms A and B, the activated complex being diatomic molecule so that the frequency factor A is given by

$$\text{PA} = \frac{kT}{h}\frac{q^{\#}}{q_A q_B}$$

where $q^{\#} / q_A q_B$ are the various partition functions. On substitution the full formed of partition functions it reduces to

$$\text{A} = \sigma^2 \, [8 \, \pi \, \text{RT} \, (\text{M}_\text{A} + \text{M}_\text{B})/\text{M}_\text{A}\text{M}_\text{B}] \qquad \text{....(2.59)}$$

where R is gas constant per mole, M_A M_B as molar masses

This expression is similar to the expression given by Eq. 2.46 for collision state theory. This treatment is for two atoms but can be extended to reactions involving molecules will be adopted here. In the first place the partition function for each type of energy will be assumed to consist of a number of equal terms one for each degree of freedom so that

$$\text{A} = \frac{kT}{h}\frac{q_R^2}{q_T^3} \qquad \text{...(2.60)}$$

where q_R and q_T are rotational and translational partitions function for reaction molecules. In these circumstances, A becomes identical with the collision number Z, and so the quantity $\frac{kT}{j}\frac{q_R^2}{q_T^3}$ may be taken as equivalent to the latter. If this treatment is extended to the general case where A and B non-linear molecules containing a and *b* atoms, respectively. On substitution of partition function it changes to

$$\text{A} = \frac{kT}{h}\frac{q_V^5}{q_T^3 q_T^3} \qquad \text{...(2.61)}$$

where q_T, q_R and q_v are translational, rotational and vibrational partition function and if represented by PZ and noting that Z is equivalent to $\frac{kT}{h}\frac{q_R^2}{q_T^3}$ it follows that so called probability factor P is

$$P = q_V^5 / q_R^5 \tag{2.62}$$

At ordinary temperature q_v is generally little different from unity where as q_R may be about 10 to 100 so that according to equation 2.62 the P factor in the reaction between two or more molecules must be of the order of 10^{-5} to 10^{-10}. The more complex the reacting molecules the greater the value of harmony with experimental findings. If the reacting molecules are diatomic molecules q_R is generally, less than 10 and thus probability factor may will be of the order of 10^{-1}. This explains why the simple collision hypothesis accounts for the rates of reaction

$$2HI \rightarrow H_2 + I_2$$

With in a factor of about 10 and good agreement should also be obtained for reactions between an atom and a simple molecule. The pre-exponential factors for some bimolecular gaseous reactions are shown in the following table:

Table: *Pre-exponential factors for simple Bimolecular gaseous reactions calculated by Transition State Theory, compared with experimental values.*

Reaction	***A_{cal} (cm^3 mol^{-1} s^{-1})***	***A_{expt} (cm^3 mol^{-1} s^{-1})***
$H + H_2 \rightarrow H_2 + H$	75 10^{13}	5.4 10^{13}
$Br + H_2 \rightarrow HBr + H$	1 10^{14}	3 10^{13}
$H + CH_4 \rightarrow H_2 + CH_3$	2 10^{13}	1 10^{13}
$CH_3 + H_2 \rightarrow CH_4 + H$	1 10^{12}	2 10^{12}

The pre-exponential factors obtained from collision theory are in the range 10^{13}-10^{15} cm^3 mol^{-1} s^{-1}. The agreement between the transition state theory and the collision theory is quite satisfactory. However, for reaction involving complex molecules, the collision theory fails while transition state theory still gives meaningful results. The transition state theory when developed to its most sophisticated form does permit a detailed treatment of reaction rates.

When two polyatomic molecules react, the formation of the activated complex requires the disappearance of three translational and three rotational degrees of freedom of the reactant and the formation of five new vibrational molecule complex will be formed in a collision between the reaction only if the necessary arrangement of the activation ever into the new degrees of freedom can occur. Further for atoms and simple molecules the energy transfer takes place readily, since few degrees of freedom are involved and almost every collision with the requisite ever results in reaction. With more complicated reactants the chances of formation of activated complex are small. Since energy transitions in six degrees of freedom are necessary only a small fraction of the activated collision will lead to chemical reactions. The P factor is thus connected with the activated state, which is an essential intermediate in all reactions, is to be formed even when total energy is available. In a sense the latter treatment is an elaborated collision theory for it provided a feasible approach to the problem of evaluating the number of encounters between the molecules in which conditions the reaction is possible.

Unimolecular Reactions and Lindemann

It is easy to understand a bimolecular reaction on the basis of collision theory. Thus, when two molecules A and B collide their relative kinetic energy exceeds the *threshold energy,* the collision may result in the breaking of bonds and the formation of new bonds. But how can one account for a unimolecular reaction ? If we assume that in such a reaction (A → P) the molecule A acquires the necessary activation energy by colliding with another molecule, then the reaction should obey second-order kinetics and not the first-order kinetics which is actually observed in several unimolecular gaseous reactions. A satisfactory theory of these reactions was proposed by F.A. Lindemann in 1922. According to him, a unimolecular reaction

$$A \rightarrow P \qquad ...(2.63)$$

proceeds via the following mechanism:

$$\left.\begin{array}{l} A + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A^* + A \\ A^* \xrightarrow{k_2} P \end{array}\right\} \qquad ...(2.64)$$

Here A* is the energised A molecule which has acquired sufficient vibrational energy to enable it to isomerise or decompose.

In other words, the vibrational energy of A exceeds the threshold energy for the overall reaction A → Products. It must be borne in mind that A* is simply a molecule in a high vibrational energy level and not an activated complex. In the first step, the energised molecule A* is produced by collision with another molecule A.

What actually happens is that the kinetic energy of the second molecule is transferred into the vibrational energy of the first. (In fact, the second molecule need not be of the same species; it could be a product molecule or a foreign molecule present in the system which, however, does not appear in the overall stoichiometric reaction A → P). The rate constant for the energisation step is k_1. After the production of A *, it can either be de-energised back to A (in the reverse step, with rate constant k_{-1}) by collision in which case its vibrational energy is transferred to the kinetic energy of an A molecule or be decomposed or isomerised to products (in the step with rate constant k_2) in which case the excess vibrational energy is used to break the appropriate chemical bonds.

In the Lindemann mechanism, a time lag exists between the energisation of A to A* and the decomposition (or isomerisation) of A* to products. During this time lag, A* can be de-energised back to A. According to the steady-state approximation (s.s.a), whenever a reactive *(i.e.,* short-lived) species is produced as an intermediate in a chemical reaction, its rate of formation is equal to its rate of decomposition. Here, the energised species A* is short-lived. Its rate of formation = $k_1[A]^2$ and its rate of decomposition k_{-1} [A][A*] + k_2 *[A*].* Thus,

$$\frac{d\left[A^*\right]}{dt} = k_1 [A]^2 - k_{-1} [A] [A^*] - k_2 [A^*] = 0 \qquad ...(2.65)$$

So that

$$\left[A^*\right] = \frac{k_1 [A]^2}{k_{-1} [A] + k_2} \qquad ...(2.66)$$

The rate of the reaction is given by

$$r = -d[A]/dt = K_2[A^*] \qquad ...(2.67)$$

Substituting Eq. 2.66 in Eq. 2.67

$$r = \frac{k_1 k_2 [A]^2}{k_{-1} [A] + k_2} \qquad ...(2.68)$$

The rate law given by Eq. 2.68 has no definite order. We can, however, consider two limiting cases depending upon which of the two terms in the denominator of Eq. 2.68 is greater. If $k_{-1}[A] >> k_2$, then the k_2 term in the denominator can be neglected giving

$$r = -(k_1k_2/k_{-1})[\mathrm{A}] \qquad ...(2.69)$$

which is the rate equation for a first-order reaction. In gaseous reaction this is the high-pressure limit because, at very high pressures, [A] is very large so that $k_{-1}[\mathrm{A}] >> k_2$.

If $k_2 >> \mathrm{k}_{-1}[\mathrm{A}]$, then the k_{-1} [A] term in the denominator can be neglected to give

$$r = k_1 [\mathrm{A}]^2 \qquad ....(2.70)$$

which is the rate equation for a second-order reaction. This is the low pressure limit. The experimental rate is defined as

$$r = \mathrm{k}_{\mathrm{uni}}[\mathrm{A}] \qquad ....(2.71)$$

where k_{uni} is the unimolecular rate constant. Comparing Eqs. 2.68 and 2.71, we have

$$k_{uni} = \frac{k_1k_2[A]}{k_{-1}[A]+k_2} = \frac{k_1k_2}{k_{-1}+k_2/[A]} \qquad ...(2.72)$$

Note: The Lindemann mechanism was also suggested independently by Christiansen. Hence, it is also sometimes referred to as the Lindemann-Christiansen mechanism. The theory of unimolecular reactions was further developed by Hinshelwood and refined by Rice, Rampsberger, Kassel and Marcus.

Example: Consider the following Lindemann mechanism for the unimolecular decomposition of a molecule A in the presence of a species M (which may be any molecule such as an inert gas like helium or even A itself):

$A + M \xrightarrow{k_1} A^* + \mathrm{M}$ (activation)

$\mathrm{A}^* + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$ (deactivation)

$A^* \xrightarrow{k_2} P$ (reaction)

Using the steady-state approximation (s.s.a), derive the rate law for the formation of the product.

Solution: $r = -d[A]/dt = +d[P]/dt = \mathrm{k}_2[\mathrm{A}^*]$

Applying s.s.a. to the transient species A *,

$$k_1\,[\mathrm{A}]\,[\mathrm{M}] - k_{-1}\,[\mathrm{A}^*]\,[\mathrm{M}] - k_2\,[A^*] = 0$$

or
$$k_1\,[\mathrm{A}]\,[\mathrm{M}] = (k_{-1}\,[M] + k_2)\,[\mathrm{A}^*]$$

$$[\mathrm{A}^*] = \frac{k_1[A][M]}{k_{-1}[M]+k_2}$$

Substituting this expression in Eq. *(i),* we obtain

$$r = k_x k_2 \frac{k_1[A][M]}{k_{-1}[M]+k_2}$$

Complex Reactions: their Kinetics

The study of chemical kinetics becomes highly complicated due to the occurrence of *complex reactions* which involve more than one step. Important among such reactions are the following categories:

1. Opposing or Reversible Reactions
2. Consecutive Reactions
3. Competing or Parallel Reactions

We shall discuss here the kinetics of these reactions briefly.

1. ***Kinetics of Opposing or Reversible Reactions*****:** The kinetics of such reactions are usually studied in the initial stages of the process when the products are at too low a concentration to set up the opposing reaction at a noticeable rate. However, when the opposing reaction also takes place at a comparable rate, the problem becomes complicated and the rate constant obtained is not quite reliable.

Consider the simplest case of an opposing reaction in which the forward as well as the reverse reactions are both first-order:

$$A \underset{k_b}{\overset{k_f}{\rightleftarrows}} B$$

where k_f and k_{-b} are the rate constants of the forward and the reverse reactions, respectively. Let *a* be the initial concentration of the reactant A. (It is assumed that initially the concentration of B = 0). Then, after time *t,* the concentration of A will be ($a - x$) and that of the product B will be x. The rate of the forward reaction is equal to $k_f\,(a - x)$ while that of the reverse reaction is $k_{-b}x$. Hence, the net rate of the formation of B is given by

$$dx/dt = k_f(a - x) - \mathrm{k}_{-\mathrm{b}}x \qquad \text{...(2.73)}$$

A second order reaction opposed by a first order reaction rate follow:

$$\frac{dx}{dt} = k_f(a-x)^2 - k_{-b}x$$

where both direct and reverse reaction are of second order, then the net rate for forward reaction is

$$\frac{dx}{dt} = k_f(a-x)^2 - k_{-b}x^2$$

An interesting example of this is the reaction

$$H_2 + I_2 \underset{k_{-b}}{\overset{k_f}{\rightleftarrows}} 2HI$$

2. ***Kinetics of Consecutive Reactions*****:** Reactions which take place in two or more steps, one after the other are called *consecutive reactions*. Their characteristic features are illustrated with an example consider two consecutive first order reaction. Thus, the sequence

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

could be regarded as typical consecutive reaction involving first order steps. Let the concentrations (in moles/lt) of the species involved be

	[A]	**[B]**	**[C]**
Initial concentration	a_0	0	0
Concentration at time t	a	b	c

The rate of consumption of A, $-\frac{d[A]}{dt}$ given by $-k$, or

$$a = a_0 \exp[-k_1 t] \qquad ...(2.74)$$

i.e., the concentration of A falls off exponentially with time. Since the net rate of consumption of B = Rate of consumption – Rate of formation

Therefore, $$\frac{d[B]}{dt} = k_2 b - k_1 a$$

Substituting the value of a from equation 2.74

$$-\frac{d[B]}{dt} = k_2 b - k_1 a_0 \exp(-k_1 t) \qquad ...(2.75)$$

This is a linear differential equation of first order, whose solution is

$$b = a_0 \frac{k_1}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right] \qquad \text{...(2.76)}$$

As during the reaction, there is no change in the number of moles

$$a + b + c = 0$$

or

$$\begin{aligned} c &= a_0 - (a + b) \\ &= \frac{a_0 k_1}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t) - a_0 \exp(-k_1 t)\right] \\ &= a_0\left[1 - \frac{k_2}{k_2 - k_1}\exp(-k_1 t) + \frac{k_1}{k_2 - k_1}\exp(-k_2 t)\right] \end{aligned} \qquad \text{...(2.77)}$$

The variation of the concentration of the constituents with time are presented in the following figure.

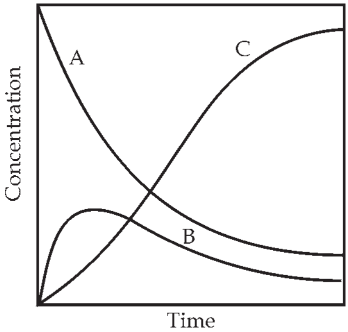


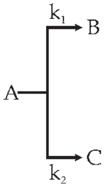
Fig. *Concentration-time graph in a consecutive reaction*

$A \xrightarrow{k_1} B \xrightarrow{k_2} c$, *when* $k_1 \neq k_2$

Concentration of A decreases exponentially (Eq. 2.74) irrespective of the fate of its product B. Concentration of B increases to a maximum and when the rate of decomposition due to accumulation, becomes greater than its rate of formation, it falls to zero. The concentration C increases steadily until it attains a limiting value. The simplest examples of consecutive reactions of first order are those involving radioactive series. Other examples include hydrolysis of various esters, *e.g.,* of polybasic acids or polyhydric alochols, in the presence of HCl.

Some connective reactions start after a little time of mixing. This time interval is called *Period of Induction*. This period, however, depends upon the concentration of the substances in solution.

3. ***Competing or Parallel Reactions*:** Some time a given substance reacts or decomposes in more than one way. Then the alternate/parallel reaction must also be taken into consideration in analysing the kinetic data. Consider the simplest case of a first order irreversible reactions A → B + C leading to the formation of two products through different path ways of first order.



The overall rate of reaction

$$\frac{dx}{dt} = k_1(a - x) + k_2(a - x) \qquad \text{...(2.78)}$$

where $(a - x)$ is the concentration of A at any instant during the course of reaction

or
$$\frac{dx}{dt} = (k_1 + k_2)\ (a - x)$$

Integration under the condition that at $t = 0$ $x = 0$, gives

$$k = (k_1 + k_2) = \frac{1}{t}\ln\left(\frac{a}{a-x}\right) \qquad \text{...(2.79)}$$

This is a typical *first order* kinetic equation.

Since, the rates of formation of the products B and C are given by

$$\frac{db}{dt} = k_1(a - x)$$

$$\frac{dc}{dt} = k_2(a - x)$$

the ratios of their concentrations at any instant, would equal the ratio k_1/k_2. Thus, if the concentration ratio is determined at any stage and k is found from the kinetic equation, individual rate constants can be determined.

This type of reactions are very common in organic chemistry (substitution reaction). For example the chlorination of methane may give mono, di, tri and/or tetra halogen derivative.

Concept of Femtochemistry

In 1872, an English photographer Eadward Muybridge was trying to capture on film a horse flying through the air. It was challenging enough for him in those days since the eye could not follow such a motion and he was given a handsome grant by a businessman to do that. After many attempts, Muybridge developed a camera shutter, which opened and closed for only two thousandths of a second. To do the experiment Muybridge spaced 12 of these cameras half a metre apart alongside the horse track. A string was stretched across the track to a mechanism that would trigger the camera when the horse broke through the string. This shutter speed allowed him to attain a resolution of about 2 centimetres in each picture for a horse that was galloping at 10 metres per second (resolution is defined as the speed of the horse multiplied by the exposure time). The speed divided by the spacing between the cameras equals the number of frames per second, which is 20 in this example. The motion within a picture becomes sharper as the shutter speed becomes faster.

The resolution of the motion improves as the spacing between the cameras is reduced. Two aspects of high-speed photography described above are relevant to femtosecond molecular spectroscopy pioneered by Zewail and his co-workers at Caltech. First a continuous motion is broken up into a series of snapshots or frames. In this way a fast motion is slowed down so that the eye can see it. Second, both methods must produce enough snapshots in rapid succession in such a way that the frames can be arranged to produce an illusion of a continuous motion. In fact, approximately 30 frames are necessary to provide one second of animation.

Molecular Photography

The time resolution or shutter speed needed to capture bond making and bond breaking processes is beyond any conventional scale. When a molecule dissociates into fragments or when it combines with another molecule to form a new molecule, it passes through transition states which last less than a trillionth of a second, or one picosecond (10^{-12} second). At a molecular level a reaction starts when two molecules, A and B come close to each other and begin to interact. Finally, through an event of trans-substantiation, a new molecule C which is chemically distinct from A or B is formed. This simple reaction can be depicted as:

$$A + B \rightarrow [A.....B]^{\#} \rightarrow C$$

where the species $[A....B]^{\#}$ conceptualise the full family of configurations through which the reaction evolves *en route* from reagents to products and what Henry Eyring in 1931 called the 'transition state'of the reaction. Conversely, a molecule of C can be excited with light from a source (say a laser) and A and B can be produced. The whole trip from reagents to products involves change in internuclear separation of the order of 10 Angstroms or 1 nanometre. If the typical velocity of the reagents at room temperature were 1000 metres per second, then the entire trip through the transition state would take about 1 picosecond. Therefore, molecular photography as described above would demand a time resolution (shutter speed) which is less than a picosecond or a few femtoseconds. A femtosecond (10^{-15} second) is to a second what a second is to 32 million years. In one femtosecond light travels 0.3 micrometre—about the diametre of a bacterium.

The Apparatus

Although the idea behind these femtosecond experiments is simple, the experimental setup to carry out the experiments is not at all trivial. In brief, it consists of a pulsed laser source capable of generating two femtosecond pulses of various duration (at the moment the world's shortest pulse is 6 femtosecond) a high vacuum chamber where a beam of molecules is flowing, and a sophisticated detector. A start laser flash called the 'pump' pulse intercepts an 'isolated' molecule in a molecular jet and sets the experimental clock at zero. A second flash called the 'probe' pulse suitably delayed with respect to the 'pump' pulse hits the 'same molecule' and captures a photograph of the reaction in progress at that particular instant. Like the cameras in Muybridge's experiment, a femtosecond camera takes snapshots at different delay times to record the progress of the entire reaction from reagents (zero time) to products (long time).

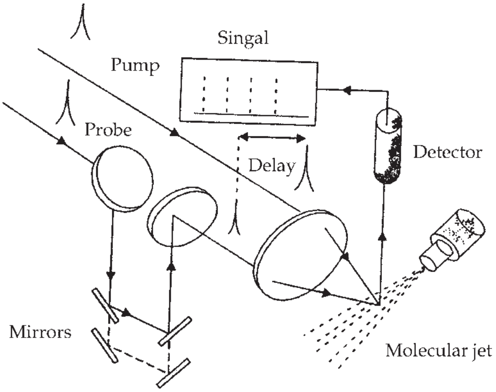
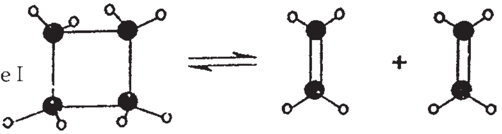


Fig. *Schematic diagram of the femtosecond apparatus used by Ahmed H. Zewail and his co-workers. The femtosecond pump and probe pulses delayed suitably in time with respect to each other are combined and focused on a molecular jet inside a high vacuum chamber. The signal from the interaction region is detected in another direction which can distinguish between events starting at different times.*

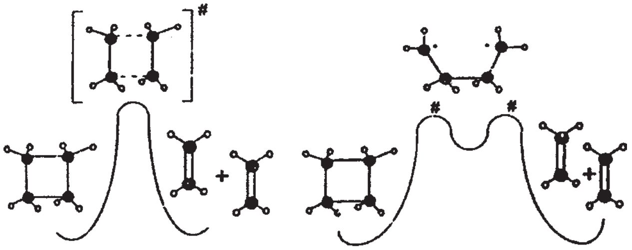
Two Examples

For more than a century, one of the most well studied addition/ elimination reactions is the addition of two ethylene molecules to from cyclobutane or the reverse reaction, involving the ring opening of cyclobutane to produce two ethylene molecules. This is a classic example of a concerted reaction, which is photochemically allowed by Woodward-Hoffman rules. The chemical transformation is shown in *Scheme I.* This reaction, however, may proceed directly through a transition state or it could proceed through a diradical intermediate beginning with the rupture of one σ-bond in cyclobutane to yield tetramethylene, which in turn goes through a transition state to give ethylene. Thus the stability of the diradical as an intermediate is crucial to our understanding of the mechanism of this simple reaction: a concerted single-step process vs a two-step process with an intermediate.

Scheme I



Zewail and his co-workers addressed this question in their laboratory and studied the stability of the tetramethylene diradical generated from various precursors in real time. He showed with femtosecond spectroscopy that intermediate product was in fact formed and had a lifetime of 700 fs. Using cyclopentanone as the precursor they have shown that with two photons at 310 nm (pump) carbon monoxide is eliminated through an α-cleavage.



a b

Fig. *How does the reaction from cyclobutane molecule to two ethylene molecules actually proceed. The left hand figure shows how the state energy varies if both bond are stretched and broken simultaneously. The right hand figure shows the state where one bond at a time breaks.*

The tetramethylene diradical intermediate has been clearly identified by mass spectrometry as a stable species having a lifetime of 700 femtoseconds.

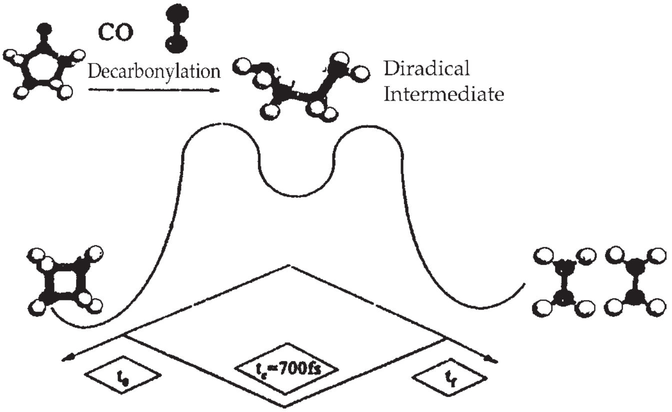


Fig. *The diradical reaction shown shcmatically in an energy diagram. After elimination of carbon ntortoxide from the parent cyclopentanone phtochemically the tetramethylene diradical is created; this can undergo ring closure to yield cyclobutane or can produce two ethylenes.*

By varying the 'pump' wavelength (total energy) and using different substitutions on the ring, they have concluded that this cycloaddition reaction, contrary to the current belief, proceeds in a non-concerted fashion through an intermediate via a two-step process. This approach is general for the study of other, reaction intermediates.

Another example where the femtosecond dynamics of bond breaking and bond making was examined is a simple exchange reaction between bromine atom and iodine molecule which goes through a collision complex (intermediate) as follows:

$$Br + I_2 \rightarrow [Br - I - I]^{\#} \rightarrow BrI + I$$

The time evolution of this reaction was followed by detecting the product BrI with probe-pulse induced fluorescence. The reaction is found to go through a stable collision complex [Br – I – I]. The complex lasts for about 50 picoseconds.

Quantum chemical calculations along with the experimental data predicts that the $[Br - I - I]^{\#}$ complex is bent and the Br – I – I angle is 150 . The energy (depth) of the potential well in which Br – I – I is trapped, as well as the activation energy barrier to go to the final products, have also been determined.

Femtochemistry following Zewail's work has become a 'Buzz word' in experimental physical chemistry research today. It has changed our view of chemical reactions and we can ask detailed questions which could not be asked before.

We can now follow the individual atoms and molecules as they react to produce new molecules or atoms. They are no longer elusive.

A variety of processes and their mechanisms are now being 'clocked' using femtosecond 'pump' and 'probe' experiments. It includes catalysis (to probe mechanism end improve catalysts), liquid phase reactions (to understand reactions in solution), polymers (to improve physical properties of polymers), and biological processes *(e.g.,* to understand the primary photochemical step in vision).

With the development of the world's fastest camera, Zewail has let loose a stream of dreams where only imagination can limit new problems to be explored.

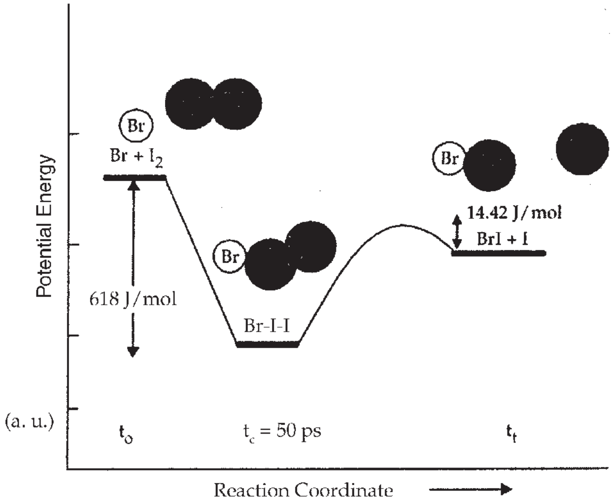


Fig. *The femtosecond dynamics of the iodine atom abstraction reaction. The corresponding structures are shown with emphasis on three molecular photographs at* t_0, t_c *and* t_t *as the reaction proceeds to completion. The calculated well depth and barrier height are also noted.*

Role of Enzyme Catalysis

A very important type of homogeneous catalysis includes reactions catalysed by certain complex organic substances known as *enzymes*. Enzymes are proteins with high relative molar mass of the order of 10,000 or even more and are derived from living organisms.

Each Enzyme can Catalase a Specific Reaction: For instance, the enzyme *diastase* produced in the germinated barley seeds converts starch into maltose sugar.

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Diastase}} nC_{12}H_{22}O_{11}$$

Starch Maltose

Another enzyme known as *maltase* converts maltose into glucose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} 2C_6H_{12}O_6$$

Maltose Glucose

The enzyme known as *zymase,* produced by living yeast cells, converts glucose into ethyl alcohol.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

The enzyme *urease* present in soyabeans brings about quantitative hydrolytic decomposition of urea into ammonia and carbon dioxide.

$$\underset{\text{Urea}}{NH_2CONH_2} + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

All these reactions are consecutive reactions, in which intermediate attains an equilibrium with the reactants; this is called a pre-equilibrium and reactions as pre-equlibrium reactions. The entire Biotechnology is nothing but study of enzyme catalysed reaction. Hence, study of this type of reactions have attained an added importance.

Mechanism and Kinetics of Enzyme-Catalysed Reactions: In 1913, biochemists L. Michaelis and Mary Menten proposed a mechanism for the kinetics of enzyme-catalysed reactions which envisages the following steps:

Step 1. Formation of the Enzyme-Substrate Complex:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\text{(complex)}}{ES} \qquad \text{(fast)}$$

Step 2. Decomposition of the Complex: $ES \xrightarrow{k_2} P + E$ (slow)

where E is the (free) enzyme; S is the substrate *(i.e.,* the reactant); ES is the enzyme-substrate complex and P is the product. In the overall reaction S → P, the enzyme is consumed in step 1 and regenerated in step 2.

The problem can be handled using either the *equilibrium approximation* on the *steady state approximation.* Experiment shows, however, that true equilibrium is not achieved in the fast step because, the subsequent slow reaction is constantly removing the intermediate enzyme-substrate complex, ES. Generally, the enzyme concentration is far less than the substrate concentration, *i.e.,* [E] << [S], so that [ES] << [S]. Hence, we can use the steady state approximation for the intermediate, ES.

According to the slow rate-determining step, the rate of the reaction is given by

$$r = -\frac{d[S]}{dt} = +\frac{d[P]}{dt} = k_2\,[ES] \qquad ...(2.80)$$

Using steady state approximation for ES, we have

$$d[ES]/dt = k_1\,[E][S] - k_{-1}\,[ES] - k_2\,[ES] = 0 \qquad ...(2.81)$$

Now, [E] cannot be measured experimentally. The equilibrium between the free and bound enzyme is given by the *enzyme conservation equation, viz.,*

$$[E]_0 = [E] + [ES]$$

where $[E]_0$ is the total enzyme concentration (which can be measured); [E] is the free enzyme concentration and [ES] is the bound (or reacted) enzyme concentration. Thus,

$$[E] = [E]_0 - [ES] \qquad ...(2.82)$$

Substituting for [E] in Eq. 2.81

$$d[Es]/dt = k_1\left\{[E]_0 - [ES]\right\}[S] - k_{-1}\,[ES] - k_2\,[ES] = 0 \quad ..(2.83)$$

Collecting terms and simplifying,

$$k_1\,[E]_0\,[S] = \left\{k_{-1} + k_2 + k_1\,[S]\right\}[ES] \qquad (2.84)$$

$$[ES] = \frac{k_1 k_2\,[E]_0\,[S]}{k_{-1} + k_2 + k_1\,[S]} \qquad ...(2.85)$$

Substituting for [ES] in Eq. 2.80

$$r = \frac{k_1 k_2\,[E]_0\,[S]}{k_{-1} + k_2 + k_1\,[S]} \qquad ...(2.86)$$

Dividing the numerator and the denominator by k_1,

$$r = \frac{k_1 k_2\,[E]_0\,[S]}{(k_{-1} + k_2)/k_1\,[S]} = \frac{k_2\,[E]_0\,[S]}{K_m + [S]} \qquad ...(2.87)$$

where the new constant K_m, called the *Michaelis constant,* is given by

$$k_m = \left(k_{-1} + k_2\right)/k_1 \qquad ...(2.88)$$

Note that K_m is not an equilibrium constant.

Eq. 2.87 is known as the *Michaelis-Menten equation.*

Further simplification of Eq. 2.87 can be made. When all the enzyme has reacted with the substrate *at high concentration,* the reaction will be going at *maximum rate.* No free enzyme will remain so that $[E]_0$ = [ES]. Hence, from Eq. 2.80.

$$r_{max} = V_{max} = k_2[E]_0 \qquad ...(2.89)$$

where V_{max} is the maximum rate, using the notation of enzymology.

The Michaelis-Menten equation can now be written as

$$r = V_{max}[S]/(K_m + [S]) \qquad ...(2.90)$$

Two cases arise:

(a) $K_m >> [S]$ so that [S] can be neglected in the denominator of Eq. 2.87, giving

$$r = V_{max}[S]/K_m = k'[S] \text{ (first-order reaction)} \qquad ...(2.91)$$

(b) $[S] >> K_m$ so that K_m can be neglected in the denominator, giving

$$r = V_{max} = \text{constant (zero-order reaction)} \qquad ...(2.92)$$

These two cases are shown diagrammatically in the following figure:

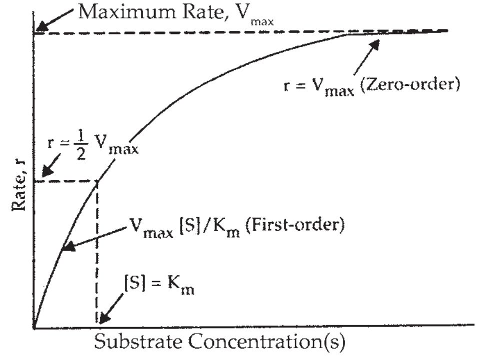


Fig. *Kinetics of an enzyme-catalysed reaction.*

Again, if K_m = [S], $r = \frac{3}{2} V_{max}$ ...(2.93)

Thus Michaelis constant *is equal to that concentration of S at which the rate of formation of product is half the maximum rate obtained at high Concentration of S.*

The constant k_2 in Eq. 2.89 is called the *turnover number of the enzyme.* The turnover number is the number of molecules converted in unit time by one molecule of enzyme. Typical values of k_2 are 100–1,000 per second though they may be as large as 10^5 to 10^6 per second. We would like to know the physical reason why the reaction rate of an enzyme-catalysed reaction changes from first-order to zero-order as the substrate concentration is increased. The answer is that each enzyme molecule has one or more 'active sites' at which the substrate must be bound in order that the catalytic action may occur. At low substrate concentration, most of these active sites remain unoccupied at any time. As the substrate concentration is increased, the number of active sites which are occupied increases and hence the reaction rate also increases. However, at very high substrate concentration, virtually all the active sites, are occupied at any time so that further increase in substrate concentration cannot further increase the formation of enzyme-substrate complex. It is rather difficult to determine V_{max} (and hence K_m) directly from the plot of r against [S]. If is, however, possible to rearrange Equation (2.87) so as to permit some alternative plots for easy determination of V_{max}. Two of the best known methods which make use of the rearranged equations are as follows:

1. ***The Lineweaver-Burk Method***: This method uses the rearranged equation

$$1/r = K_m/[S]V_{max}) + 1/V_{max} \qquad ...(2.94)$$

A plot of 1/r against 1/[S] gives a straight line whose intercepts on the x-axis and y-axis are ($-1/K_m$) and $1/V_{max}$, respectively and whose slope is (K_m/V_{max}), as shown in the following figure:

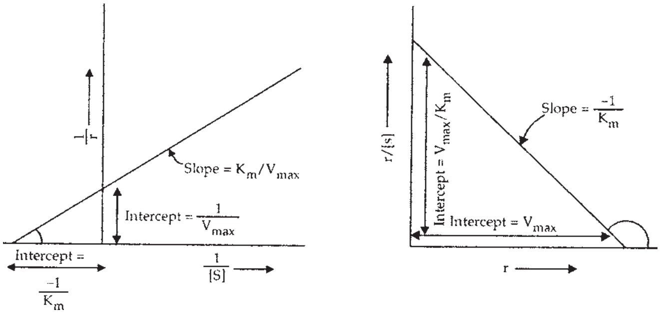


Fig. *(first) The Lineweaver-Burk method of plotting enzyme kinetic data (second) Eadie-Hofstee method of plotting enzyme kinetic data.*

2. ***The Eadie-Hofstee Method***: This method uses the rearranged equation

$$r/[Sl = V_{max}/K_m - r/K_m \qquad ...(2.95)$$

A plot of *r/[S]* against *r* gives a straight line with slope equal to $-1/K_m$ and an intercept on the y-axis equal to V_{max}/K_m, as shown in the figure above. From the graph, both K_m and V_{max} can be determined.

Enzyme Catalysis and Temperature

Like chemical catalysts, the enzyme catalysts also decrease the activation energy of a reaction at a given temperature. In fact, the decrease of activation energy by an enzyme catalyst is far greater than that by a non-enzyme catalyst. While the rate of a reaction generally increases with an increase in temperature, this condition would be highly unfavourable for a living cell. Enzymes are, in fact, very sensitive to high temperatures. Because of the proteinous nature of an enzyme, increase in temperature results in *denaturation* of the enzyme protein which leads to a decrease in effective concentration of the enzyme and hence a decrease in reaction rate. Upto about 45 C, the reaction rates of enzyme-catalysed reactions increase with temperature.

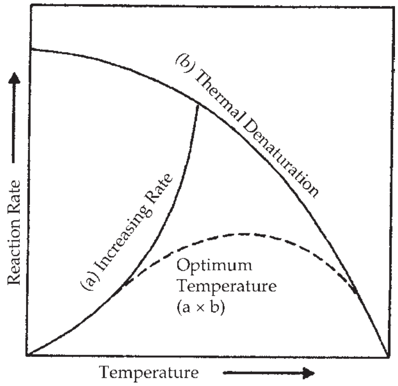


Fig. *Temperature-dependence of the rate of an enzyme-catalysed reaction, (a) represents the increase in rate with increase in temperature* (b) *represents the decrease in rate as a result of thermal denaturation of the enzyme; the dashed line curve shows the combination of* (a) *and* (b).

At temperatures greater than 45 C, thermal denaturation of the enzyme becomes increasingly significant. At about 55 C, rapid denaturation completely destroys the catalytic function of the enzyme protein. The effect of temperature on the rates of enzyme-catalysed reactions is illustrated in the figure above.

3

State of Gas and Liquid

Formation of Gases

Amongst the three common states of matter the gaseous state is the simplest. The laws of gaseous behaviour are more uniform and are better understood. The well-known laws of gaseous behaviour are Boyle's law, Charles's law, Graham's law, Dalton's law and Avogadro's law. At the time of their enunciation, these laws were only empirical generalisations based on experimental observations. There was no theoretical background to justify them. In the nineteenth century, however, Kronig, Clausius, Maxwell and Boltzmann developed a theory, known as Kinetic Molecular Theory of Gases, which provided sound theoretical basis for the various gas laws.

The Kinetic Molecular Theory of Gases

The kinetic molecular theory is based on the following postulates:

1. A gas consists of a large number of minute particles, called molecules. The molecules are so small that their actual volume is a negligible fraction of the total volume (space) occupied by the gas.
2. The molecules are in a state of constant rapid motion in all possible directions, colliding in a random manner with one another and with the walls of the vessel.

3. The molecular collisions are perfectly elastic so that there is no net loss of energy when gas molecules collide with one another or against the walls of the vessel. The kinetic energy may be transferred from one molecule to another but it is not converted into any other form of energy, such as heat.
4. There are no attractive forces between molecules or between molecules and the walls of the vessel in which the gas is contained. The molecules move completely independent of one another.
5. The pressure of a gas is due to the bombardment of the molecules on the walls of the containing vessel.
6. The laws of classical mechanics (in particular the Newton's second law of motion) are applicable to the motion of gaseous molecules.

It may be emphasised that the above postulates are meant for an ideal gas only. These are only approximately valid for a real gas. From the above postulates and classical mechanics, expression $\mathrm{PV} = \frac{1}{3} m N_A c^2$ can be derived. From this equation gas laws can be easily derived.

Kinetic Energy and Temperature: Suppose one mole of a gas is under consideration. The number of molecules involved will then be N_A (the Avogadro's number), *c* is molecular velocity gas molecules. The kinetic gas equation for N_A molecules may be written as

$$PV = \frac{1}{3} m N_A c^2 = \frac{2}{3} \times \frac{1}{2} m N_A c^2 = \frac{2}{3} \times E_t \qquad \text{...3.1}$$

where E_t is the translational kinetic energy of one mole of the gas.

Since for one mole of an ideal gas, $PV = RT$,

$$E_t = 3/2\ RT \qquad \text{...3.2}$$

Thus, the translational kinetic energy of an ideal {perfect) gas is directly proportional to the absolute temperature. This is also known as the Maxwell generalisation.

Further, since translational kinetic energy $\propto c^2$, it follows that

$$c^2 \propto T \qquad (\textit{cf}\ \text{Eq. 3.1})$$

$$\text{or } c \propto \sqrt{T}$$

Thus, the molecular velocity of any gas is proportional to the square root of the absolute temperature. The molecular motion is, therefore, often termed as thermal motion of molecules. At absolute zero *(i.e., $T = 0$)*, kinetic energy is zero. In other words, thermal motion ceases completely at absolute zero.

It readily follows from Eq. 3.2 that the translational kinetic energy of a gas is independent of the volume (or pressure), the molar mass or the nature of the gas. It depends only on temperature (T). Thus, a hydrogen molecule has the same average translational kinetic energy as a molecule of nitrogen, ammonia or methane. The molecular velocity, of course, would be different in each gas.

The average translational kinetic energy of one molecule of an ideal gas will be given by

$$\varepsilon_t = E_t/N_A = (3/2)\, RT/N_A = 3/2\, kT \qquad ...3.3$$

where k (= R/N_A) is the Boltzmann constant whose numerical value = 1.38 10^{-23} J K^{-1}.

Example: Calculate the average translational kinetic energy of an ideal gas per molecule (s,) and per mole (E_t) at 25 C.

Solution: ε_t = 3/2 kT = 3/2 (1.38 10^{-23} J Kr^{-1}) (298 K).

= 6.17 10^{-23} J per molecule

E_t = 3/2 RT= 3/2 (8.314 J K^{-1} mol^{-1}). (298 K)

= 3.716 10^3 J mol^{-1}.

Molecular Velocities: Role of Maxwell

As a result of random collisions of gaseous molecules, the molecular velocities keep on changing. Consider a gas molecule of mass m having a velocity component u. Then, the kinetic energy, e, associated with this velocity component is $1/2\, mu^2$. The probability that this molecule has its velocity component between u and $u + du$ is given by $p(u)\, du$. In the 19th century, Boltzmann had shown that the probability for a molecule to have an energy ε was proportional to $e^{-\varepsilon/KT}$. It is apparent that we can equate this probability with $p(u)\, du$. Thus,

$$p(u)du \propto e^{-\varepsilon/KT} \propto e^{-mu^2/2kT} \qquad (\text{Q}\ \varepsilon = 1/2mu^2)$$

$$p(u)du = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mu^2/2kT} du \qquad ...3.4$$

Eq. 3.4 is called the Maxwell's distribution of molecular velocities in one dimension. It is easy to derive the Maxwell's distribution of molecular velocities in three dimensions by multiplying the three one-dimension distributions with one another. Thus,

$$p(u, v, w) = p(u)p(v)p(w) \qquad \text{...3.5}$$

where v and *w* are the velocity components in the other two dimensions.

$$\therefore \quad p(u, v, w)\, dudvdw = p(u)\, du \quad p(v)dv \quad p(w)dw$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m\left(u^2 + v^2 + w^2\right)}{2kT}\right] dudvdw \qquad \text{...3.6}$$

We are, however, interested in an expression which gives the fraction of molecules with a velocity between *c* and *c + dc* ($c^2 = u^2 + v^2 + w^2$) regardless of the direction. These are molecules whose velocity points lie within a spherical shell of thickness *dc* at a distance *c.* This shell has the volume $4\pi c^2 dc$, which is the integral of *dudvdw* in Eq. 3.6, over the spherical shell. Hence, we find that

$$p(c)dc = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} c^2 \exp\left(-mc^2 / 2kT\right) dc \qquad \text{...3.7}$$

This result was obtained by Maxwell in 1860 and is called the Maxwell's distribution of molecular velocities. It is customary to write *p(c)dc* as *dNIN,* where *N* is the total number of gas molecules. The quantity *dN/N* or *p*(*c*)*dc* gives the fraction of molecules with speeds between *c* and *c + dc.* The molecular mass $m = M_n/N_A$ where M_m is the molar mass and N_A is the Avogadro number. Accordingly, Eq. 3.7 may also be written as

$$p(c)dc = \frac{dN}{N} = 4\pi\left(\frac{M_m}{2\pi RT}\right)^{3/2} c^2 \exp\left(-\frac{M_m c^2}{2RT}\right) dc \qquad \text{...3.8}$$

The Maxwell's distribution of molecular velocities is plotted in the following figure.

We see that the fraction of molecules having velocities greater than zero increases with an increase in velocity, reaches a maximum and then falls off towards zero again at higher velocities.

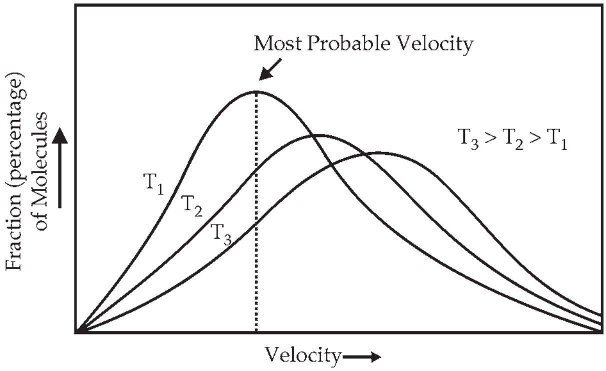


Fig. *Maxwell's distribution of molecular velocities.*

The important features of these curves are as follows:

1. The fraction of molecules with too low or too high velocities is very small.
2. There is a certain velocity for which the fraction of molecules is maximum. This is called the most probable velocity.

The most probable velocity of a gas is the velocity possessed by maximum number of molecules of the gas at a given temperature. It corresponds to the peak of the curve. Its value, at a given temperature, depends upon the volume of the gas.

Molecular Velocities: Temperature Effect

The most probable velocity increases with rise in temperature, as shown in the figure given above. The entire distribution curve, in fact, shifts to the right with rise in temperature, as shown. The rise in temperature, therefore, increases the fraction of the molecules having high velocities considerably. This can readily be understood from the presence of the factor, $\exp(-mc^2/2kT)$, in Eq. 3.7. The exponent has a negative sign and the temperature T is in the denominator. The factor, therefore, increases markedly with increase in temperature. This factor is known as the Boltzmann factor.

Further, knowing that $1/2\ mc^2$ is the kinetic energy of one molecule of the gas having velocity c, the factor

$$\exp(= mc^2/2\text{kT}) = \exp(-\varepsilon/\text{kT}) \qquad ...3.9$$

where ε $(= 1/2\ mc^2)$ gives the kinetic energy per molecule of the gas. Evidently, the greater the temperature, the greater is the value of ε. Hence, there is rapid increase of the Boltzmann factor with increase in temperature. This conclusion finds application in the theory of reaction rates also.

Types of Molecular Velocities: Three types of molecular velocities are reckoned with in the study of gases. These are: (i) the most probable velocity, c_p (ii) the average velocity, $<c>$, and (iii) the root mean square velocity $<c^2>^{1/2}$.

The most probable velocity is defined as the velocity possessed by maximum number of molecules of a gas at a given temperature.

The average velocity is given by the arithmetic mean *of t*he different velocities possessed by the molecules of the gas at a given temperature. If $c_1, c_2, c_3, ...c_n$ are the individual velocities of the gas molecules and n is their total number, then, average velocity is given by

$$\langle c \rangle = \frac{c_1 + c_2 + c_3 + ...c_n}{n} \qquad ...3.10$$

If, however, $c_x, c_2, c_3, ...$ are the velocities possessed by groups of $n_1, n_2, n_3, ...$ molecules of the gas, respectively, then, average velocity is given by

$$\langle c \rangle = \frac{n_1c_1 + n_2c_2 + n_3c_3 + ...}{n_1 + n_2 + n_3 + ...} \qquad ...3.11$$

The root mean square velocity is defined as the *square root of the mean of the squares of different velocities possessed by molecules of a gas at a given temperature.* Evidently, the root mean square velocity would be given by

$$\langle c^2 \rangle^{1/2} = \left[\frac{c_1^2 + c_2^2 + c_3^2 + ...c_n^2}{n}\right]^{1/2} \qquad ...3.12$$

where $c_1\ c_2, c_3 ....c_n$ are the individual velocities of n molecules of the gas. Alternatively,

$$\langle c^2 \rangle^{1/2} = \left[\frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + ...}{n_1 + n_2 + n_3 + ...}\right]^{\frac{1}{2}} \qquad ...3.13$$

where $c_1, c_2, c_3 .....$ are velocities possessed by groups of $n_1, n_2, n_3, ...$ molecules, respectively.

With the help of the Maxwell equation Eq. 3.8, it is possible to derive mathematical expressions for the three types of velocities, *viz.,* the *most probable velocity,* c_p; the *average velocity,* $<c>$ *and the root-mean-square velocity,* $<c^2>^{1/2}$. *These expressions are as follows:*

$$c_p = \left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{2RT}{M_m}\right)^{1/2} \qquad ...3.14$$

$$\langle c \rangle = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M_m}\right)^{1/2} \qquad ...3.15$$

$$\langle c^2 \rangle^{1/2} = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3RT}{M_m}\right)^{1/2} \qquad ...3.16$$

It is found that

$<c^2>^{1/2}:<c>:c_p = 1.00:0.92:0.82$

The molecular distribution of the three types of velocities is shown in the following figure.

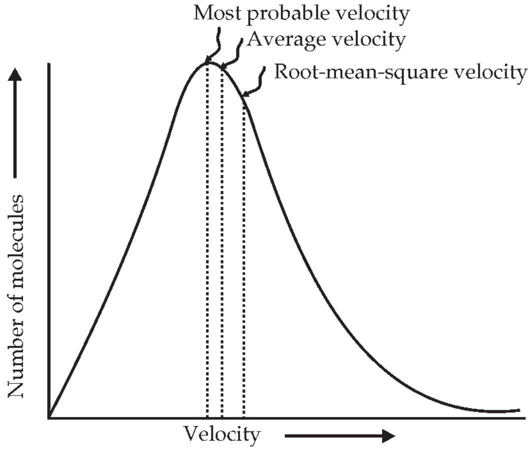


Fig. *Molecular distribution of the three types of velocities.*

Example: For hydrogen gas, calculate (a) the root mean square velocity $<c^2>^{1/2}$ (b) the average velocity $<c>$ and (c) the most probable velocity c_p at 0 C.

Solution: The molar mass M_m of H_2 = 2.016 g mol^{-1} = 2.016 10^{-3} kg mol^{-1} From Eq. 3.16

(a) $$\langle c^2\rangle^{1/2} = \left[\frac{3RT}{M_m}\right]^{1/2} = \left(\frac{(3)\left(8.314\,\mathrm{JK^{-1}\,mol^{-1}}\right)273.15K}{2.016\times10^{-3}\,\mathrm{kg\,mol^{-1}}}\right)^{1/2}$$

Recalling that J = kg m^2 s^{-2}, we find that

$<c>^{1/2}$ = 1.84 10^3 m s^{-1}

(b) From Eq. 3.15

$$<c> = \left(\frac{8RT}{\pi M_m}\right)^{1/2} = \left(\frac{\left(8.314K^{-1}\,\mathrm{mol^{-1}}\right)(273.15K)}{(3.1416)\left(2.016\times10^{-3}\,\mathrm{kg\,mol^{-1}}\right)}\right)^{1/2}$$

= 1.69 10^3 m s^1

(c) From Eq. 3.14

$$c_p = \left(\frac{2RT}{M_m}\right)^{1/2} = \left(\frac{(2)\left(8.314\,\mathrm{JK^{-1}\,mol^{-1}}\right)(273.15\,\mathrm{K})}{2.016\times10^{-3}\,\mathrm{kg\,mol^{-1}}}\right)^{1/2}$$

= 1.50 10^3 m s^1

The average velocities of some gaseous molecules are given in the following table.

Table: Average Velocities (m s^{-1}) of Some Gaseous Molecules at 0 C

Gas	<c>	Gas	<c>
Hydrogen	1692	Mercury vapour	170.0
Deuterium	1196.0	Argon	380.0
Helium	1204.0	Methane	600.6
Nitrogen	454.2	Ammonia	562.7
Oxygen	425.2	Carbon dioxide	362.5
Chlorine	285.6	Carbon monoxide	454.5

***Example*:** Calculation the temperature at which the root mean square velocity, the average velocity and the most probable velocity of oxygen gas are all equal to 1,500 m s^{-1}.

***Solution*:** Let the respective temperatures be T_1, T_2 and T_3.

(i) cms = $<c^2>^{1/2}$ $= \left(3RT_i / M_m\right)^{1/2} = 1.5\times10^3\,\mathrm{ms^{-1}}$

$$T_1 = \frac{\left(1.5\times10^3\ \mathrm{ms^{-1}}\right)^2\left(32\times10^{-3}\ \mathrm{kg\,mol^{-1}}\right)}{3\times8.314\,\mathrm{JK^{-1}\,mol^{-1}}}$$

$$\left[\mathrm{Q}\ M_m = 32\,\mathrm{mol^{-1}}\right]$$

$$= 2886\ \mathrm{K}$$

(ii) $$\langle c\rangle = \left(8RT_2/\pi M_m\right)^{1/2} = 1.5\times10^3\ \mathrm{ms^{-1}}$$

$$T_2 = \frac{\left(1.5\times10^3\ \mathrm{ms^{-1}}\right)^2\left(32\times10^{-3}\ \mathrm{kg\,mol^{-1}}\right)(3.1416)}{8\times8.314\,\mathrm{JK^{-1}\,mol^{-1}}}$$

$$= 3399\ \mathrm{K}$$

(iii) $$c_p = \left(2RT_3/M_m\right)^{1/2} = 1.5\times10^3\ \mathrm{ms^{-1}}$$

$$T_3 = \frac{\left(1.5\times10^3\ \mathrm{ms^{-1}}\right)^2\left(32\times10^{-3}\ \mathrm{kg\,mol^{-1}}\right)}{2\times8.314\,\mathrm{JK^{-1}\,mol^{-1}}}$$

Example: Calculate the temperature at which the average velocity of oxygen equals that of hydrogen at 300K.

Solution: $\langle c\rangle = (3RT/M_m)^{1/2}$, *i.e.*, $\langle c\rangle \propto (T/M_m)^{1/2}$

Let $\langle c\rangle_1$ and $\langle c\rangle_2$ be the average velocities of O_2 and H_2, respectively.

$$\frac{\langle c\rangle_1}{\langle c\rangle_2} = \left(\frac{T_1/M_{m1}}{T_2/M_{m2}}\right)^{1/2} = 1$$

$$T_1/M_{m1} = T_2/M_{m2}$$

or $$T_2\ /\ 32\mathrm{g\ mol^{-1}} = T_2/2\mathrm{g\ mol^{-1}}$$

$$T_1 = (32/2)\ T_2 = 16\quad 300\ \mathrm{K} = 4800\ \mathrm{K}$$

Example: Calculate the value of p(c) for oxygen molecules at 27 C when $c = c_p$, where c is the most probable velocity.

Solution: The Maxwell equation for distribution of molecular velocities may be put as

$$p(c) = \frac{dN}{Ndc} = 4\pi\left(\frac{M_m}{2\pi RT}\right)^{3/2} c^2 \exp\left(-\frac{M_m c^2}{2RT}\right)$$

From Eq. 3.15,

$$c_p \equiv c = \left(\frac{2RT}{M_m}\right)^{1/2} = \left[\frac{2\times 8.314\,\text{JK}^{-1}\,\text{mol}^{-1}\times 300K}{32\times 10^{-3}\,\text{kg}\,\text{mol}^{-1}}\right]^{1/2}$$

$$= 3.948 \quad 10^{2}\ \text{ms}^{-1} \qquad \left(J = \text{kg}\,\text{m}^{2}\,\text{s}^{-2}\right)$$

$$\left(\frac{M_m}{2\pi RT}\right)^{3/2} = \left[\frac{32\times 10^{-3}\,\text{kg}\,\text{mol}^{-1}}{2\times 3.1416\times\left(8.314\,\text{JK}^{-1}\,\text{mol}^{-1}\right)(3000K)}\right]^{3/2}$$

$$\frac{M_m c^2}{2RT} = \frac{\left(32\times 10^{-3}\,\text{kg}\,\text{mol}^{-1}\right)\left(3.948\times 10^{2}\,\text{ms}^{-1}\right)^{2}}{(2)\left(8.314\,\text{JK}^{-1}\,\text{mol}^{-1}\right)(300K)} = 0.999$$

$$\therefore \quad \exp\left(-\frac{M_m c^2}{2RT}\right) = \exp(-0.999) = 0.3679$$

$$\therefore \ p(c) = (4\pi)\left(2.92\times 10^{-9}\,m^{-3}s^{2}\right)\left(3.948\times 10^{2}\,ms^{-1}\right)^{2}(0.3679)$$

$$= 2.10\times 10^{3}\,m^{-1}$$

Example: Derive an expression for the root mean square velocity $<c^2>^{1/2}$ of an ideal gas in terms of pressure and density of the gas.

Solution: From Eq. 3.16

$$\left\langle c^2\right\rangle^{1/2} = \left(\frac{3RT}{M_m}\right)^{1/2} \qquad \text{...(i)}$$

For an ideal gas, $PV = nRT = mRT/M_m$

where m is the mass of the gas and M_m its molar mass.

$\therefore \quad P = \dfrac{mRT}{VM_m} = \dfrac{\rho RT}{M_m}$ where $\rho = (= m/V)$ is the density of the gas.

$\therefore$ RT/Mm = P/ρ

Substituting in Eq. (i),

$\langle c\rangle^{1/2} = (3P/\rho)^{1/2}$ which is the desired expression.

Example: Calculate the root mean square velocity of nitrogen at 27 C and 70 cm pressure. Density of Hg 13.6 g cm^{-3}.

Solution: Volume V_2 at 27 C and 70 cm pressure is given by

$$\frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1}$$

$$\frac{70\,\text{cm} \times V_2}{300K} = \frac{76\,\text{cm} \times 0.0224\,\text{m}^3}{273K}$$

$$\text{V}_2 = 0.026725\,\text{m}^3$$

$$\langle c \rangle = \left(\frac{3RT}{M_m}\right)^{1/2} = \left(\frac{3PV}{M_m}\right)^{1/2}$$

$$= \left(\frac{(3)(70/76) \times \left(101{,}325\,\text{Nm}^{-2}\right)\left(0.026725\,\text{m}^3\,\text{mol}^{-1}\right)}{28 \times 10^{-3}\,\text{kg mol}^{-1}}\right)^{1/2}$$

$$= 517\text{ms}^{-1} \text{ (Newton, N = kg m s}^{-2}\text{)}$$

It is evident that gases have very high molecular velocities. The root mean square velocities for nitrogen and hydrogen, as calculated in the above problems, when expressed in other units, amount to approximately 30 and 110 km per minute, respectively.

Role of Collision Diameter

The kinetic theory of gases treats molecules as point masses. When two such molecules approach each other, a point is reached at which the mutual repulsion between the molecules (resulting from, electronic and nuclear repulsions) becomes so strong that it causes reversal of the direction of their motion.

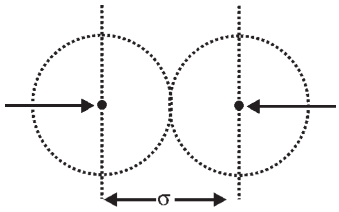


Fig. *Collision of two molecules, concept of collision diameter.*

The distance between the centres of the two molecules at the point of their closest approach is known as collision diameter. It is represented by sigma *(σ),* as shown in the figure given below. Evidently, a gaseous molecule can be regarded as a rigid (or hard) sphere of radius σ. The volume $(4/3)\pi\sigma^3$ is known as the effective volume of the molecule.

It can be easily seen that if the distance between the centres of two molecules is less than σ, there would be a collision between them. Thus, collision is an event in which the centres of two identical molecules come within a distance σ from each other.

Collision Cross-Section: The model of gaseous molecules as hard, non-interacting spheres of diameter σ can satisfactorily account for various gaseous properties such as the transport properties (viscosity, diffusion and thermal conductivity), the mean free path and the number of collisions the molecules undergo. It can be easily visualised that when two molecules collide, the effective area of the target is $\pi\sigma^2$. The quantity $\pi\sigma^2$ is called the collision cross-section of the molecule because it is the cross-sectional area of an imaginary sphere surrounding the molecule into which the centre of another molecule cannot penetrate.

Collision Number: It can be shown on kinetic considerations that in a gas the number of molecules with which a single molecule will collide per unit time is given by $\sqrt{2}\pi\sigma^2 <c> \rho$ where <c> is the average velocity of the molecules and ρ is the number density, *i.e.,* the number of molecules per unit volume of the gas. This expression, evidently, gives the number of collisions suffered by a single molecule per unit time per unit volume of the gas. This is known as the collision number. Thus,

$$Z_1 = \sqrt{2}\pi\sigma^2 <c> \rho \qquad ...3.17$$

The total number of molecules colliding per unit time per unit volume of the gas is, therefore, given by $\sqrt{2}\pi\sigma^2 <c> \rho$. Since each collision involves two molecules, the number of collisions of like molecules occurring per unit time per unit volume of the gas is given by

$$Z_{11} = \frac{1}{2}\left(\sqrt{2}\pi\sigma^2 <c> \rho^2\right) = \frac{1}{\sqrt{2}}\left(\pi\sigma^2 <c> \rho^2\right) \qquad ...3.18$$

Collision Frequency: The number Z_{11} in Eq. 3.18 gives the *collision frequency* of the gas. Thus, collision frequency is the *number of molecular collisions occurring per unit time per unit volume of the gas.*

It readily follows that the number of collisions of molecules of type 1 with those of type 2 would be given by

$$Z_{12} = \frac{1}{\sqrt{2}}\left(\pi\sigma^2 <c> \rho_1\rho_2\right) \qquad ...3.19$$

where ρ_1, and ρ_2 are the *number densities* of molecules of type 1 and 2, respectively. The number density ρ is equal to P/kT, as shown below:

For an ideal gas, $PV = nRT = nN_AkT$

$$P = nN_AkT/V = NkT/V \qquad ...3.20$$

where $N (= nN_A)$ is the total number of molecules in n moles of the gas. Since ρ is the number of molecules per unit volume, hence $\rho = N/V$. Thus, $P = pkT$.

$$\therefore \quad \rho = P/kT \qquad ...3.21$$

Eqs. 3.17 and 3.18 may thus be written as

$$Z_1 = \sqrt{2}\pi\sigma^2 <c> P/kT \qquad ..3.22$$

$$Z_{11} = \frac{\pi\sigma^2 <c> P^2}{\sqrt{2}(kT)^2} \qquad ...3.23$$

It may be noted that while units of Z_1, are s^{-1}, those of Z_{11} are s^{-1} m^{-3}.

Mean Free Path: the Concept

A very important quantity in kinetic theory of gases is the mean free path, λ, defined as *the mean distance travelled by a gas molecule between two successive collisions.* Evidently,

$$\lambda = \frac{<c>}{Z_1} = \frac{<c>}{\sqrt{2}\pi\sigma^2 <c> P/kT} = \frac{kT}{\sqrt{2}\pi\sigma^2 P} \qquad ...3.24$$

From Eq. 3.24 we see that $\lambda \propto .1/P$, *i.e., the mean free path of a gas molecule is inversely proportional to pressure.* This fact is of tremendous importance in vacuum systems. It should be borne in mind that at 1 atm pressure, λ is very small compared with the macroscopic dimensions (such as 1 cm) which implies that the molecules collide with one another far more frequently than they collide with the walls of the container and that a molecule moves a distance of several molecular diameters before colliding with another molecule.

In a good vacuum where the pressure is of the order of 10^{-3} atm, a simple calculation shows that λ is very large compared with the dimensions of the container. Thus, in a good vacuum the gas molecules collide far more frequently with the walls of the container than with one another. Under such conditions, the gas is called a *Knudsen gas.*

Example: For oxygen gas at 25 C, calculate, (a) the mean free path at 1 atm pressure, (b) the mean free path at 10^{-3} mm Hg pressure, (c) the number of collisions per second per molecule, (d) the number of collisions per cubic metre per second and (e) the number of moles of collisions per dm^3 per second. In parts (c), (d), and (e), the pressure is 1 atm. The collision diameter of oxygen molecule is 361 picometre.

Solution:

(a) 1 atm = $1.01325 \quad 10^5$ Nm^{-2} $\quad T = 25$ C = 298 K

$\sigma = 361$ pm $= 361 \quad 10^{-12}$ m $= 3.61 \quad 10^{-10}$ m

From Eq. 3.24

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 P} = \frac{\left(1.38\times10^{-23}\,JK^{-1}\right)(298K)}{(1.4142)(3.1416)\left(3.61\times10^{-10}\,m\right)^2\left(1.01325\times10^5\,Nm^{-2}\right)}$$

$= 7.02 \quad 10^{-8}$m = 70.2 nm $\qquad$ [J = kg m^2 s^{-2} = 1N m]

(b) $P = 10^{-3}$ mm Hg

$$\frac{\left(10^{-3}\,\text{mm Hg}\right)\left(1.01325\times10^5\,\text{Nm}^{-2}\,\text{atm}^{-1}\right)}{760\,\text{mm Hg atm}^{-1}} = 0.1333\ \text{Nm}^{-2}$$

$$\therefore \qquad \lambda = \frac{\left(1.38\times10^{-23}\,JK^{-1}\right)(298K)}{(1.4142)(3.1416)\left(3.61\times10^{-10}\,m\right)^2\left(0.1333\,Nm^{-2}\right)}$$

$= 5.3 \quad 10^{-2}$ m

(c) From. Eq. 3.17 $Z_1 = \sqrt{2}\pi\sigma^2 <c> \rho = \sqrt{2}\pi\sigma^2 <c> P/kT$

$[\therefore \rho = P/(kT)]$

From Eq. 3.14

$$<c> = \left(\frac{8RT}{\pi M_m}\right)^{\frac{1}{2}} = \left[\frac{(8)\left(8.314\,JK^{-1}\,\text{mol}^{-1}\right)(298K)}{(3.1416)\left(32\times10^{-3}\,\text{kg mol}^{-1}\right)}\right]^{-1/2}$$

$= 444.0$ ms^{-1} $\qquad$ [J = kg m^2 s^{-2}]

$$Z_1 = \frac{(1.4142)(3.1416)\left(3.61\times10^{-10}\ \mathrm{m}\right)^2\left(444.0\,\mathrm{ms}^{-1}\right)\left(1.01325\times10\,\mathrm{Nm}^{-2}\right)}{\left(1.35\times10^{-23}\ \mathrm{JK}^{-1}\right)(298\,\mathrm{K})}$$

$= 6.32 \quad 10^{9}\ \mathrm{s}^{-1}$

(d) From Eq. 3.18

$$Z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2 <c> \rho^2 = \frac{\pi\sigma^2 <c> P^2}{\sqrt{2}(kT)^2} \qquad [\therefore\ \rho = P/kT]$$

$= 7.77 \quad 10^{34}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1}$

(e) $N_A = 6.022 \quad 10^{23}\ \mathrm{mol}^{-1} \quad 1\mathrm{dm}^3 = 10^3\ \mathrm{m}^{-3}$

$$\therefore \qquad Z_{11} = \frac{\left(7.77\times10^{34}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1}\right)\left(10^{-3}\ \mathrm{m}^2\ \mathrm{dm}^{-3}\right)}{6.022\times10^{23}\ \mathrm{mol}^{-1}}$$

$= 1.29 \quad 108\ \mathrm{mol\ dm}^{-3}\ \mathrm{s}^{-1}$

***Example*:** Astronomers have suggested that intergalactic space contained hydrogen atoms at a temperature of 7.8 10^5 K, with about 1 atom per 100 dm^3, (a) Calculate the mean free path of a hydrogen atom in the intergalactic space in light-years, (b) Calculate the approximate average time in years, between collisions of an atom. Assume that the collision diameter of a hydrogen atom is 200 pm.

Solution: A- light-year is the distance travelled by light in the year. It can be shown that 1 light year = 9.464 10^{15} m

(a) From Eq. 3.24

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 P} = \frac{1}{\sqrt{2}\pi\sigma^2\rho} \qquad (\therefore\ \rho = P/(kT))$$

$\sigma = 200\ \mathrm{pm} = 200 \quad 10^{-12}\ \mathrm{m} = 2 \quad 10^{-10}\ \mathrm{m}$

$$\rho = \frac{1\,\mathrm{atom}}{100\,\mathrm{dm}^3} = 10\ \mathrm{atoms\ m}^{-3} \qquad [\therefore\ 1\mathrm{m}^3 = 10^3\ \mathrm{dm}^3]$$

$$\lambda = \frac{1}{(1.4142)(3.1416)\left(2\times10^{-10}\ \mathrm{m}^2\right)\left(10\,\mathrm{atoms\,m}^{-3}\right)} \frac{\mathrm{light-yr}}{9.464\times10^{15}\ \mathrm{m}}$$

= 59 light-year.

(b) The average time between collisions of an atom is given by $t = \lambda/\langle c \rangle$, where $\langle c \rangle$, is the average velocity which according to Eq. 3.16 is given by

$$\langle c \rangle = \left(\frac{8RT}{\pi M_m}\right)^{1/2}$$

$$= \left(\frac{(8)(8.31\,\text{JK}^{-1}\,\text{mol}^{-1})(7.8 \times 10^5\,\text{K})}{3.1416 \times 1.0078 \times 10^{-3}\,\text{kgmol}^{-1}}\right)^{1/2}$$

$$= 1.28 \quad 10^5\text{ms}^{-1}$$

$$\therefore \qquad t = \frac{\lambda}{\langle c \rangle}\left(\frac{(59\,\text{light-yr}) \times 9.464 \times 10^{15}\,\text{m}\,(\text{light-yr})^{-1}}{1.28 \times 10^5\,ms^{-1}}\right)\left(\frac{1\,\text{yr}}{3.156 \times 10^7\,s}\right)$$

$$= 1.38 \quad 10^5 \text{ years} \qquad [\text{Q} \;\; 1 \text{ yr} = 3.156 \quad 10^7\text{s}]$$

Comment: Under conditions of extremely low pressure prevailing in the intergalatic space, the mean free paths of atoms are tremendously large so that it takes 1,38,000 years for a hydrogen atom to collide with another hydrogen atom!

Some properties of gas molecules derived from the kinetic theory of gases are given in the following table.

Table: Gas Properties at 25 C and 1 atm Pressure

Gas	***Collision Diameter $\sigma(m)$***	***Mean Free Path $\lambda(m)$***	***Collision Frequency Z_1 (s^{-1})***	***Collision Frequency Z_n (m^{-1} s^{-1})***
He	$2.18 \quad 10^{-10}$	$19.0 \quad 10^{-8}$	$6.6 \quad 10^{9}$	$8.1 \quad 10^{34}$
H_2	2.73	12.3	14.4	17.7
Ar	3.96	5.8	6.9	8.5
N_2	3.74	6.5	7.3	9.5
O2	3.5	7.1	6.1	7.5
CO_2	4.56	4.4	8.6	10.6

Gases and their Viscosity

Viscosity is a characteristic property of all fluids – liquids or gases. It is defined as the property by virtue of which it tends to oppose the relative motion between two adjacent layers of the fluid. It originates from the internal friction existing between the molecules of the gas or the liquid. In gases, the viscosity arises from the transfer of momentum between two adjacent layers of the gas. The coefficient of viscosity, η, is given by the equation

$$F = -\eta\,(dv_y/dz) \qquad ...3.25$$

and is defined as *the force per unit area required to establish a unit velocity gradient between two adjacent layers of a fluid, a unit distance apart.* The negative sign comes from the fact that if F is in the positive y-direction, the velocity v_y decreases in successive layer and dv_y/dz is negative. If F has the units of m s^{-2}/m^2 and dv_y/dx has the unit of m s^{-1}/m, then η has the units of kg m^{-1} s^{-1}. The c.g.s. unit of η is called a *poise* (P). A poise is equal to one-tenth of the SI unit, *i.e.,* 1P = 0.1 kg m^{-1} s^{-1}. Since 1 poise represents very high viscosity, the viscosity data of gases are often given in terms of *micropoise (μP)* units and for liquids in terms of *centipoise* (cP) units. It is useful to remember that

$$1\ \text{cP} = 10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1};\ 1\ \mu\text{P} = 10^{-7}\ \text{kg m}^{-1}\ \text{s}^{-1} = 10^{-7}\ \text{Pa s}$$

where 1 kg m^{-1} s^{-1} = 1 Pa s *(i.e.,* Pascal second).

***Viscosity in Terms of Momentum Transfer*:** Molecules of a gas are associated with a certain momentum depending upon their mass and viscosity. As a result of intermolecular collisions, the momentum of the faster layer is decreased by the entrance of molecules from the slower layer. This implies that the viscous drag tending to bring the two layers to the same speed depends upon the rate of transfer (or transport) of momentum from a region of higher momentum to one of lower momentum. The collisions between the molecules are responsible for the transfer of momentum. Hence, we expect the rate of momentum transfer to depend on the average molecular speed, the mean free path, λ and the concentration of molecules. This is, indeed, the case. Maxwell showed, using the simple kinetic theory, that for gaseous molecules considered as hard spheres, the coefficient of viscosity, η, is given by

$$\eta = 1/3\lambda <c> m\rho \qquad ...3.26$$

where m is the mass of the molecules and ρ is the *number density* defined as $\rho = N/V$, *i.e.,* number of molecules per unit volume. For an ideal gas, as shown earlier, $\rho = P/kT$ where P is the pressure and k is the Boltzmann constant. Recalling that $\lambda = kT/\sqrt{2}\left(\pi\sigma^2\right)P$ (cf. Eq. 3.24) where $\pi\sigma^2$ is the *collision cross-section* and σ is the *collision diameter of the molecule* and since $\langle c\rangle = (8\,kT/\pi m)^{1/2}$, we have

$$\eta = \frac{1}{3}\left(\frac{kT}{\sqrt{2}\pi\sigma^2 P}\right)\left(\frac{8kT}{\pi m}\right)^{1/2}(m)\left(\frac{P}{kT}\right) = \frac{2\left(M_mRT\right)^{1/2}}{3\pi^{1/2}N_A\left(\pi\sigma^2\right)} = \frac{2\left(M_mRT\right)^{1/2}}{3\pi^{3/2}N_A\sigma^2} \quad \text{... 3.27}$$

Eq. 3.27 shows that η is independent of pressure. The experimental verification of this conclusion was one of the greatest triumphs of the kinetic theory of gases.

A more rigorous treatment, given by Chapman, shows that the numerical coefficient in Eq. 3.26 is 1/2 so that

$$\eta = 1/2\lambda \langle c\rangle m\sigma \quad \text{...3.28}$$

The equation is known as the Chapman equation.

***Calculation of Mean Free Path*:** The Chapman equation permits calculation of mean free path from viscosity measurements. According to this equation

$$\lambda = \frac{2\eta}{\langle c\rangle\rho'} \quad \text{...3.29}$$

where ρ' (= mρ where ρ is the number density) is the usual density of the gas.

$$\text{Since } V_m = \frac{RT}{P}\text{, hence } \rho' = \frac{M_m}{V_m} = \frac{PM_m}{RT} \quad \text{...3.30}$$

$$\text{Also } \langle c\rangle = \left(\frac{8RT}{\pi M_m}\right)^{1/2}$$

Substituting the values of <c> and ρ′ in Eq. 3.29, we get

$$\lambda = \frac{1}{\sqrt{2}P}\left[\frac{\pi RT}{M_m}\right]^{1/2}\eta \quad \text{...3.31}$$

Thus, knowing η, λ can be calculated at a given temperature and pressure.

***Calculation of Collision Diameter*:** As already described, the mean free path is given by the relation

$$\lambda = \frac{kT}{\sqrt{2}P\pi\sigma^2} \qquad \text{(cf Eq. 3.24)...3.32}$$

From Eqs. 3.31 and 3.32

$$\frac{1}{\sqrt{2}P}\left[\frac{\pi RT}{M_m}\right]^{1/2}\eta = \frac{kT}{\sqrt{2}P\pi\sigma^2}$$

Since the Boltzmann constant, $k = R/N_A$, hence

$$\sigma^2 = \frac{\left(M_m RT\right)^{1/2}}{\pi^{3/2}N_A\eta} \qquad \text{...3.33}$$

Thus, knowing the viscosity of a gas, the collision diameter σ can be easily calculated.

The reason why η is independent of pressure is that though under increased pressure more molecules are available to transport the momentum, Only a few molecules can do so because of their reduced mean free paths.

Eq. 3.27 shows that η is directly proportional to $T^{1/2}$, *i.e.,* η increases with *T*. This peculiar behaviour of gases can be explained by saying that at higher temperatures, the momentum is transported more rapidly through a given area and hence force has to increased to maintain the motion of the layers of the gas. In case of liquids, on the other hand, η decreases with increase in temperature. The difference arises from the fact that the viscosity of liquids is dominated by intermolecular forces. In order to flow, the molecules in a liquid need energy to escape from their neighbours. Evidently, this energy is more freely available at high temperatures than at low temperatures.

***Example*:** Calculate the coefficient of viscosity of air at (a) 0 K (b) 298 K (c) 1,000 K. Assume that the collision cross-section ($\pi\sigma^2$ of air is 0.28 (nm)^2 and average molar mass of air is 29 g mol^{-1}.

Solution: $\pi\sigma^2 = 0.28(\text{nm})^2 = 0.28 \quad 10^{-18}\text{m}^2$

$M_m = 29 \text{ g mol}^{-1} = 29 \quad 10^{-3} \text{ kg mol}^{-1}$

From Eq. 3.27

$$\eta = \frac{(M_m RT)^{1/2}}{\pi^{1/2} N_A (\pi\sigma^2)}$$

$$= \frac{\left[(29 \times 10^{-3}\,\mathrm{kg\,mol^{-1}})(8.314\,\mathrm{JK^{-1}\,mol^{-1}})(\mathrm{T})\right]^{1/2}}{(3.1416)^{1/2}(6.022 \times 10^{23}\,\mathrm{mol^{-1}})(0.28 \times 10^{-18}\,\mathrm{m^2})}$$

$= 1.65 \quad 10^{-6}$ kg m^{-1} s^{-1} (T/K)$^{1/2}$ [J = kg m^2 s^{-2}]

(a) $T = 0$ K: The air is not a gas at this temperature, hence, the above formula for η is not applicable.

(b) = 298 K: η = (1.65 10^{-6} kg m^{-1}s^{-1}] (298 K/K)$^{1/2}$
= 2,835 10^{-5} kg m^{-1} s^{-1}

(c) = 1000 K: η = (1.65 10^{-6} kg m^{-1} s^{-1}) (1000 K/K)$^{1/2}$
= 5.19 10^{5} kg m^{-1} s^{-1}

***Example*:** At 27 C and 1 atm pressure, the coefficient of viscosity of nitrogen gas is 178 μP (i.e., micropoise). Calculate, (a) the mean free path λ, and (b) the collision diameter σ of nitrogen molecule using the Chapman equation.

***Solution*:**

(a) According to the Chapman equation,

$\eta = 1/2\ \lambda <c> m\rho$ [cf. Eq. 3.28]

where $<c> = (8\,kT/\pi m)^{1/2}$ and $\rho = P/kT$; $P = 101{,}325$ N m^{-2}

$$\therefore \qquad \lambda = \frac{2\eta}{<c> m\rho} = \frac{2\eta}{(8kT/\pi m)^{1/2}(m)(P/kT)}$$

$$= \frac{2\eta}{2P}\left(\frac{\pi kT}{2m}\right)^{1/2}$$

Here $m = 28 \quad 1.6605 \quad 10^{-27}$ kg. η = 178 μP = 1.78 10^{-3} kg m^{-1} s^{-1}. Substituting the given data.

$$\lambda = \frac{2 \times 1.78 \times 10^{-5}\,\mathrm{kg\,m^{-1}}\,s^{-1}}{1.01325 \times 10^{5}\,\mathrm{Nm^{-2}}}$$

$$\left[\frac{3.416 \times (1.38 \times 10^{-23}\,\mathrm{JK^{-1}})(300\,\mathrm{K})}{2 \times 28 \times 1.6605 \times 10^{-27}\,\mathrm{kg}}\right]$$

$= 6.602 \quad 10^{8}\text{m} = 66.02$ nm [J = kg m^2 s^{-2}; N = kg m s^{-2}]

(b)
$$\lambda = \frac{kT}{\sqrt{2}\left(\pi\sigma^2\right)P}$$

$$\therefore \ \sigma = \left(\frac{kT}{\sqrt{2}\pi\lambda P}\right)^{1/2} = \left[\frac{\left(1.38\times10^{-23}\,\text{JK}^{-1}\right)(300\,\text{K})}{\sqrt{2}\pi\left(66.02\times10^{-9}\,\text{m}\right)\left(1.01325\times10^{5}\,\text{Nm}^{-2}\right)}\right]^{1/2}$$

$$= 3.72 \quad \text{I}0^{-10}\text{ m} = 373 \text{ pm} \qquad [\therefore\ 1 \text{ pm} = 10^{-12}\text{m}]$$

***Example*:** At 20 C, the coefficient of viscosity of CO_2 gas is 1.48 $\quad 10^5$ kg m^{-1} s^{-1}. Calculate the collision diameter of CO_2.

Solution: M_m = 44.01 g mol^{-1} = 44.01 $\quad 10^{-3}$ kg

From Eq. 3.27

$$\sigma^2 = \frac{\left(M_m RT\right)}{\pi^{3/2} N_A \eta}$$

$$= \frac{\left[44.01\times10^{-3}\,\text{kg mol}^{-1}\left(8.314 JK^{-1}\,\text{mol}^{-1}\right)(293.15\,\text{K})\right]^{1/2}}{(3.416)^{3/2}\left(6.022\times10^{23}\,\text{mol}^{-1}\right)\left(1.48\times10^{-5}\,\text{kg m}^{-1}\,s^{-1}\right)}$$

$$= 20.865 \quad 10^{-20}\text{ m}^2$$

$$\therefore \qquad \sigma = 4.568 \quad 10^{10}\text{ m} = 456.8 \text{ pm}$$

Example: The coefficient of viscosity η has the units of kg m^{-1} s^{-1} in the SI system. Show that it can be written as Pa s (i.e., Pascal second).

Solution: Pa s = Pressure time = (N m^{-2}) s = (kg m s^{-2} m^2) s = kg m^{-1} s^{-1}.

Gaseous Molecule: Levels of Freedom

The motion of atoms and molecules is generally described in terms of the degrees of freedom they possess: The degrees of freedom of a molecule are defined as the independent number of parameters required to describe the state of the molecules completely. When a gaseous molecule is heated, the energy supplied to it may bring about three kinds of motion in it. These are: 1. The Translational Motion, 2. The Rotational Motion, and 3. The Vibrational Motion. This is expressed by saying that the molecule possesses translational rotational and vibrational degrees of freedom.

Freedom and some Degrees

Atoms possess only translational degrees of freedom. If we consider an atom as a *mass point,* then the mass point requires three coordinates (such as *x, y, z* in the Cartesian coordinates system) to specify its position. The atom has thus *three translational degrees of freedom* in the *x, y* and z-directions. If the atom is moving with a velocity *c,* then

$$c^2 = c_x^2 + c_y^2 + c_z^2 \qquad ...3.34$$

where c_x, c_y and c_z are the components of velocity c in the three directions,

Multiplying Eq. 3.34 by *m/2,* where *m* is the mass of the atom, we have

$$\frac{1}{2}mc^2 = \frac{1}{2}mc_x^2 + \frac{1}{2}mc_y^2 + \frac{1}{2}mc_z^2 \qquad ...3.35$$

or

$$\varepsilon_k = \varepsilon_{k,x} + \varepsilon_{k,y} + \varepsilon_{k,z} \qquad ...3.36$$

Thus, the kinetic energy ε_k, too, can be resolved into three components along the three Cartesian axes.

It may be noted that the rotational motion of an atom about an axis perpendicular to it and passing through its 'centre contributes negligible energy compared with its translational motion.

As in the case of atoms, three coordinates are needed to specify the centre of gravity of a molecule. Thus, the centre of gravity of any molecule has *three translational degrees of freedom.*

Degree of Rotation

A gaseous molecule can rotate along infinite number of axis but all these motions can be resolved along the three axis. In other word a molecule can have three rotational motions, motion along x-axis, y-axis, z-axis. A diatomic molecule lying along the x-axis can under go rotation about the mutually perpendicular y-axis and z-axis passing through its centre of gravity as shown in the following figure. However rotation along the x-axis is rotation about internuclear axis is no motion and thus cannot be considered as rotation. Thus diatomic molecule has two rotational degrees of freedom. Similarly for any linear molecule, rotation about internuclear axis is no rotation. Consequently will have two rotational degrees of freedom.

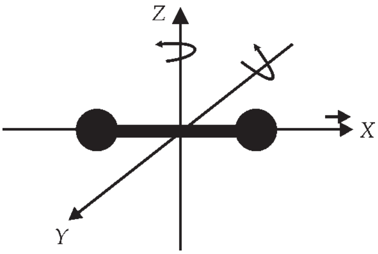


Fig. *Rotation of a diatomic molecule*

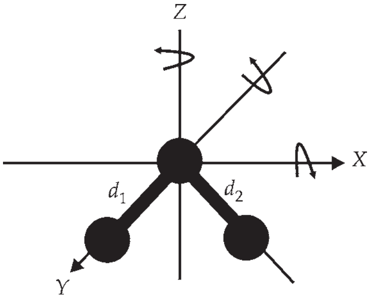


Fig. *Rotation of triatomic non-linear H_2O molecule*

However, non-linear molecules such as H_2O, H_2S, CH_4 and C_6H_6 can undergo rotation about the three Cartesian axes and so that they have three rotational degrees of freedom. The rotational motions of H_2O molecule is shown in the figure given above. Rotational motions of molecules are observed in rotational spectrum which will be taken up in third year.

Degrees of Vibration

As already mentioned, atoms possess only translational degrees of freedom.

In a diatomic molecule, the masses m_1, and m_2 vibrate back and forth relative to their centre of mass in opposite directions, as shown in the following figure. The two masses reach the extremes of their respective motions at the same time. The diatomic molecule has only *one vibrational degree of freedom, i.e.,* it has only one frequency, called the fundamental vibrational frequency. During vibrational motion, the bond of the molecule behave like a spring and the molecule exhibits a simple harmonic motion provided the displacement of the nuclei from the equilibrium configuration is not too much. At the two extremes of motion which correspond to extension and compression of the chemical bond between the two atoms, *the potential energy is maximum.* On the other hand, when the atoms are in their equilibrium position, *the kinetic energy is maximum.* Thus, during vibration, there is a constant interchange of kinetic and potential energy.

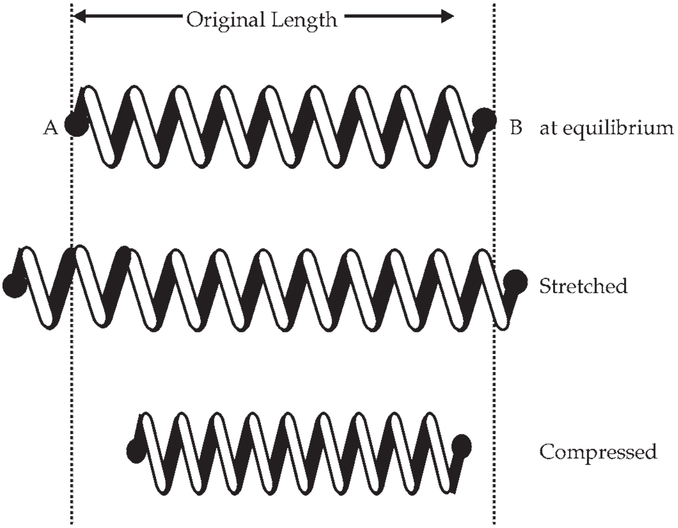


Fig. *A vibrating diatomic molecule AB. Bonding between A and B is like a massless spring. AB goes from equilibrium state to stretched state, comes back to equilibrium state, gets compressed comes back to equilibrium state, that makes one vibration*

A polytomic molecule containing n atoms or nuclei, has 3n degrees of freedom since each atom requires 3 degrees of freedom in the x, y and z-directions to specify its position. It we subtract the translational and rotational degrees of freedom from the total 3n degrees of freedom, we find that we are left with 3n – 6 internal degrees of freedom for a non-linear molecule and 3n – 5 internal degrees of freedom for a linear molecule. The 3n – 6 internal degrees of freedom of a non-linear molecule correspond to its 3n – 6 normal modes of vibrations. Similarly, the 3n – 5 normal degrees of freedom of a linear molecule correspond to its 3n – 5 normal modes of vibrations, A normal mode of vibration is defined as the molecular motion in which all the atoms in the molecule vibrate with the same frequency and all the atoms pass through their equilibrium positions simultaneously. The relative vibrational amplitudes of individual atoms may be different in magnitude and direction but the centre of gravity of the molecule does not change.

The various vibrational motions are observed in the infrared region of electromagnetic spectrum. This vibrational spectrum will be taken up in third year.

Example: Calculate the various degrees of freedom of the following molecules:

(a) He; (b) H_2; (c) HCl; (d) H_2O; (e) CO_2; (f) C_2H_2; (g) C_6H_6; and (h) a protein molecule containing 44,700 atoms.

Solution: Let N be the total number of degrees of freedom and n the number of atoms in a molecule. Then,

(a) He: $n = 1$ $N_{tr} = 3$ $N_{rot} = 0$ $N_{vib} = 0$
(b) $H_{2:}$ $n = 2$ $N_{tr} = 3$ $N_{rot} = 2$ $N_{vib} = 3 \quad 2 - 5 = 1$
(c) HCl: $n = 2$ $N_{tr} = 3$ $N_{rot} = 2$ $N_{vib} = 3 \quad 2 - 5 = 1$
(d) H_2O: It is a non-linear molecule.
$n = 3$ $N_{tr} = 3$ $N_{rot} = 3$ $N_{vib} = 3 \quad 3 - 6 = 3$
(e) CO_2: It is a linear molecule.
$n = 3$ $N_{tr} = 3$ $N_{rot} = 2$ $N_{vib} = 3 \quad 3 - 5 = 4$
(f) $HC \equiv CH$: It is a linear molecule.
$n = 4$ $N_{tr} = 3$ $N_{rot} = 2$ $N_{vib} = 3 \quad 4 - 5 = 7$
(g) C_2H_6: It is non-linear molecule.
$n = 12$ $N_{tr} = 3$ $N_{rot} = 3$ $N_{vib} = 3 \quad 12 - 6 = 30$
(h) Protein molecule: It is a macromolecule.
$n = 44{,}700$ $N_{tr} = 3$ $N_{rot} = 3$ $N_{vib} = 3 \quad 44700 - 6 = 134{,}100$
(We can neglect 6 in comparison with 134,100)

The transitional, rotational and vibrational degrees of freedom can be written in the shortened notation as follows:

(a) He: (3, 0, 0); (b) H_2: (3, 2, 1);
(c) HCl: (3, 2, 1); (d) H_2O: (3, 3, 3);
(e) CO_2: (3, 2, 4); (f) C_2H_2: (3, 2, 7);
(g) $C_6H_{6:}$ (3, 3, 30), etc.

It should be remembered that the rotational degrees of freedom are associated with substances in both the gaseous and liquid states. However, in the solid state, the molecules possess only vibrational degree of freedom, The translational and rotational motions in solids are converted into vibrational motion where the atoms in the lattice vibrate to and fro about their equilibrium positions.

Division of Energy

From the kinetic theory of gases we know that the average translational kinetic energy of a molecule of an ideal gas is given by

$$\varepsilon_k = \frac{3}{2}kT \qquad \text{(cf. Eq. 3.2)} \qquad ...3.37$$

According to the law of equipartition of energy, *the total energy of a molecule is divided equally amongst the various degree of freedom of the molecule.*

The distribution of kinetic energy along the *x, y* and z-directions is given by

$$\varepsilon_k = \varepsilon_{k,x} + \varepsilon_{k,y} + \varepsilon_{k,z} \qquad ...3.38$$

Since the motion to gas molecules is random and the motion along the three Cartesian axes is equally probable, hence from Eqs. 3.37 and 3.38(a).

$$\varepsilon_{k,x} = \varepsilon_{k,y} = \varepsilon_{k,z} = 1/3rd\ of\ \varepsilon_k = \frac{1}{2}kT \qquad ...\ 3.39$$

Eq. 3.39 shows that each component of kinetic motion contributes equal by to the total kinetic energy and that the kinetic energy for each degree of freedom is 1/2 kT per molecule or 1/2 RT per mole.

As regards the vibrational motion, the two atoms oscillate against each other. The molecule, therefore, possesses both potential and kinetic energy. This means that the energy of vibration involves two degrees of freedom. The vibrational motion in a molecule is, thus, associated with energy = 2 1/2 $kT = kT$ per molecule or RT per mole.

Thus, if a gaseous species has n_x translational degrees of freedom, n_2 rotational degrees of freedom and n_3 vibrational degrees of freedom, then the total energy of the species is given by n_1 (kT/2) + n_2 (kT/2) + n_3 *(kT).*

Example: Using the principle of equipartition of energy, estimate the energy of (a) H_2, (b) H_2O, and (c) CO_2 at room temperature, assuming that all the degrees of freedom are excited and contribute towards the energy of the molecules.

Solution: Ordinarily, at room temperature only translational and rotational degrees of freedom are excited and hence they contribute to the energy of the molecule. Here, however, we shall assume that vibrational degrees of freedom, too, are excited. According to the principle of equipartition of energy, each translational and rotational degree of freedom contributes 1/2kT and each vibrational degree of freedom contributes 2 1/2kT = *kT* to the total energy.

(a) H_2 (3, 2, 1): *E* = 3 (1/2kT) + 2 (1/2kT) + 1 *(kT)*
= 7/2 *kT* per molecule or 7/2 *RT* per mole

(b) H_2O (3, 3, 3): E = 3 (1/2kT) + 3 (1/2kT) + 3 *(kT)*
= 6kT per molecule or 6*RT* per mole.

(c) CO_2 (3, 2, 4): *E* = 3 (1/2kT) + 2 (1/2kT) + 4 *(kT)*
= 13/2kT per molecule or *13/2RT* per mole.

Importance of Real Gases

Deviation from Ideal Gas Behaviour

The equation of state, *PV = nRT,* derived from the postulates of the kinetic theory, is valid for an ideal gas only. Real gases obey this equation only approximately and that too under conditions of low pressure and high temperature. The higher the pressure and the lower the temperature, the greater are the deviations from the ideal behaviour. In general, the most easily liquefiable and highly soluble gases show larger deviations. Thus, gases like carbon dioxide, sulphur dioxide and ammonia show much larger deviations than hydrogen, oxygen, nitrogen, etc.

The deviations from ideal behaviour are best represented in terms of the compressibility factor (also called the compression factor) Z, which is defined as:

$$Z = \frac{PV}{(PV)_{ideal}} = \frac{PV}{nRT} = \frac{PV_m}{RT}$$

For an ideal gas, Z = 1 under all conditions of temperature and pressure. The deviation of Z from unity is, thus, a measure of the imperfection of the gas under consideration.

The graphs plotted for the compressibility factors determined for a number of gases over a range of pressure at a constant temperature (0 C) are shown in the following figure. At extremely low pressure, all the gases have Z close to unity which means that the gases behave almost ideally. At very high pressures, all the gases have Z more than unity indicating that the gases are less compressible than an ideal gas. This is due to the fact that at high pressures, the molecular repulsive forces are dominant.

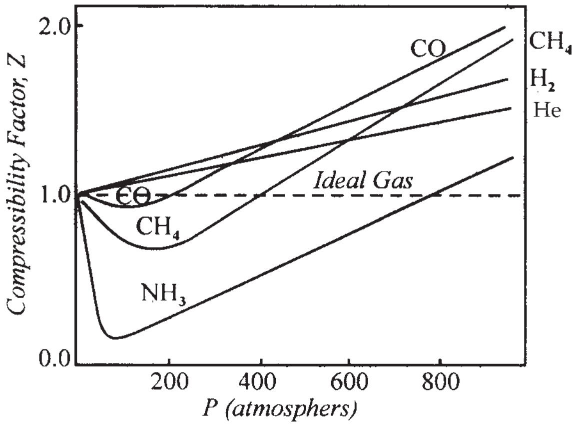


Fig. *Deviations of real gases from ideal behaviour*

As can be seem from the figure given above at moderately low pressures, carbon monoxide, methane and ammonia are more compressible than an ideal gas, *i.e., PV* is less than (PV_{Ideal}) so that Z < 1. This is due to the fact that at low pressures, the long range attractive forces are dominant and favour compression. The compressibility factor Z goes on decreasing with increase in pressure, passes through a minimum at a certain stage and then begins to increase with increase in pressure. The gases now become less compressible than an ideal gas, *i.e., PV* is more than (PV_{ideal}) so that Z > 1. It is evident from the figure that while carbon monoxide and methane exhibit marked deviations from ideal behaviour only at high pressures, ammonia shows large deviation even at low pressure.

Hydrogen and helium at 0 C, however, are seen to be less compressible than the ideal gas *at all pressure, i.e.,* $Z > 1$. However, if the temperature is sufficiently low *(e.g.,* below –165 C for hydrogen and below –240 C for helium) these gases also give the same type of *Z-P* plots as are shown by ammonia, carbon monoxide and methane at 0 C. On the other hand, if the temperature is sufficiently high, at Z – *P* plots of ammonia, carbon monoxide and methane will be similar to those of hydrogen and helium at 0 C, *i.e.,* the value of Z will increase continuously with increase in pressure.

Effect of Temperature on Deviations from Ideal Behaviour

The *Z-P* plots of nitrogen at different temperatures varying between –70 and 400 C, are shown in the following figure.

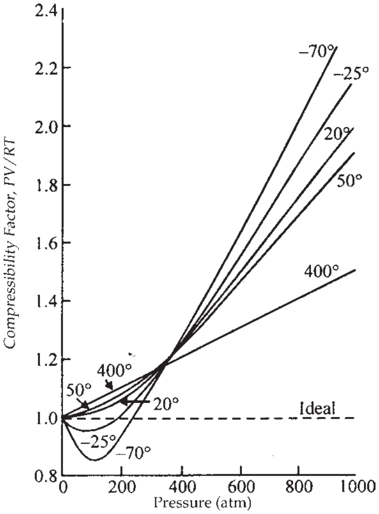


Fig. *Compressibility factors for one mole of* N_2 *at different temperatures.*

It is seen that as the temperature is raised, the dip in the curve becomes smaller and smaller. At 50 C, the curve seems to remain almost horizontal for an appreciable range of pressure varying between 0 and about 100 atmosphere showing thereby that the compressibility factor Z becomes almost equal to unity under these conditions. In other words, the product *PV* remains constant and hence *Boyle's law is obeyed within this range of pressure at* 50 C.

This temperature is called the Boyle point or Boyle temperature T_{Boyle}. Below this temperature, the value of Z at first decreases, approaches a minimum and then increases as the pressure is increased continuously. Above 50 C, the value of Z shows a continuous rise with increase in pressure.

The Boyle temperature is different for different gases. For example, the Boyle temperature for hydrogen is –165 C and for helium it is –240 C. Thus, at –165 C, hydrogen gas obeys Boyle's law for an appreciable range of pressure. However, at any temperature below –165 C, the plot of Z *vs P* first shows a fall and then a rise as pressure is increased continuously. At a temperature above –165 C, however, Z shows a continuous rise with increase in pressure.

Explanation for the Deviations

In order to explain deviations from ideal behaviour, it is necessary to modify the kinetic theory of gases. The following two postulates of the kinetic theory do not appear to hold good under all conditions. Let us examine them more critically.

Postulate No. 1: *The volume occupied by the molecules themselves is negligibly small as compared to the total volume occupied by the gas.* This postulate can be justified only under ordinary conditions of temperature and pressure. It can be shown by calculations that in some of the common gases, the volume occupied by the molecules themselves, under ordinary conditions, is only 0.014 per cent of the total volume of the gas. This is a negligible fraction indeed. But if the pressure becomes to high (say, 100 atmosphere or more), the total volume of the gas will decrease appreciably whereas the volume of the molecules will remain almost the same because the molecules are *incompressible.* Hence, *under conditions of high pressure, the volume occupied by the gas molecules will no longer be negligible in comparison with the total volume of the gas.*

The same thing happens when the temperature is lowered to a large extent. The total volume of the gas decreases considerably, no doubt, but the volume occupied by the molecules themselves remains practically the same. In this case, too, *the volume occupied by the molecules will no longer be negligible.*

The postulate No. 1, *therefore, is not valid at high pressure and low temperatures.*

Postulate No. 2: The forces of attraction between gas molecules are negligible. This assumption is valid at low pressures or at high temperatures because under these conditions the molecules lie far apart from one another.

But at high pressures or at low temperatures, the volume is small and molecules lie closer to one another. The intermolecular forces of attraction, therefore, are appreciable and cannot be ignored.

Hence, *the postulate No.* 2 *also does not hold under conditions of high pressure and low temperature.*

It is necessary, therefore, to apply suitable corrections to the ideal gas equation so as to make it applicable to real gases.

Equations of State for Real Gases

A number of equations of state have been suggested to describe the P-V-T relationship in *real gases.* The earliest and the best known equation is that of van der Waals.

Concept of Van der Waals Equation

In 1873, J.D. van der Waals proposed his famous equation of state for a non-ideal, *i.e.,* real gas. He modified the ideal gas equation by suggesting that the gas molecules were not mass points but behave like rigid spheres having a certain diameter and that there exist intermolecular forces of attraction between them. The two correction terms introduced by van der Waals are described below.

***Correction Due to Volume of Gas Molecules*:** The ideal gas equation $PV = nRT$ is derived on the assumption that the gas molecules are mass points, *i.e.,* they do not have finite volume. Van der Waals abandoned this assumption and suggested that a correction term nb should be subtracted from the total volume V in order to get the ideal volume which is compressible. In order to understand the meaning of the correction term nb, let us consider two gas molecules as unpenetrable and incompressible spheres, each of which has a diameter d, as shown in the following figure.

It is evident that the centres of the two spheres cannot approach each other more closely than the distance *d.* For this pair of molecules, therefore, a sphere of radius *d,* and hence of volume $\frac{4}{3}\pi d^3$, constitutes what is known is the excluded volume. The excluded volume per molecule is thus half the above volume, *i.e.,* equal to $\frac{2}{3}\pi d^3$. The actual volume of gas molecule of radius *r* is $\frac{4}{3}\pi r^3 = \frac{4}{3}\pi(d/2)^3 = \frac{1}{6}\pi d^3$.

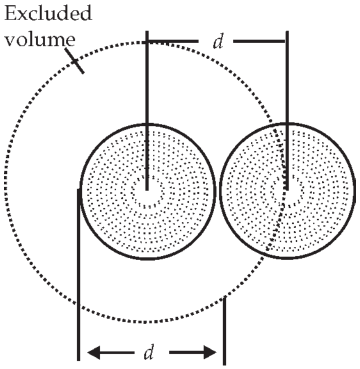


Fig. *Illustration of excluded volume*

$\therefore$ Excluded volume per molecule $\frac{2}{3}\pi d^3 = 4 \times \frac{1}{6}\pi d^3 = 4$ times the actual volume of the gas molecule.

The excluded volume per mole of the gas would be $N_A \times 4 \times \frac{4}{3}\pi d^3 = b$, where N_A is the Avogadro number. The compressible volume per mole of the gas would thus be $V - b$. If volume V of the gas contains n moles, then the excluded volume would be nb. Hence the *ideal volume which is compressible* would be $V - nb$.

The *volume b* per mole is also known as co-volume.

***Correction Due to Intermolecular Force of Attraction*:** In the derivation of the ideal gas equation, it was assumed that there are no intermolecular forces of attraction. Actually it is not so. In order to take into account the effect of intermolecular forces of attraction, let us consider a molecule lying somewhere in the midst of the vessel, as shown at the Point A. As can be seem, it is being surrounded uniformly on all sides by the neighbouring molecules. These forces neutralise one another and there is no resultant attractive force on the molecule.

However as the molecule approaches the wall of the vessel as shown at B, it experiences attractive forces from the bulk of the molecules behind it. Hence, *it will strike the wall with a lower velocity and will exert a lower pressure than it would have done if there was no force of attraction.* It is, therefore, necessary to add a certain quantity to the pressure of the gas in order to get the *ideal pressure.* The correct pressure, therefore, should be $P + p$.

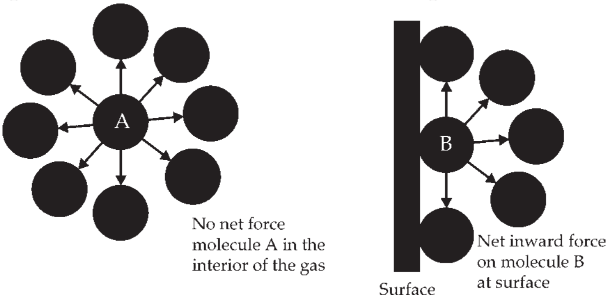


Fig. *Intermolecular forces in a gas*

***Calculation of the Correction Factor, p*:** The force of attraction exerted on a single molecule which is about to strike the wall evidently depends upon the *number of molecules per unit volume in the bulk of the gas, i.e.,* it depends directly upon the *density* of the gas. Further, the number of molecules striking the wall at any given instant also depends directly upon the *density* of the gas. Thus, the total inward attractive pull on the molecules which gives a measure of the correction factor, *p,* is proportional to the square of the density (p) of the gas, *i.e.,*

$$P \propto \rho^2 \qquad ...3.41$$

But, density is inversely proportional to the volume and if V is the volume occupied by *one mode* of a gas, the value of p for *one mole* of a gas will be inversely proportional to the square of volume.

Hence,

$$p \propto 1/V^2 = a/V^2 \qquad ...3.42$$

where *a* is a *constant* depending upon the nature of the gas.

The kinetic gas equation for one mole of a real gas, therefore, takes the form

$$\left(P + a/V_m^2\right)\left(V_m - b\right) = RT \qquad \text{...3.43}$$

where V_m stands for the *molar volume* of the gas.

This is known as the van der Waals equation. The constants *a* and *b* are known as the van der Waals constants. These are characteristics of each gas.

Eq. 3.43 is valid for one mole of a gas only. If there are *n* moles of a gas occupying volume *V*, then, as illustrated above, the *excluded volume* will be given by *nb* and the compressible volume, therefore, will be $V - nb$. The pressure correction factor *p* for *n* moles, in the light of Eq. 3.41 will be proportional to n^2p^2, *i.e.,*

$$p \propto n^2p^2 \propto n^2 \quad 1/V^2$$

$$= an^2/V^2 \qquad \text{...3.43(a)}$$

Hence, the van der Waals equation for *n* moles of a gas becomes

$$\left(P + \frac{n^2 a}{V^2}\right)\left(V - nb\right) = nRT \qquad \text{...3.44}$$

Eq. 3.44 is more accurate than the ideal gas equation $PV = nRT$ for expressing the $P - V - T$ behaviour of real gases. Thus, if we take one mole of carbon dioxide at 47 C and compress it to different pressures, the volume, as observed by experiment, is found to be closer to that calculated from the van der Waals equation than to that calculated from the ideal gas equation. The departure from ideal gas equation becomes more and more wide as the pressure increases.

Table: Volume of Carbon Dioxide at 47 C under Different Pressures

	Volume (dm^3) of the gas		
Pressure (atm)	***Observed experimentally***	***Calculated from the van der Waals equation***	***Calculated from the ideal gas equation***
1	27.20	26.20	26.30
10	2.52	2.53	2.63
40	0.54	0.54	0.66
100	0.098	0.10	0.20

Van der Waals was awarded the 1910 Physics Nobel prize for developing this equation.

The Units for the van der Waals Constants: The units for the van der Waals constants *a* and *b* depend upon the units in which *P* and *V* are expressed. It is evident that the constant *a* is expressed by the factor pV^2/n^2, *i.e., pressure (volume)*^{2}*/mol*^{2}. If pressure is expressed in atm and volume in dm^3, the value of *a* will be in dm^6 atm mol^{-2}. As regards *b,* it is incompressible *volume* per mole of a gas. Hence, it must have the same units as volume per mole, *e.g.,* dm^3 mol^{-1}.

The van der Waals constants for some common gases are given are below.

Table: The van der Waals Constants for Some Common Gases.

Gas	***a* (dm^6 atm mol^{-2})**	***b* (dm^3 mol^{-1})**
Ammonia	4.17	0.0371
Argon	1.35	0.0322
Carbon dioxide	3.59	0.0427
Carbon monoxide	1.49	0.0399
Chlorine	6.49	0.0562
Ethane	5.49	0.0638
Ethylene	4.47	0.0571
Helium	0.034	0.0237
Hydrogen	0.024	0.0266
Hydrogen chloride	3.67	0.0408
Hydrogen bromide	4.45	0.0443
Methane	2.25	0.0428
Neon	0.21	0.0171
Nitric oxide	1.34	0.0279
Nitrogen	1.39	0.0319
Oxygen	1.36	0.0318
Sulphur dioxide	6.71	0.0564

The constant a is a *measure of the van der Waals forces of cohesion,* existing between the molecules of a given gas. The greater the value of *a,* the greater is the strength of a van der Waals forces.

The values of *a* for hydrogen and helium are very small, being 0.024 and 0.034, respectively, indicating that the cohesive force (van der Waals forces) in these gases are very weak. The values of a for ammonia, carbon dioxide, chlorine and sulphur dioxide are very high being 4.17, 3.59, 6.49 and 6.71, respectively. This shows that the van der Waals forces in these gases are very strong. The greater the value of a, the greater is the ease with which a gas can be liquefied.

Example: Calculate the pressure exerted by one mole of carbon dioxide gas in a 1.32 cm^2 vessel at 48 C using (a) the ideal gas equation, and (b) the van der Waals equation. The van der Waals constants are: a = 3.59 dm^6 atm mol^{-2} and b = 0.042 dm^3 mol^{-1}.

Solution:

(*a*) For an ideal gas, $PV = nRT$, so that

$$P = \frac{nRT}{V} = \frac{(1\,\text{mol})\left(0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}\right)(321\,\text{K})}{1.32\,\text{dm}^3}$$

$$= 19.9 \text{ atm}$$

(*b*) For a van der Waals gas, from Eq. 3.44,

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$= \frac{(1\,\text{mol})\left(0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}\right)(321\,\text{K})}{\left(1.32\,\text{dm}^3\right) - (1\,\text{mol})\left(0.0427\,\text{dm}^3\,\text{mol}^{-1}\right)}$$

$$- \frac{(1\,\text{mol})^2\left(3.59\,\text{dm}^6\,\text{atm}\,\text{mol}^{-2}\right)}{\left(1.32\,\text{dm}^3\right)}$$

$$= 20.62 \text{ atm} - 2.06 \text{ atm} = 16.56 \text{ atm}$$

The experimental value of the pressure is 16.40 atm. Thus, the van der Waals equation gives a better agreement with experiment than the ideal gas equation.

Discussion of van der Waals Equation

We are now in a position to discuss the departure to real gases from ideal behaviour at different pressures and temperatures.

1. ***When the pressure is not Too High***: When the pressure is not very high, the volume V_m will be sufficiently large and *b* may be ignored in comparison. The van der Waals equation for one mole of a gas, *viz.,*

$$\left(P+\frac{d}{V_m^2}\right)-\left(V_m-b\right)=RT \qquad ...3.45$$

may then be written as

$$\left(P+\frac{d}{V_m^2}\right)V_m = RT$$

or $$PV_m + a/V_m = RT$$

or $$PV_m = RT-a/V_m \qquad ...3.46$$

Thus, the product PV_m is less than *RT* by an amount equal to a/V_m. As pressure increases, V_m, decreases, a/V_m increases and, therefore, PV_m becomes smaller and smaller. This explains the dip in the isotherms of most of the gases for carbon monoxide, methane and ammonia.

2. ***When the Pressure is Too High***: When the pressure is considerably high, the volume V_m will be quite small. Now it may not be possible to ignore *b.* But, as *P* is quite high, the quantity a/V_m^2 may becomes negligible in comparison with *P* in Eq. 3.43 which, therefore reduces to

$$\mathrm{P(V_m - b) = RT}$$

or $$PV_m = RT+Pb \qquad ...3.47$$

Thus, PV_m is now greater than *RT* by an amount equal to *Pb.* As the pressure increases, the product *Pb* increases and, therefore, PV_m increases. This explains why the value of PV_m, after reaching a minimum, increases with further increases of pressure.

At the ordinary temperatures, while the effect of the term a/V_m^2 is predominant at low pressures, that of *Pb* is predominant at high pressures. At some intermediate range of pressure, therefore, the two effects balance each other. *In this range of pressure, the gas shows the ideal behaviour.* This explains the existence of a small horizontal portion in the isotherms of gases like carbon monoxide and methane.

3. **When the Temperature is High:** If at a given pressure, tire temperature is considerably high, the volume will become sufficiently large to make the value of a/V_m^2 negligibly small.

At high temperature, b may also be negligible in comparison to V_m, which is now sufficiently large. Under these conditions, the van der Waals equation approaches the ideal gas equation, $PV_m = RT$. This explains why the deviations becomes less at high temperatures.

4. **Exceptional Behaviour of Hydrogen and Helium:** Since both hydrogen and helium have comparatively small masses, the attractive forces between their molecules are too small, In other words, the correction term a/Vm^2 due to the attraction factor remains negligible at ordinary temperatures. Thus,

$$PV_m = RT + Pb \qquad ...3.48$$

This explains why there is a continuous increases in PV_m with increase of pressure in the case of these two gases at ordinary temperatures.

The van der Waals equation explains fairly satisfactorily the behaviour of real gases.

The Boyle Temperature: As already mentioned, the temperature at which a real gas obeys Boyle's law, is known as the Boyle temperature T_B It is given by the expression

$$T_B = a/bR \qquad ...3.49$$

where a and b are the van der Waals constants.

Example: Calculate the Boyle temperature T_B for CO_2 gas, assuming it to be a van der Waals gas.

Solution: The van der Waals constants for CO_2 are

$$a = 3.59 \text{ dm}^6 \text{ atm mol}^{-2} \text{ and } b = 0.0427 \text{ dm}^3 \text{ mol}^{-1}$$

$$T_B = \frac{a}{bR} = \frac{3.59\,\text{dm}^6\,\text{atm}\,\text{mol}^{-2}}{(0.0427\,\text{dm}^2\,\text{mol}^{-1})(0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1})}$$

$$= 1026 \text{ K}$$

Various Equations

Several other equations have been proposed from time to time to account for the $P - V - T$ behaviour of real gases. A 'good' equation of state should be able to express the $P - V - T$ behaviour under moderate ranges of pressure and temperature. Other criteria of a workable equation of state are its simplicity of form and the use of only a few adjustable constants or parameters. However, to represent the behaviour of gases to a sufficient degree of accuracy, the number of such parameters has to be at least more than two. A brief description of some of the equations of state, other than the van der Waals equation, is given below. In all these equations, the quantity of the gas is *one mole.*

***The Dieterici Equation*:** Dieterici introduced an exponential factor to account for the effect of molecular attraction on the pressure. He suggested the following relationship to account for the behaviour of real gases:

$$Pe^{a/RTV_m}(V_m - b) = \text{RT} \qquad \text{...3.50}$$

$$\text{or} \quad P(V_m - b) = RTe^{-a/RTv_m} \qquad \text{...3.51}$$

This equation agrees with the van der Waals equation at moderate pressures but differs appreciably at high pressures and gives more satisfactory agreement with the experimental data.

***Berthelot Equation*:** Berthelot proposed the following empirical equation to explain the behaviour of real gases:

$$\left\{P + \frac{a}{TV_m^2}\right\}(V_m - b) = RT \qquad \text{...3.52}$$

This equation is virtually the same as the van der Waals equation except that the correction term for intermolecular attraction is a/TV_m^2 instead of a/V_m^2.

The Berthelot equation has been found to be more accurate than the van der Waals equation for determining molar masses of gases.

A feature common to all the equations of state described above is that regardless of the number of parameters occurring in them, they reduce to the ideal gas equation under conditions of low pressure. Thus, for all the above equations:

$$\lim_{P \to 0}(PV_m/RT) = 1$$

***The Virial Equation of State*:** The most general equation of state for real gases is the virial equation, proposed by Kammertirghones.

He expressed the product PV_m as a power series in 1/K as shown below:

$$PV_m = RT\left(1+\frac{B_2(T)}{V_m}+\frac{B_3(T)}{V_m^2}+\frac{B_4(T)}{V_m^3}+....\right)$$

where $B_2(T)$, $B_3(T)$, $B_4(T)$, etc., are the temperature-dependent second, third, fourth, etc. *virial coefficients,* respectively.

The various virial coefficients can be determined from the $P - V - T$ data for real gases. It is possible to calculate them from a knowledge of intermolecular potential energy. Unfortunately, however, this potential is not accurately known and hence the calculation of higher virial coefficients is a formidable problem in theoretical chemistry. The first virial coefficient is, evidently, equal to *RT.*

Example: Express the van der Waals equation in the virial form as a power series in $1/V_m$ and derive an expression for the Boyle temperature.

***Solution*:** The van der Waals equation for *one mole* of a gas is

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT$$

(where, for convenience, we have written molar volume as *V)*

$$\therefore \qquad P=\frac{RT}{V-b}-\frac{a}{V^2}=\frac{RT}{V(1-b/V)}-\frac{a}{V^2}$$

$$\text{or} \qquad PV=\frac{RT}{(1-b/V)}-\frac{a}{V}=RT\left(1-\frac{b}{V}\right)^{-1}-\frac{a}{V}$$

Since $b < V$, we can use the binomial theorem to expand the quantity $(1 - b/V)^{-1}$ obtaining

$$PV = RT\left(1+\frac{b}{V}+\frac{b^2}{V^2}+\frac{b^3}{V^3}+...\right)-\frac{a}{V}$$

Taking the term - a/V inside the bracket, we get

$$PV = RT\left(1+\frac{b}{V}-\frac{a}{VRT}+\frac{b^2}{V^2}+\frac{b^3}{V^3}+....\right)$$

$$= RT\left(1+\frac{b-a/RT}{V}+\frac{b^2}{V^2}+\frac{b^3}{V^3}+....\right)$$

Comparing this equation with the virial equation of state, *viz.,*

$$PV = RT\left(1+\frac{B_2(T)}{V}+\frac{B_3(T)}{V^2}+\frac{B_4(T)}{\left(V^3\right)}....\right)$$

we see that

$$B_2(T) = b-\frac{a}{RT}; B_3(T)=b^2; B_4(T)=b^3, etc.$$

Since the van der Waals constant b is very small, the terms involving b^2, b^3, can be neglected so that the van der Waals equation can be written in the virial form as

$$PV = RT\left(1+\frac{b-(a/RT)}{V}\right)$$

Since at the Boyle temperature, the second virial coefficient is zero, that is,

$$\frac{b-(a/RT_B)}{V} = 0$$

hence T_{Boyle} (the Boyle temperature) = a/Rb for a gas obeying the van der Waals equation of state.

Significant Process

***Critical Constants of a Gas*:** The most characteristic property of gases is that their molecules lie far apart from one another and are in continuous rapid motion. Each molecule, therefore, leads almost an independent existence. This is particularly so when temperature is high and pressure is low.

However, as the temperature of a gas is lowered, the kinetic energy of the molecules decreases. The volume occupied by the gas also decreases. At a sufficiently low temperature, some of the slow moving molecules cannot resist the force of attraction and they come closer and closer and ultimately the gas change's into the liquid state. Thus, liquefaction of gases results from decrease of temperature.

Increase of pressure has also the effect of bringing the gaseous molecules closer and closer to one another (due to decrease in volume). This is an additional helpful factor in converting a gas into liquid. Thus, increase of pressure and decrease of temperature both tend to cause liquefaction of gases. For instance, sulphur dioxide can be liquefied at –8 C if the pressure is 1 atm. But it can be liquefied even at a higher temperature of 20 C if the pressure is increased to 3.24 atm.

The effect of temperature, however, is more important than that of the pressure because for each gas there is a certain temperature above which it cannot be liquefied, no matter how high a pressure may be applied. This temperature is known as the *critical temperature.* Thus, the critical temperature of a gas may be defined, as that temperature above which it cannot be liquefied howsoever high the pressure may be. For instance, the critical temperature of carbon dioxide is 31.1 C. This means that it is not possible to liquefy carbon dioxide above 31.1 C by any means.

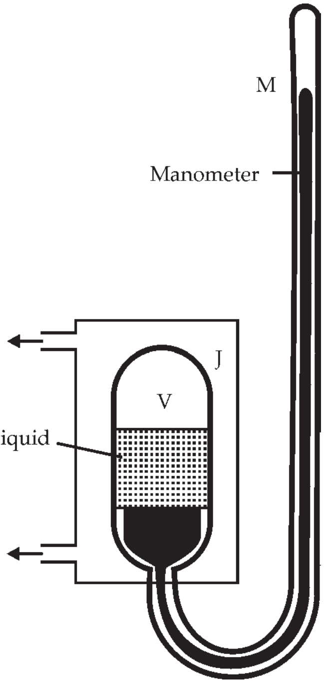


Fig. *Determination of critical temperature and critical pressure.*

At the critical temperature, a certain pressure is needed to liquefy the gas. This pressure is called the critical pressure. For instance, at 31.1 C, carbon dioxide can be liquefied under a pressure of 72.9 atm. Thus, the critical pressure of the gas is 72.9 atm.

The critical temperature of oxygen is –118 C and that of hydrogen is –240 C. These gases, therefore, cannot be liquefied at ordinary temperatures. Their critical pressures are 49.7 and 12.8 atm, respectively.

The volume occupied by *one mole* of a gas at its critical temperature and critical pressure is known as the critical volume. For example, critical volumes of carbon dioxide, oxygen and hydrogen are 940.0, 78.2 and 61.5 ml per mole, respectively.

Determination of Critical Temperature and Critical Pressure: These constants can be determined together by a simple method described below. It is generally used when "the substance is in liquid state at ordinary temperatures.

The method is based on the principle that at the critical temperature, the surface of separation (i.e. the meniscus) between the liquid and vapour phases disappears.

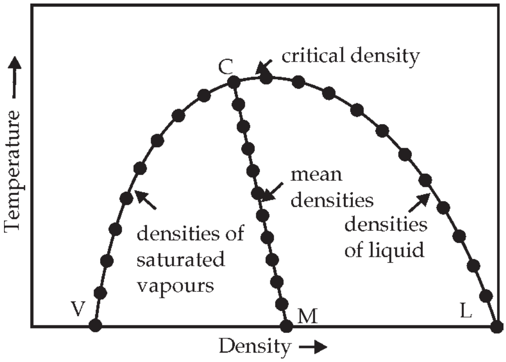


***Fig.** Determination of the critical volume.*

The liquid under examination is taken in vessel V enclosed in as jacket *J* the temperature of which can be varied gradually by circulating a suitable liquid from a thermostat. The vessel *V* is attached to a mercury manometer *M* containing air. The temperature is first lowered so that the vessel is cooled and the surface of separation between the liquid and its vapour becomes sharp. The temperature of the jacket is then raised gradually. This is continued until the meniscus between the liquid and its vapour just disappears. The temperature is noted. The jacket is then cooled gradually until cloudiness due to the condensation of vapour appears again. This temperature is also noted. The mean of the two temperatures gives the critical temperature.

The mean of the pressures read from the manometer, M corresponding to the two temperatures gives the critical pressure.

Determination of Critical Volume: In the determination of critical volume, advantage is taken of the observation made by Cailletet and Mathias that *when the mean densities of liquid and saturated vapour of a substance are plotted against the corresponding temperature of a substance a straight line is obtained.*

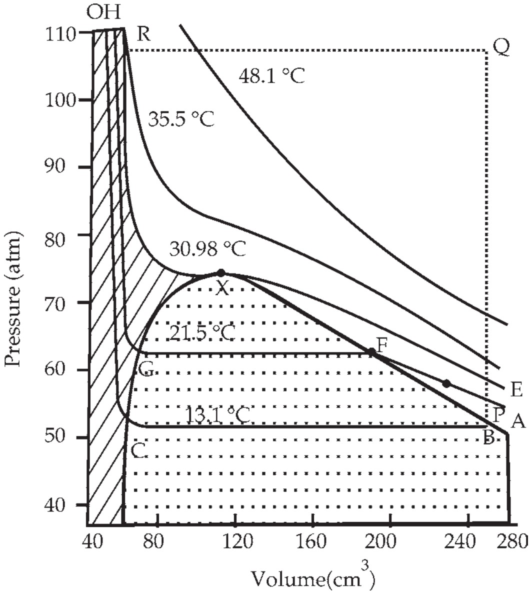


Fig. *Liquefaction isotherms for CO_2. The gaseous region is white, the liquid region is hatched portion, and the two-phase region is dotted,* T_c = 304.IK; P_c = 72.9 *atm;* V_c = 94 *cm^3/mole.*

The point C where the two curves meet gives the critical temperature. Obviously, this point is not sharp as the curve in this range is flat, as shown. The means densities are then plotted against the various temperatures when a straight line MC is obtained. The point C where this line cuts the curve VCL, gives the critical temperature as the densities of the liquid now becomes identical with that of the vapour. The point C also gives the critical density. The critical volume is then obtained by dividing the molar mass of the substance by the critical density.

The P-V Isotherms of Carbon Dioxide: The importance of critical temperature of a gas was first discovered by T. Andrews in his experiments on pressure-volume relationships (isotherms) of carbon dioxide gas at a series of temperatures. The isotherms of carbon dioxide determined by him at different temperatures is shown in the figure given above. Consider first the isothermal at the lowest temperature, *viz.,* 13.1 C. The point A represents carbon dioxide in gaseous state occupying a certain volume under a certain pressure. On increasing the pressure, its volume diminishes as is indicated by the curve AB. At B which represents a pressure of 49.8 atm, liquefaction of the gas commences and thereafter a rapid decrease in volume takes place at the same pressure, as more and more of the gas is converted into the liquid state. At C, the gas has been completely liquefied. Now, as the liquid is only slightly compressible, further increase of pressure produces only a very small decrease in volume. A steep line CD that is almost vertical shows this.

Thus, *along the curve AB, carbon dioxide exists as gas; along BC, it exists partly as gas and partly as liquid while along CD, it exists entirely as liquid.* It may also be noted that a considerable decrease of volume (represented by *BC)* takes place when the gas changes into the liquid state at a constant pressure.

The isotherm *EFGH* at 21.5 C shows a similar behaviour except that now the liquefication commences at a higher pressure and the horizontal portion *FG,* representing decrease in volume, becomes smaller. At still higher temperatures, the horizontal portion of the curve becomes shorter and shorter until at 31.1 C *it reduces just to a point* (represented by *X).* At this temperature, therefore, the gas passes into liquid state *imperceptibly.* Above 31.1 C, the isotherm is continuous. There is no evidence of liquefaction at all. Andrews concluded that if the temperature of carbon dioxide is above 31.1 C, it cannot be- liquefied, no matter how high the pressure may be. He called 31.1 C as the critical temperature of carbon dioxide. Since then, other gases have been found to behave similarly. There is no fundamental difference between the so called 'permanent' gases such as hydrogen, oxygen, nitrogen, etc., and 'temporary' gases such as carbon dioxide, chlorine, hydrochloric acid, ammonia, etc. The difference lies in the fact that while the so-called 'permanent' gases have very low critical temperatures much below the ordinary range of temperature, the so called 'temporary' gases have critical temperatures well within the range of ordinary temperatures.

Continuity of State

A careful examination of the isotherms plotted in the figure given above shows that it is possible to convert liquid carbon dioxide into gas and *vice versa, without any 'discontinuity',* that is, without having, at any time, more than one phase present. On joining the ends of the horizontal portions of the various isotherms, a boundary curve *CGXFB,* represented by a line, is obtained. At the top lies the critical point *X* (31 C). Within the area of the boundary curve, both liquid and gaseous states can coexist but outside this area, either liquid or gaseous state alone can exit. Suppose, a certain volume of carbon dioxide, represented by a point *P* on the 13.1 C isotherm *ABCD* is heated *at constant volume* to a temperature at which the pressure increases to a point *Q,* lying above the critical pressure of the gas. Let the gas be now cooled at the *same pressure.*

The temperature and volume both will decrease along *QR.* At *R,* the temperature is 21.5 C and carbon dioxide exists as liquid. During this transition from gas to liquid, there has never been more than one phase present at any time. As the temperature is decreased from Q to R, trie volume of the gas decreases gradually till the molecules are close enough for the van der Waals forces of attraction to cause their condensation into the liquid state. *The process of transition from gaseous state to liquid state (or vice versa);* therefore, is *regarded as* continuous.

The van der Waals Equation and the Critical State: For one mole of a gas, the van der Waals equation

$$\left(P+\frac{a}{(V_m)^2}\right)(V_m-b) = RT \qquad ...3.55$$

may be written as

$$PV_m - Pb - \frac{a}{V_m} - \frac{ab}{(V_m)^2} - RT = 0 \qquad \text{...3.56}$$

Multiplying $(V_m)^2$ and dividing by P and rearranging in decreasing powers of V_m, it may be

$$(V_m)^3 - \left(b + \frac{RT}{P}\right)(V_m)^2 + \frac{a}{P}V_m - \frac{ab}{P} = 0 \qquad \text{...3.57}$$

This is a cubic equation in the variable V_m and, therefore, for any single set of the values of P and T, there should be three values of V_m, all of which may be real or only one may be real and the other two imaginary. If, at a constant temperature, the values of V are plotted against P, then, according to Eq. 3.57 a curve similar to that marked I in the figure given below should be obtained. It will be seen readily that, for a certain pressure, there are three values of V marked as L, N and Q. As the temperature increases, the isotherm moves up. When it is in position II, the three values of V get closer to one another. At a certain temperature (isotherm III), the three values of V become identical as shown by the point X. At a still higher temperature (isotherm IV), there is only one real value of V corresponding to a given pressure. Thus, below the critical temperature of a gas, the isotherm indicates three values of V for a given pressure t in accordance with the above equation.

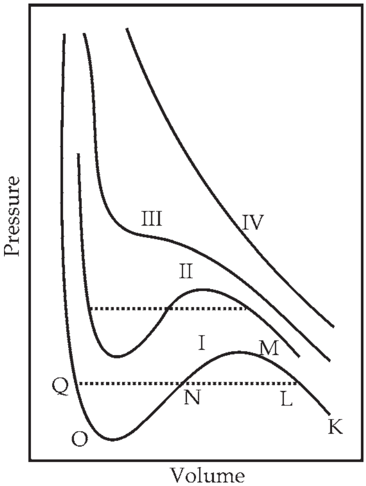


Fig. *The theoretical* P–V *isotherms of carbon dioxide*

It may be pointed out that the isotherms plotted in the figure given above are based on *theoretical calculations* of V corresponding to different values of P obtained by using the van der Waals equation. The isotherms for carbon dioxide, obtained by Andrews *experimentally,* were in close resemblance with these curves, with the difference that the wavelike portion *LMNOQ* was replaced by a horizontal line. Since then more careful experiments have shown that small portions corresponding to curves *LM* and *OQ* can be realised in practice also. These represent supersaturated vapour and superheated liquid, respectively.

As the temperature is raised, the loops become smaller and smaller, as already stated. At the critical point X, all the three values of V become identical. Since the temperature is now critical this value of V represents the *critical volume* of the gas, that is

$$V_m = V_{m,c} \qquad ...3.58$$

$$(V_m - V_{m,c})^3 = 0$$

Expanding and writing in decreasing powers of V_m, we have

$$V_m^3 - 3V_{m,c}(V_m)^2 + 3(V_{m,c})^2 V_m - (V_{m,c})^3 = 0 \qquad ...3.59$$

Eq. 3.59 must be identical with the van der Waals equation at critical temperature and pressure, which for 1 mole of the gas may be written as

$$(V_m)^3 - \left(b + \frac{RT_c}{P_c}\right)(V_m)^2 + \frac{a}{P_c}V_m - \frac{ab}{P_c} = 0 \qquad ...3.60$$

Hence, the coefficients of equal power of V_m in Eqs. 3.59 and 3.60 must be equal to one another. Thus,

$$3V_{m,c} = b + \frac{RT}{P_c} \qquad ...3.61$$

$$3(V_{m,c})^2 = a/P_c \qquad ...3.62$$

$$(V_{m,c})^2 = ab/Pc \qquad ...3.63$$

From Eqs. 3.61, 3.62 and 3.63 the critical constants T_c P_c *and* V_{mc} of a gas can be calculated in terms of the van der Waals constants *a* and *b,* as shown below.

Dividing Eq. 3.63 by Eq. 3.62 we have

$$V_{mc} = 3b \qquad ...3.64$$

Substituting this value in Eq. 3.62 we get

$$P_c = a/27b^2 \qquad ...3.65$$

Inserting these values of V_{mc} and P_c in Eq. 3.61 we have

$$Tc = 8a/27Rb \qquad ...3.66$$

Thus, knowing the critical constants of a gas, it is possible to calculate the van der Waals constants and *vice versa.*

***Critical Compressibility Factor*:** The critical compressibility factor, Z_c, of a van der Waals gas is given by

$$Z_c = \frac{P_c V_{m,c}}{RT_c} = \frac{\left(a/27b^2\right)(3b)}{R[8a/28Rb]} = 0.375$$

Thus, we can test whether a gas behaves as a van der Waals gas by seeing whether its critical compressibility factor is equal to 0.375.

The critical constants of some common gases are given in the following table. We see that although Z_c is less than 0.375, the disprepancy is rather small.

***Table*:** *Critical Constants of Gases*

Gas	*P_c(atm)*	*$V_{m,c}$(cm^{3}mol^{-1})*	*T_c(K)*	*Z_c*
He	2.26	57.9	5.2	0.307
Ne	26.9	41.7	44.4	0.308
Ar	48.1	75.2	150.7	0.292
Xe	58.0	119.0	289.7	0.290
H_2	12.8	65.5	33.0	0.309
O_2	50.1	78.2	154.8	0.308
N_2	33.5	90.1	126.2	0.291
CO_2	72.8	94.0	304.2	0.274
NH_3	111.5	72.5	405.0	0.243
CH_4	45.6	98.7	190.6	0.288
C_2H_6	48.2	148.0	305.4	0.284
C_6H6	48.4	254.0	562.3	0.266

Example: Calculate the critical temperature of a Van der Waals gas for which P_c is 100 atm and b is 50 cm^3 mol^{-1}.

Solution: From Eq. 3.65, $a = P_c 27b^2$

From Eq. 3.66 $$T_c = \frac{8a}{27Rb} = \frac{(8)\left(P_c 27 b^2\right)}{27Rb} = \frac{8P_c b}{R}$$

$$= \frac{(8)(100\,\text{atm})\left(0.050\,\text{dm}^3\,\text{mol}^{-1}\right)}{0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}} = 487.2\text{K}$$

Example: The van der Waals constants of a gas are:

a = 0.751 am^6 atm mol^{-2} and b = 0.0226 dm^3 mol^{-1}. Calculate its critical constants.

Solution: V_{mc} = 3b = 3 (0.0226 dm^3 mol^{-1}) = 0.0678 dm^3 mol^{-1}

$$P_c = \frac{a}{27b^2} = \frac{\left(0.751\,\text{dm}^6\,\text{atm}\,\text{mol}^{-2}\right)}{27\left(0.0226\,\text{dm}^3\text{mol}^{-1}\right)^2} = 54.5\,\text{atm}$$

$$T_c = \frac{8a}{27Rb}$$

$$= \frac{8\left(0.751\,\text{dm}^6\,\text{atm}\,\text{mol}^{-2}\right)}{27\left(0.08206\,\text{dm}^2\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}\right)\left(0.0226\,\text{dm}^3\,\text{mol}^{-1}\right)} = 120\text{K}$$

Example: A certain gas has the following values of its critical constants: P_c = 45.6 atm, $V_{m,c}$ = 0.987 dm^3 mol^{-1} and T_c = 190.6 K. Calculate the van der Waals constants of this gas. Also, estimate the radius of the gas molecules assuming that they are spherical.

Solution:

$$b = \frac{V_{m,c}}{3} = \frac{0.0987\,\text{dm}^3\,\text{mol}^{-1}}{3} = 0.0329\,\text{dm}^3\,\text{mol}^{-1}$$

$$a = 3P_c\left(V_{m,c}\right)^2 = 3(45.6\,\text{atm})\left(0.0987\,\text{dm}^3\,\text{mol}^{-1}\right)^2$$

$$= 1.333\ \text{dm}^6\ \text{atm mol}^{-2}$$

The critical volume of *one molecule* $V_{m,c}$ is, evidently, b/N_A where N_A is the Avogadro number.

$$V_{m,c} = \frac{0.0329\,dm^3\,mol^{-1}}{N_A} = \frac{0.0329\times 10^{-3}\,m^3\,mol^{-1}}{6.022\times 10^{23}\,mol^{-1}}$$

The volume of a sphere = $(4/3)\pi r^3$, where *r* is its radius, so that

$$4/3\pi r^3 = 5.46 \times 10^{-29}\, m^3$$

$$r = \left(\frac{3 \times 5.46 \times 10^{-29}\,\mathrm{m}^3}{4\pi}\right)^{1/3} = 2.35 \quad 10^{-10}\ \mathrm{m}$$

$$= 2.35\text{Å} = 235\ \mathrm{pm} \qquad [1\text{Å} = 100\ \mathrm{pm}\ (\text{micometres})]$$

It may be of interest to know that *normal boiling point T_b of a liquid is proximately two-thirds of its critical temperature T_c when both are expressed on Kelvin scale, i.e..*

$$T_b/T_c \approx 2/3 \qquad ...(3.66)$$

Example: Estimate the critical temperature of w-hexane at its boiling point is 68.9 C.

Solution: From Eq. 3.66 $T_b = 111\ T_c$

$$T_c = 3/2\ T_b = 3/2\ (68.9 + 273)\ \mathrm{K}$$

= 512.85 K = 239.85 C (Experimental value is 234.7 C)

It can also be shown that for a van der Waals gas, the Boyle temperature T_{Boyle} = (27/8) T_c.

Relevant States

In 1881, van der Waals showed that if the pressure, 'volume and temperature of a gas are expressed in terms of its critical pressure, critical volume and critical temperature, we can obtain an important generalisation called the principle of corresponding states.

Let $P/P_c = P_r$, $V_m/V_{m,c} = V_r$, $T/T_C = T_r$, where P_r, V_r and T_r are called the *reduced pressure,* the *reduced volume* and the *reduced temperature,* respectively. Substituting in the van der Waals equation for one mole of a gas, *viz.,*

$$\left(P + \frac{a}{(V_m)^2}\right)(V_m - b) = RT, \text{ we have}$$

$$\left(P_r P_c + \frac{a}{(V_r)^2 (V_{m,c})^2}\right)(V_r V_{m,c} - b) = \mathrm{RT_r T_c} \qquad ...3.69$$

Substituting for P_c, $V_{m,c}$ and T_c from Eqs. 3.64, 3.65 and 3.66 we have

$$\left(\frac{aR_r}{27b^2}+\frac{a}{9(V_r)^2 b^2}\right)(3V,b-b)=\mathrm{RT_r}\left(\frac{8a}{27Rb}\right)$$

$$\text{or}\quad \left(P_r+3/V_r^2\right)\left(3V_r-1\right)=8\mathrm{T_r} \qquad \text{....3.70}$$

Eq. 3.70 involves neither *R* nor the van der Waals constant *a* and *b* and is called *reduced equation of state. It is a general equation applicable to all substances.* It follows from this equation that if *two more substances have the same reduced temperature and the same reduced pressure, they have the same reduced volume.* This statement is known as the principle of corresponding states.

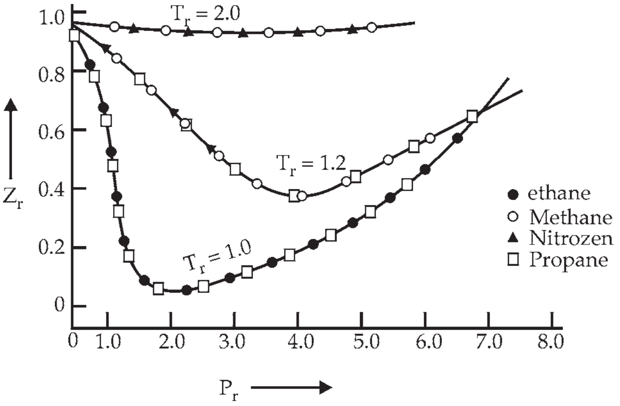


Fig. *The compressibility factors as a function of reduced pressures and reduced temperatures.*

Two or more substances having the same reduced temperature and the same reduced pressure and thus having the same reduced volume are said to be in corresponding states.

When compressibility factors are plotted in terms of the reduced variables, the same curve should be obtained for all gases. The principle of corresponding states thus enables the properties of real gases to be plotted on a single diagram.

***Example*:** Calculate the pressure exerted by one mole of CO_2 gas at 40 C, confined to a volume of 0.107 dm^3, using the law of corresponding states, given that the critical constants of the gas are $V_{m,c}$ = 0.0957 dm^3, T_c = 304 K and P_c = 73.0 atm.

Solution: From Eq. 3.70

$$P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2} = \frac{8(T/T_c)}{3(V_m/V_{m,c}) - 1} - \frac{3}{(V_m/V_{m,c})^2}$$

$$= \frac{8(313/304)}{3(0.107/0.0957) - 1} - \frac{3}{(0.0107/0.00957)^2}$$

$$= \frac{(8)(1.03)}{3 \times 1.18 - 1} - \frac{3}{(1.1)^2} = 3.51 - 2.40 = 1.11$$

$$P = P_r P_c = 1.1\ 1 \quad 73.0 \text{ atm} = 81.03 \text{ atm}$$

Example: Calculate the temperature and pressure that one mole of (a) ammonia and (b) helium will have in states corresponding to 1 mole of H_2 at 25 C and 1 atm.

Solution: The critical constants of the given gases are

H_2: $T_c = 33.0$ K $\quad P_c = 12.8$ atm

He: $T_c = 5.2$ K $P_c = 2.26$ atm

NH_3 – $T_c = 405.0$ K $P = 111.5$ atm

Now for H_2 at 298 K and 1 atm pressure, the reduced parameters are

$T_r = T/T_c = 298 \text{ K}/33.0 \text{ K} = 9.030$

$P_r = P/P_c = 1 \text{ atm}/12.77 \text{ atm} = 0.078$

Ammonia and helium will be in their corresponding states when their reduced temperatures and pressures are the same as those of H_2. Thus,

(a) For NH_3: $T = T_rT_c = 9.030 \quad 405 \text{ K} = 3657.15 \text{ K}$

$P = P_tP_c = 0.078 \quad 111.5 \text{ atm} = 8.697 \text{ atm}$

(b) For He: $T = T_rT_c = 9.030 \quad 5.2 \text{ K} = 46.956 \text{ K}$

$P = P_rP_c = 0.078 \quad 2.26 \text{ atm} = 0.176 \text{ atm}$

Liquifaction of Gases

As has already been explained, it is necessary to cool a gas below its critical temperature before it can be liquefied. In the case of a gas like ammonia, chlorine, sulphur dioxide or carbon dioxide, which has a fairly high critical temperature the application of a suitable pressure alone is sufficient to cause liquefaction. Gases such as hydrogen, oxygen, nitrogen and helium which have very low critical temperatures could not be liquefied by this simple technique. As the significance of critical temperature was not properly understood at that time, these gases were regarded as 'permanent'. But, now it is known that these gases can also be liquefied *if they are first cooled below their respective critical temperatures and then compressed.*

Two principles are usually applied in cooling gases below their critical temperatures.

***The Joule-Thomson Effect*:** The English physicists, James Joule and William Thomson (later Lord Kelvin), observed that *when a gas under high pressure is permitted to expand into a region of low pressure it suffers a fall in temperature.* This phenomenon is known as the Joule-Thomson effect.

The Joule-Thomson effect *offers further support to the view that attractive forces do exist between gas molecules.* As the gas expands, the molecules fall apart from one another. Therefore, work has to be done in order to overcome the cohesive or attractive forces which tend to hold the molecules together. Thus work is done by the system at the expense of the kinetic energy of the gases molecules. Consequently, the kinetic energy decreases and since this is proportional to temperature, cooling results. It may be noted that in this case no external work has been done by the gas in expansion.

Experiment has shown that gases become cooler during the Joule-Thomson expansion only if they are below a certain temperature known as the inversion temperature, T_r The inversion temperature is characteristic of each gas. It is related to the van der Waals constants *a* and *b* of the gas concerned by the following expression:

$$T_i = 2a/Rb \qquad \text{...3.71}$$

At the inversion temperature there is no Joule-Thomson effect. Thus, if a gas under pressure passes through a porous plug and expands adiabatically into a region of very low pressure at the inversion temperature, there is neither fall nor rise in temperature. If, however, the expansion takes place above the inversion temperature, there is a small rise of temperature and if it takes place below the inversion temperature there is a small fall of temperature.

In most gases, this temperature lies within the range of ordinary temperature. Hence, they get cooled in the Joule-Thomson expansion. Hydrogen and helium, however, have very low inversion temperatures. Thus, at ordinary temperatures, these gases get warmed up instead of getting cooled in the Joule-Thomson expansion. But if hydrogen is first cooled to –80 C which is its inversion temperature and helium is first cooled to –240 C which is its inversion temperature, then these gases also get cooled on expansion in accordance with the Joule-Thomson effect.

State of Liquid

On cooling gases below their respective critical temperature, followed by the treatment of high-pressure liquid is obtained. Cooling decrease the thermal energies of molecule and decrease the volume of the system so as to allow the molecules to come closer, thereby are increasing the binding energies amongst them. Alternatively, liquids can be obtained by heating solids up to or beyond there melting points. In solids, molecules do not possess any translational energy but posses only vibrational energy. The binding forces amongst them are very strong. The effect of heating solids is to impart sufficient energy to molecules so that they can overcome these strong binding forces.

Liquids are neither characterised by the random chaotic motion of molecules, which one find in gases, nor by the perfect order of moleculars arrangement in solids. They occupy an intermediary position where molecules are more disorderly than those of a solid, but much less disorderly than those of gases. Because of this fact the enthalpy change when a crystal melts is always positive and the corresponding entropy change is also positive. This implies that there is less of order when a crystal melts. The liquid is thus intermediate between the complete order of the crystalline state and the complete disorder of the gaseous state. Because of this fact, the development of a molecular theory for liquids has posed formidable difficulties.

Properties of liquids also lie in between those of solids and gases. For example, liquids are less compressible than gases but a little more compressible than solids. The two important properties of liquid, namely fixed volume but no fixed shape, arise mainly because of the following two facts:

(i) The energies binding the molecules are larger than their average Thermal energy.

(ii) These binding energies are not strong enough to stop the motion of the molecules altogether, as is the case in solids, with the result that molecules can move from one place to another but cannot escape from the liquid unless they are present on the surface.

The origin of Surface Tension Viscosity in liquids is basically due to the existence of strong intermolecular attractions.

Concept of Surface Tension

The existence of strong intermolecular forces of attraction in liquids gives rise to another important property known as surface tension. The phenomenon of surface tension may be explained by reference in the following figure.

Consider a molecule *P* somewhere in the body of the liquid. This is attracted *equally* in all directions by other molecules which surround it as shown and, therefore, cancel the effect of one another.

Consider, next, a molecule near the surface, as at *R*. The downward attractive forces are greater than the upward forces because there are more molecules of the liquid below than in the air above the surface. These unbalanced attractive forces acting downward tend to draw the surface molecules into the body of the liquid and, therefore, tend to reduce the surface to a minimum.

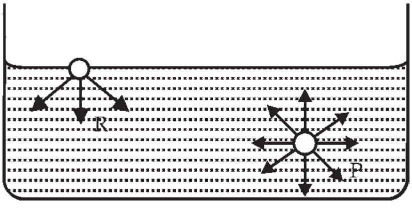


Fig. *Molecular attraction*

On dipping a capillary tube in a liquid, there occur either a rise or a fall of the liquid in the tube. The phenomenon is known as capillary action and is basically due to surface tension of the liquid. If the forces attraction between the molecules of a liquid and those of solid of tube are greater than those existing amongst the molecule of the liquid, then the liquid has a tendency to spread on the solid surface and its menscus in the tube is concave upwardly. Such types of liquids are known as wetting liquids and they rise in the capillary tube.

The surface tension forces act all around the capillary tube in the upward direction and liquid rises in the tube. This rise continues till the upward lifting force becomes equal to the weight of the liquid in the capillary tube. If the cohesive forces in liquid are greater than the solid-liquid and those of the solid surface, the liquid detaches from the surface of the solid and a fall of liquid in the tube is observed.

It is well known that forces of attraction tend to decrease the energy of a system. In the present case, the attractive forces are more predominant in the bulk of the liquid than at the surface. Therefore, the molecules in the bulk of the liquid are associated with lower energy than those at the surface.

In other words, the molecules at the surface possess greater energy than those in the bulk. It is the extra energy of surface molecules which gives rise to their tendency to move into the bulk of the liquid, *i.e.,* the molecules tend to move from a state of higher energy to a state of lower energy. As a consequence of this transfer, the number of molecules at the surface becomes less than that in the bulk.

The distance between any two molecules at the surface therefore, becomes greater than that in the bulk. Consequently, the surface molecules tend to move closer to one another in order to acquire a normal distance between them as before. It is for this season that drops of a liquid or bubbles of a gas are spherical in space. A sphere has minimum surface for a given volume. As a result of the tendency to contract, surface of a liquid behaves as if it were in a state of tension.

The force that tends to contract the surface of a liquid is known as surface tension, Mathematically, surface tension may be defined as the force in dynes acting at right angles to the surface of a liquid along one centimetre length of the surface. It is generally represented by the symbol γ and is expressed in dynes cm^{-1}. In SI units surface tension is defined as the force in newtons acting at right angles to the surface of a liquid along 1 metre length of the surface (1 dyne $cm^{-1} = 10^{-3}$ Nm^{-1}).

Table: *Surface Tension of Some Common Liquids at 20 C*
(Values without brackets are in dynes cm^{-1} while those within brackets are in N m^{-1})

Liquid	***Surface Tension***	***Liquid***	***Surface Tension***	***Liquid***	***Surface Tension***
Water	72.8	Toluene	28.4	Acetone	23.72
	(0.0728)		(0.0284)		(0.0237)
Nitrobenzene	41.8	Acetic acid	27.6	Methyl alcohol	22.55
	(0.0418)		(0.0276)		(0.0225)
Carbon-	32.25	Chloroform	27.1	Ethyl alcohol	22.3
disulphide	(0.0322)		(0.0271)		(0.0223)
Benzene	28.9	Carbon tetra	26.8	Ethyl ether	17.0
	(0.0289	chloride	(0.0268)		(0.017)

As can be seen, for most liquids, surface tension at room temperature varies between 15 to 50 dynes cm^{-1}. For water, however, γ is 72.8 dynes cm^{-1} at 20 C. This high value is obviously due to strong intermolecular forces which exist in water as a result of extensive hydrogen bonding.

***Effect of Temperature on Surface Tension*:** According to the kinetic theory, molecular kinetic energy is proportional to absolute temperature. The rise in temperature of a liquid, therefore, is accompanied by increase in energy of its molecules. Since intermolecular forces decrease with increase in the energy of molecules, the intermolecular forces of attraction decrease with rise of temperature.

Hence, surface tension of a liquid decrease with rise in temperature. At critical temperature, since the surface of separation between a liquid and its vapour disappears, the surface tension falls to zero.

Eotvos found that surface tension varies linearly with temperature. He suggested the following expression for the variation of surface tension with temperature:

$$\gamma\left(M_m/\rho\right)^{2/3} = a - kt \qquad \text{...3.72}$$

where M_m is molar mass, ρ is density and γ is surface tension of the liquid at the temperature, t; *a* and *k* are constants.

At the critical temperature *(i.e.,* when t = tc), the surface tension is zero. Substituting these values in Eq. 3.72, we may write

$$0 = a - kt_c$$

or

$$a = kt_c \qquad \text{...3.73}$$

The Eotvoc equation, therefore, may be written as

$$\gamma\left(M_m/\rho\right)^{2/3} = k\left(t_c - t\right) \qquad \text{...3.74}$$

This equation has been found to be satisfactory in giving variation of surface tension with temperature in the case of a number of liquids over a wide range of temperature.

Since surface tension vanishes roughly 6 C above the critical temperature rather than at the critical temperature, Ramsay and Shields proposed the following equation for the temperature-dependence of surface tension:

$$\gamma\left(M_m/\rho\right)^{2/3} = k\left(t_c - t - 6\right) \qquad \text{...3.75}$$

***Some Effects of Surface Tension*:** Some important effects of surface tension may now be considered.

1. The effect of surface tension is to reduce the area of the surface to a minimum. Hence, drops of a liquid or bubles of a gas are spherical in shape. As stated before, a sphere has minimum surface area for a given volume.
2. The rise of a liquid in a capillary tube *(e.g.,* rise of oil in the wick of a lamp, rise of underground water to the surface of earth) are well-known phenomenons. These can be explained in terms of surface tension. Capillary-rise phenomenon is partially responsible for the rise of water in plants and soils.
3. One of the most interesting consequences of surface tension is the fact that the vapour pressure of a liquid is greater when it is in the form of small droplets than when it has a

plane surface. According to the Kelvin equation, the vapour pressure P for a very small droplet of radius r is given by the relation.

$$ln(P/P_0) = 2\gamma M_m/(r\rho RT) \quad ...3.76$$

where P_o is the vapour pressure of the bulk sample of the liquid, ρ is its density and R is the gas constant. The conclusions of this equations have been verified experimentally.

How to Measure Surface Tension?

The Stalagmometer Method: The stalagmometer consists of a pipette-like tube having a very smooth capillary end with sharp edges. It is filled with the liquid upto the mark A by sucking at the upper end of the tube. The liquid is then allowed to come down in the form of drops. Each drop coming out of the capillary end goes on increasing in size to a certain point and then falls down. The ultimate size of the drop depends upon the radius of the capillary orifice and the surface tension of the liquid. The drop is supported by the force of surface tension, $2\pi r\gamma$ where r is the radius of the drop at the end of the capitallary tube.

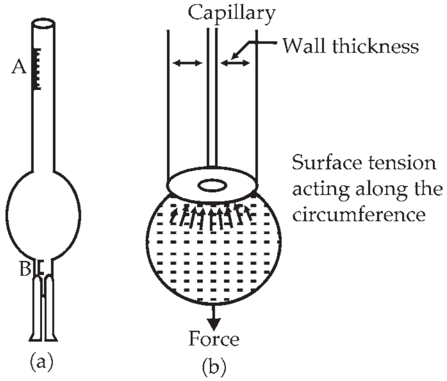


Fig. *(a) Stalagmometer with end flattened and carefully ground and polished, (b) liquid drop formation at stalagmometer*

The drop falls when its weight w just exceeds the force of surface tension. A moment before, at equilibrium,

$$w = mg = 2\pi r\gamma \quad ...3.77$$

where m is the mass of the drop and g is the acceleration due to gravity. The surface tension of the liquid may thus be determined from a knowledge of the weight of the drop and its radius.

For drops of two liquids of weight w, and w_2, we have

$$w_1 = m_1 g = \pi r \gamma_1 \qquad ...3.78$$

and

$$w_2 = m_2 g = 2\pi r \gamma_2 \qquad ...3.79$$

Hence

$$\gamma_1/\gamma_2 = w_1/w_2 \qquad ...3.80$$

Knowing the surface tension of one liquid, generally water, that of the other can be easily evaluated.

It is more convenient to count the number of drops formed by equal volumes of two liquids than determining the weights of single drops. Let n_1 and n_2 be the numbers of drops formed from the same volume V of the two liquids. Then,

Mass m_1 of a single drop of liquid 1 = $V \quad \rho_1/n_1$

Mass m_2 of a single drop of liquid 2 = $V \quad \rho_2/n_2$

where ρ_1 and ρ_2 are the densities of the two liquids. Thus, for liquid 1

$$V \rho_1 g/n_1 = 2\pi r \gamma_1 \qquad ...3.81$$

and for liquid 2,

$$V\rho_2 g/n_2 = 2\pi \, . \, r\gamma_2 \qquad ...3.82$$

Dividing Eq. 3.81 by Eq. 3.82, we get

$$\gamma_1/\gamma_2 = n_2\rho_1/n_1\rho_2 \qquad ...3.83$$

or

$$\gamma_1 = \frac{n_2\rho_1}{n_1\rho_2} \times \gamma_2 \qquad ...3.84$$

The number of drops formed per minute should not exceed 20 as otherwise they will not be properly formed. This rate can be controlled with the help of a pinch cock attached to a rubber tube fixed at the upper end of the stalagmometer, not shown here.

***Surface Active Agents*:** A number of substances are known which when added to water, lower its surface tension. These substances are called surface active agents or surfactants. Thus, liquids like methanol, ethanol, acetone and acetic acid when added to water, lower its surface tension. Similarly, soaps when mixed with water lower its surface tension. There are a host of other substances such as salts of higher sulphonic acids and higher amines which behave in this manner. They are all surface-active materials. These substances act as detergents.

Let us explain the action of soap as a detergent. Most of the dirt or dust sticks on the grease or oily materials which somehow gather on cloth. As grease is not readily watered by water, it is difficult to clean the garment by water alone. The addition of soap lowers the interfacial tension between water and grease so as to facilitate the mixing of the two. The soap molecules get oriented at the interface between water and oil (or grease in such a way that their polar end (–COONa) is dipping in water and the hydrocarbon chain (R–) in the oil. This helps in bringing the two liquid phases in more intimate contact with each other. In other words, the pressure of soap causes emulsification of grease in water. The mechanical action, such as rubbing, release the dirt.

Viscosity

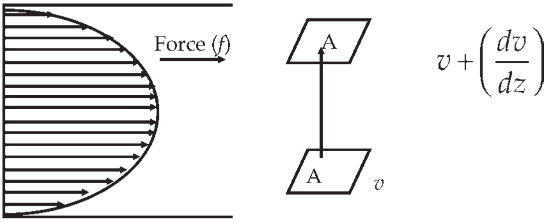
The flow is a characteristic property of liquids. Viscosity is defined as the resistance of a liquid to flow. Consider a liquid flowing through a narrow glass tube. The flow of the liquid molecules can be analysed in terms of molecular laminar layers arranged one over another. A laminar layer has negligible thickness. The layer immediately in contact with the surface of the inner wall of the tube is stationary. However, the velocity of the successive layers increases as we move away from the surface. As a result, a velocity gradient is set up along the z-axis.

If the distance between the two layers is r and the slow-moving layer moves with a velocity ν, then the faster-moving layer moves with a velocity $\nu + r dv/dz$. When a molecule moves from the faster layer to the slower layer, it transport momentum to the latter thereby speeding it up. Conversely, when a molecule moves from the slower layer to the faster layer, it retards the latter. In this way, there arises a frictional force or drag between the two layers which gives rise to viscosity which may thus be defined as the resistance that one part of a liquid flowing with one velocity offers to another part of the liquid flowing with a different velocity. In simple words viscosity *may be looked upon as the force of friction between two layers of a liquid moving past one another with different velocities.*

If we want to maintain the velocity gradient, we must apply an external force along the *y-axis.* This force is proportional to the area and the velocity gradient, that is,

$$F \propto A\,(dv/dz) = -\eta A\,(dv/dz) \qquad \text{...3.85}$$

where the constant of proportionality η is called the *coefficient of viscosity.* The minus sign shows that the viscous force on the faster layer is in the opposite direction to its motion.



(a) (b)

Fig. *The velocity profile during the flow of a liquid in a glass tube.*

Eq. 3.85 is Newton's law of viscosity. It is experimentally observed by several liquids provided their rate of flow is not very high. The fluid flow to which this equation applies is called laminar (or streamlined) flow. The equation does not apply to turbulent flow. Liquids which do not obey Eq. 3.85 are called non-Newtonian liquids. For Newtonian liquids, η is independent of dv/dz whereas for non-Newtonian liquids, η changes as dv/dz changes.

Units of viscosity is c.g.s. system: From Eq. 3.85

$\eta = F\,dz/A\,dv$

If F is measure in dynes, dz in cm, A in cm^2 and dv in cm sec^{-1}, then the units of η are $\frac{\text{dynes} \times \text{cm}}{\text{cm}^2 \times \text{cmsec}^{-1}}$ = dynes cm^{-2}sec. For simplicity, the units of viscosity, *viz.,* dynes sec cm^{-2}, are called *poise.* Still more convenient units of viscosity are *centipoises* and *millipoises* (one millipoise = 0.001 poise and 1 centipoise = 0.01 poise).

Units of Viscosity in SI system: If F is measure in newtons, dz in metres, A in square metres and dv in metres sec^{-1}, then, we get the coefficient of viscosity in units of kg m^{-1} s^{-1}, as illustrated below:

$$\eta = \frac{Fdz}{Adv} = \frac{\text{kgms}^{-2}\,\text{m}}{\text{m}^2\,\text{ms}^{-1}} = \text{kgm}^{-1}\,s^{-1}$$

It can be easily shown that 1 poise = 10^{-2} kg m^{-1} s^{-1}.

***Table:** Coefficients of Viscosity in Centipoise (20 C)*

Liquid	n	Liquid	n
Water	1.008	Benzene	0.647
Chloroform	0.563	Acetone	0.329
Ethyl alcohol	1.216	Acetic acid	1.229
Methyl alcohol	0.593	Nitrobenzene	2.010
Ethyl ether	0.233	Carbon tetrachloride	0.968

Polyhydric alcohols like glycerol have high viscosities because of the formation of a network of hydrogen bonds between the molecules. The network which extends throughout the liquid makes the flow difficult.

The reciprocal of viscosity is called fluidity and is denoted by ϕ. Thus, $\phi = 1/\eta$.

Measurement of Viscosity

The Ostwald Viscometer Method: There are a number of methods of different kinds of measuring viscosity. The method commonly employed is the Ostwald's viscometer method which is based on Poiseullie's law. This connects the rate of flow of a liquid through a capillary tube with the coefficient of viscosity of the liquid and is expressed by the equation

$$\eta = \frac{\pi r^4 tP}{8Vt} \qquad ...3.86$$

where V is the volume in ml of the liquid flowing in t seconds through a narrow tube of radius r cm and length l cm under a hydrostatic (driving) pressure of P dynes per square centimetre and η is the coefficient of viscosity in poises (i.e., dynes per square centimetre).

Since the hydrostatic pressure P of a liquid column is given by

$$P = h\rho g$$

where h is the height of the column and p is the density of the liquid, the Poiseuille's equation 3.15 may be written as

$$\eta = \frac{\pi r^4 th\rho g}{8Vl} \qquad ...3.87$$

It is not necessary to measure all quantities on the right hand side of the above equation. The viscosity of water at different temperatures has been very accurately determined. The usual procedure is to determine the viscosity of a liquid with reference to that of water.

This is termed as relative viscosity. All that is needed to be done is to measure the times of flow for equal volumes of water and the liquid under examination, through the same capillary. If t_1 and t_2 are the times of flow of the same volume of water and the liquid, respectively and η_1, and η_2 are their respective coefficients of viscosity, then,

$$\frac{\eta_1}{\eta_2} = \frac{\pi r^4 t_1 h \rho_1 g}{8Vl} \times \frac{8Vl}{\pi r^4 t_2 h \rho_2 g} \qquad ...3.88$$

where ρ_1 and ρ_2 are the densities of water and the liquid, respectively.

The value of *h* is the same in both cases since equal volumes of both liquids are taken and, therefore, they stand at the same height. Hence,

$$\eta_1 / \eta_2 = \rho_1 t_1 / \rho_2 t_2 \qquad ...3.89$$

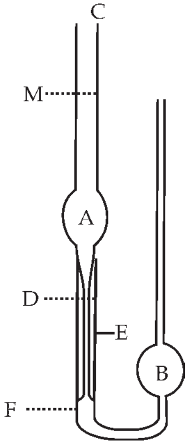


Fig. *Ostwald viscometer*

The Ostwald viscometer used for measuring viscosity by the above method is shown in the figure given above. It is first thoroughly cleaned with chromic acid mixture and dried. A known volume of water, usually 10 to 25 ml depending upon the capacity of the bulb *A*, is pipetted into the bulb *B* (bulb *B* is bigger than

A, as shown). It is then sucked into the bulb *A* with the help of a rubber tube attached at the end *C* till it rises to the mark *M.*

The time taken by this water to flow through the capillary tube *DF* is noted by means of a stop watch. Let it be t_y The viscometer is dried and the same volume of the liquid under examination is taken into the bulb *B* (so that the pressure head remains the same) and the process repeated as before. Let the time of flow be t_2.

Knowing the coefficient of viscosity of water (h_1). that of the other liquid *(η_2)* can easily be calculated with the help of Eq. 3.89.

4

Symmetry Elements

Symmetry is an idea has an aspect of universality to it. In virtually every facet of human endeavour and natural phenomena, cutting across the boundaries of time and space, we find manifestations of symmetry. As Herman Weyl said “Symmetry, as a inside or as narrow as you may define its meaning, is one idea by which mail through ages has tried to comprehend and create order, beauty and perfection.” The all-embracing nature of the concept of symmetry is staggering within its fold lie subjects as far removed from one another as particle physics, relativity, crystallography, molecular structure, spectroscopy, rangoli patterns and Islamic art. Scientists are far from being the only ones ponder about the concept, and William Blake, immortal poems reflect man’s age-old fascination with symmetry.

Tiger! Tiger! burning bright
In the forests of the night,
What immortal hand or eye
Dare frame thy fearful symmetry?

Those keen on the analysis of poetry will note that Blake’s himself chooses to break the symmetry in the end, with his use of the word ‘symmetry’. Here is Wordsworth’,

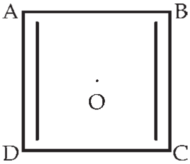
To see a World in a Grain of Sand
And a Heaven in a Wild Flower
Hold Infinity in the palm of your hand
And Eternity in an hour.

(What symmetry is being reflected in there lines?)

It has been said that 'symmetry is death'. The pun is suggestive– 'symmetry' and 'cemetery'(!) the purport presumably is that symmetry carries an association of stasis and lack of change, whereas life is ever changing, ever moving. But, in fact, some of the finest examples of symmetry come from nature itself: the striking axial symmetry of a butterfly's wings, the rotational symmetry of a flower, the astonishing 3-dimensional symmetry of certain radiolaria and pollen grains, the spiral arrangement of seeds in a sunflower, the logarithmic spiral arrangement of a snail shell, the spiralling double helix of the DNA molecule, etc. It is one of the strange facts about the world that life has the urge as well as the capacity to create symmetric forms. Another curious thing is the phenomenon of left-right asymmetry in some organic molecules like sugars and preference of living forms for one type of orientation. Why this should be so, and whether symmetry is inevitable in any form of life, is something the reader should reflect upon.

Factors and Functions of Symmetry

Symmetry is a widely distributed property in nature. The human body is symmetric; the left hand is the mirror image of the right hand. Each wing of a butterfly is the mirror image of the other half. Thus a plane of symmetry divides the two halves and a reflection in this plane transfer the left hand side to the right hand side and *vice versa*. As this operation does not cause any change or deformation in the object, the result of the operation is indistinguishable from the original. Such operation is called the symmetry operation—the rotation of the object through a definite angle about some axis, the reflection of it in some plane, and translation of the object over some distance. Of these, the translation operation is applicable only to an infinite medium as a crystal lattice. An object of finite dimensions, such as a molecule, can be symmetrical only with respect to rotation and reflection.



Symmetry operations in a molecule or any other object are carried out with respect to some fixed plane or a fixed axis. The features are called elements of symmetry. Consider the cyclobutadiene molecule as shown in the figure given above. Though all the four corners of the molecule are equivalent, yet to understand how the symmetry operations operate, these have been alphabetically named.

Although there are two fundamental types of symmetry operations, such as rotation and reflection, but an examination of different molecules reveal that there are four operations, rotation, reflection, improper rotation and inversion which will now be considered.

Rotations: A rotation through 360/n degrees about an axe is denoted by C_n. Such an axis is called *n* fold axis is symmetric. The number n can take integer value n = 1,2, 3, 4 and 6. Axis is a line drawn perpendicular to square and passing through point O can be one axis. Upon rotating the square by 360/4 = 90 about this axis brings it to a configurations 2, a further rotation of the molecule by 90 brings it to stage 3 as shown in the figure below, then on further rotation of molecule by 90 and 180 places cyclobutadiene to stage 4 and 1.

The above four configurations may be written by a symbol C_p^m which may represent rotation by $\frac{m360}{p}$. For $C_4 m = 1$, for C_4^2, $m = 2$, for C_4^4 m = 4 and is equal to identity operation. C_4^2 is equivalent to C_2.

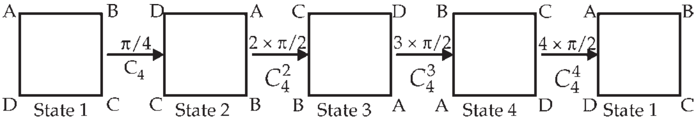
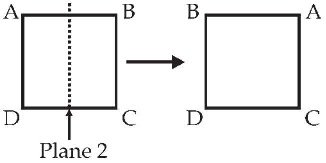


Fig. *However this molecule does not have a* C_3, C_6, *axis.*

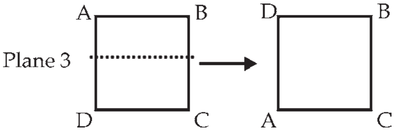
Plane of Rotation: It is denoted by letter σ.

Plane 1: Plane of the molecule which does not make any change in coordinates of the molecule and is the identity operation.

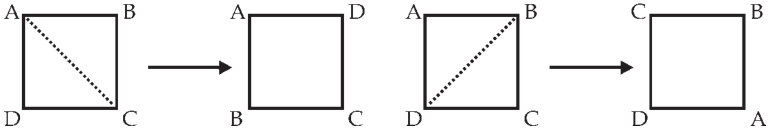
Plane 2: Plane 2 is perpendicular to the molecular plane but passing through the midpoints of line joining AB and CD. Symmetry operation will change the points as shown in the figure given below.



Plane 3: Like plane 2 it is perpendicular to the molecular plane but passing through the midpoints of AD and BC, operation will change the point as shown in the figure given below.



Plane 4 and 5: These planes are perpendicular to the molecular plane but pass through AC/BD. Symmetry operation will change points as shown in the figures given below. It maybe noted that of a second time reflection is carried out on the same plane it will return the molecule to original coordinates.



Improper Rotations: A rotation by 360/n about an axis followed by a reflection in a plane perpendicular to the axis is called rotation-reflection symmetry operation. A combined operation of this kind is called a rotation-reflection or an improper rotation and is denoted by the symbol S_n standing for the combination of a rotation through an angle $2\pi/n$ about some axis and reflection in a plane perpendicular to the axis. C_4 operation followed by reflection through the plane of molecule gives S_4 axis. If we use the symbol σ_h to denote the reflection in the plane perpendicular to rotatory-reflection axis we can write

$$S_4 = \sigma_h C_4$$

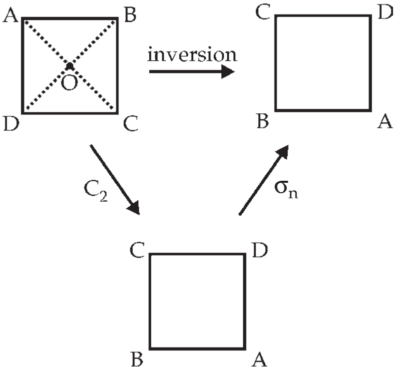
or in general $$S_n = \sigma_h C_n$$

By applying S_n twice we do two rotation C_n and two reflection σ_h; since the double reflection is equivalent to the identical operation E and result is a simple rotation through the angle 2 $(2\pi/n)$. We may, therefore write

$$S_n^2 = C_n^2$$

Maintenance of Symmetry

If a molecule can be brought into equivalent configuration by changing the coordinates of every atom where the origin of coordinates lies into (–x, –y, –z). The point at which origin lies is said to be the centre of symmetry. As in the case of cyclobutadiene point O is the centre of symmetry it will change the molecule, as shown in the figure given below.



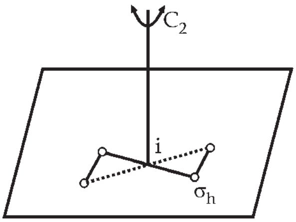
Since all the points are inverted it is called an inversion operation. This is a special case of improper rotation. It is easy to see that a rotation through an angle 180 followed by a reflection in the plane perpendicular to the axis of rotation is inversion as shown by second path in the figure given above.

Now if one of the carbons in cyclobutadiene made up to ^{12}C atom, say atom A is replaced by ^{13}C atom, now the molecule cannot remain symmetrical. Rotation operation by C_4 axis does not lead to equivalent position, hence fourfold and twofold rotation axis of symmetry, are lost.

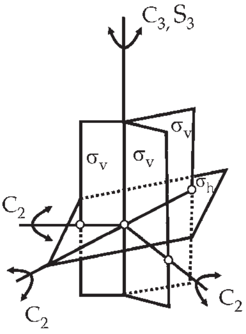
Symmetry planes–plane 2, plane 3, plane 5 do not lead to equivalent position because of the presence of atom ^{13}C at position A. The molecule does not have now centre of symmetry. In other words, introduction ^{13}C has decreased the cyclobutadiene symmetry.

All *p* and *d* atomic orbitals are symmetrical about rotation and reflection axis. However, the hybridised orbitals are highly asymmetric because they do not have any reflection plane of symmetry, rotational axis of symmetry.

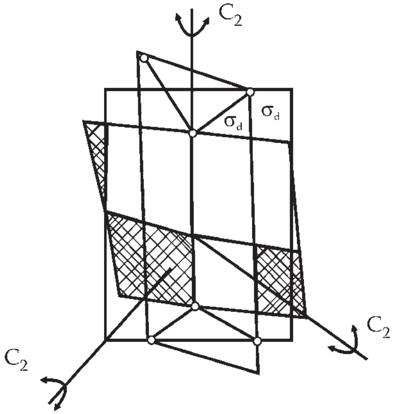
Symmetry elements of some molecules are illustrated in the figure given below.



Molecule: $N_2O_2^{-2}$ ion
Symmetry Elements C_V, σ_h, $i \equiv S_2$
Point Group : C_{2h}



Molecule: BF_3
Symmetry Elements: $2C_3$, $3S_3$, $3C_2$, $3\sigma_v$, σ_h
Point Group : C_{3h}



Molecule: B_2Cl_4
Symmetry Elements: C_2, S_4, $2C_2$, $2\sigma_d$
Point Group : D_{2d}

Fig. *Symmetry elements and point groups of three type of molecules, σ_v, σ_h, σ_d denote vertical, horizontal and diagonal plane of symmetry.*

The five kinds of symmetry elements and operation are compiled in the above table.

Table: *Various kinds of symmetry elements and operations*

Symmetry elements description	Symbol	Symmetry operation
1. Identity	E	Leaves the molecule unchanged
2. *n*-fold rotation axis of symmetry where $p = 1, 2, 3, 4$, or 6	C_p	Rotation by an angle of $360/p$ about the axis producing indistinguishable configuration from original
3. Plane of symmetry	σ	Reflection of a molecule with respect to some plane producing indistinguishable configuration from original
4. *p*-fold rotation-reflection axis of symmetry	S_p	Rotation by an angle of $360/p$ followed by reflection at a plane perpendicular to the rotation axis
5. Centre of symmetry	*i*	Reflection at the centre producing a configuration indistinguishable from original one. The centre is called centre of symmetry

Classes of Symmetry

The set of symmetry operations belonging to a given molecule has the following four properties:

(i) The product QP of the two elements P and Q of the set is an element of the set (i.e. the product, as we have defined it, of two symmetry operations of the molecule is also a symmetry operation of the molecule).

(ii) The product is associative; R(QP) = (RQ)P.

(iii) The set contains an element E with the property

$$RE = ER = R$$

where R is any element of the set. This element is called the unit element of the set; it is, of course, just the identity operation which leaves the molecule unchanged.

(iv) Each element R of the set has an inverse R^{-1} which is also an element of the set and satisfies

$$RR^{-1} = R^{-1}R = E.$$

The four properties are the defining properties of a group: A group is a set of elements of whatever kind for which we can define the product of a pair of elements and which has the properties *(i)-(iv)* above. Hence it follows that the set of all the symmetry operations belonging to a molecule forms a group, the symmetry group of the molecule, and that the methods of group theory can be used to discuss the symmetry of a molecule.

Group theory is not concerned with the nature of the group elements; it deals only with the formal structure of the group defined by the multiplication rules for the group elements. For example, we have used the geometrical shape of the BF_3 molecule to obtain its symmetry operations and have found the results of multiplying each pair of symmetry operations together. Any other molecule with the same basic symmetry will have the same set of symmetry operations, *i.e.,* the same symmetry group, and all molecules like this are treated alike from the point of view of group theory.

In this theory we abstract from the molecule its system of axes and planes of symmetry with their corresponding symmetry operations. The structure and properties of the symmetry group of the molecule depend only on the relations between its elements, the symmetry operations and these relations are completely determined by the spatial relations between the axes and planes of symmetry. Any two molecule no matter how different in form or complexity, which have the same system of axes and planes of symmetry will have the same symmetry group and those of their properties which depend on symmetry will be the same.

This is one of the reasons for the power and generality of group theoretical methods in discussing the properties of molecules; for although the number of different imaginable molecules is unbounded, this is not true of their possible systems of axes and planes of symmetry. These are severely restricted by geometrical considerations and it is possible to write down a list of all the molecular symmetry groups that can exist and to discuss their properties once and for all. To apply the results of the theory to a particular molecule, all that is necessary is to identify its symmetry group and then to use standard methods to extract the desired information from the known properties of this group.

Before going on to discuss the molecular symmetry groups in more detail we note one feature that they all possess. A symmetry operation which rotates or reflects a molecule into itself must leave the centre of mass (centre of gravity) of the molecule unmoved; if the molecule has a plane or axis of symmetry, the centre of mass must lie on this plane or axis. It follows that all the axes and planes of symmetry of a molecule must intersect in at least one common point and that at least one point remains fixed under all the symmetry operations of the molecule. For this reason, the symmetry group of molecule is generally referred to as its point group and we shall use this name, which is taken over from crystallography, from now on.

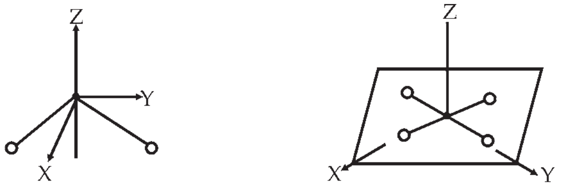
Role of Coordinate Axis

It is desirable to place every molecule in a coordinated system in such a manner as to minimise the ambiguities. The following procedure is recommended.

1. Place the origin of the coordinate system at the centre of gravity of the molecule. This point remains fixed under all symmetry operations.
2. Assignment of Z-axis
   a. The Z-axis is always considered to be vertical.
   b. If there is only one rotational axis, take this as the Z-axis. Thus in H_2O the C_2-axis becomes the Z-axis.
   c. If the molecule has several rotational axes, the one of highest order is taken as the Z-axis. The molecule is placed in a such a way that the Z-axis is vertical. Thus the axis of highest order in the square planar complex $(PtCl_4)^{-2}$ and benzene have fourfold and sixfold, respectively taken to be the Z-axis.
   d. If there are several rotational axes of highest order, the axis that passes through the largest number of atoms is taken as the Z-axis. As in ethylene and naphthalene,

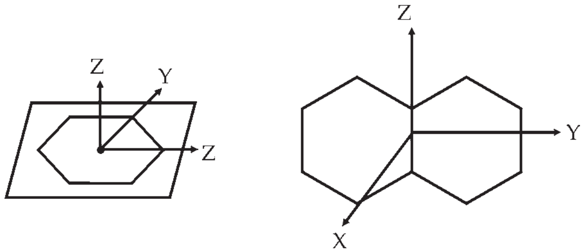
each has three the C_2-axis, the one passing through the bridging carbon atoms is considered the Z-axis.

3. Assignment of X-axis.
   a. If the molecule is planar and the Z-axis lies in this plane, the X-axis is chosen to be normal to this plane, e.g. naphthalene.
   b. If the molecule is planar and the Z-axis is perpendicular to this plane, the X-axis is chosen to pass through the largest number of atoms. In benzene, the X-axis passes through the centre of carbon-carbon atoms.
   c. In all other cases the choices are equivalent and hence the assignment is arbitrary, but preference should be given to the axis passing through the largest number of atoms, e.g.$(PtC1_4)^{-2}$.



Molecule: H_2O
Point Group: C_2v

Molecule: $(PtCl_4)^{-2}$
Point Group: D_{4h}



Molecule: Benzene
Point Group: D_{6h}

Molecule: Napthalene
Point Group: D_{2h}

***Fig.** Coordinate axis of molecules.*

4. *Assignment of Y-axis*: An axis perpendicular to the XZ planes is assigned as Y-axis.
5. The possible directions of the axes are found by extending the thumb, index and middle finger of the right hand in the three mutually perpendicular directions. The possible X, Y,

and Z lies in the direction of the thumb, index and middle finger to which these point.

Groups of Molecular Point

We are now in a position to describe and classify the various molecular point groups. In this designation bold face symbols represent the point groups and the non-bold symbols are used to denote symmetry operations. The bold face symbols are used for the point groups are based for the most part on the principal symmetry elements of the group and that subscripts added to some of the point group symbols further tie in the symbol with elements in the group.

The point groups can be classified into three broad divisions. There are, firstly, two simple groups C_s and C_i which arise when a molecule possesses just one plane of symmetry or just centre of symmetry. Secondly, there is a sequence of groups which are distinguished by possessing a single main n-fold axis of symmetry: these are the groups designated by the symbols C_n, S_{2n}, C_{nh}, C_{nv}, D_n, D_{nh}, D_{nd}. Finally, there are groups, with more than one main *n*-fold symmetry axis, which are related to the symmetry of the regular solids, in particular the tetrahedron and the octahedron.

The Groups C_s and C_i

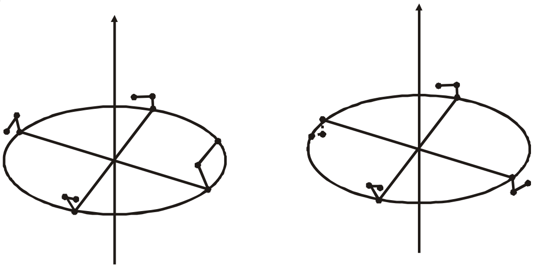
A molecule may possess just a single plane of symmetry, so that its only symmetry operations are E and the reflection a in the plane of symmetry. This group of two elements is called C_s.

Again the molecule may possess just a centre of symmetry, so that its only symmetry operations are E and the inversion *i*. This group of two elements is called C_i.

Groups with one Main Axis of Symmetry

If a molecule possesses one main *n*-fold axis of symmetry all its symmetry operations must leave the main symmetry axis unaltered or at most, reverse its direction. Apart form rotations or improper rotations about the main axis the only other symmetry operations which satisfy this condition are: a reflection in a plane perpendicular to the main axis (such a plane is called a horizontal plane and the reflection operation is denoted by σ_h; a reflection in a plane containing the main axis (such a plane is called a vertical plane and the reflection operation is denoted by a_v; or a rotation through 180 about a twofold axis perpendicular to the main axis (such a rotation is denoted by C'_2).

These operations may be combined in various ways; we obtain the following enumeration of groups with one main axis of symmetry.



(a) (b)

Fig. *(a)* C_4 *Elements* E, C_1 C_2, C_4^{-1} (b) S_4 *Elements* E, S_4 $S_4^2 = C_2$, S_4^{-1}

Group C_n: This has a single *n*-fold symmetry axis, and the elements of C_n are the *n* rotations C_n, C_n^2.... C_n^n = E. These operations all commute with each other and each elements of the group is in a class by itself.

Group S_{2n}: This has a single alternative axis of *even* order *2n* and the group elements are the improper rotations $S_{2n}, S_{2n}^2 = C_n$, $S_{2n}^3, ..., S_{2n}^{2n} = E$. They all commute with each other and each element is in a class by itself.

The simplest group of this type is S_2 which has the two elements E and S_2 = *i;* it is the same as the group C_i mentioned above.

Group C_{nh}: This group is obtained from C_n by adding a horizontal symmetry plane perpendicular to the axis of rotation. Apart from the *n* rotations of C_n, this group contains the *n* improper rotations $\sigma_h C_n^k$ including the pure reflection $\sigma_h C_n^n$. All these elements commute and each is in a class by itself.

Examples:

(i) The simplest group of this type is C_{1h} with the two elements *E* and σ_h. It is identical with the group C_s mentioned above.

(ii) The next simplest group is C_{2h} with elements E, C_2, σ_h and $\sigma_h C_2 = i$. This is the point group of molecules like trans $C_2H_2Cl_2$.

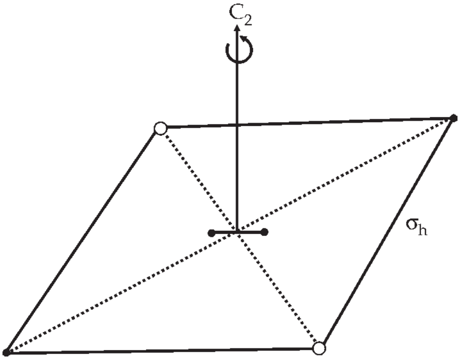


Fig. C_{2h} *trans-*$C_2H_2Cl_2$.

Group C_{nv}**:** If we add to C_n a vertical symmetry plane containing the axis of rotation, there will be altogether n such planes intersecting at angles π/n. The elements of C_{nv} are the n rotation of C_{nv} and the n reflections σ_v in these vertical planes.

The division of the n reflections σ_v into classes depends on whether n is even or odd. The operation C_n, a rotation through $2\pi/n$, moves each plane of symmetry into the next plane but one. Thus if n is odd we can move any particular plane of symmetry into the position of any other plane by successive applications of C_n, and all the reflections σ_v are in the same class. If n is even, however, there will be two independent sets of alternate planes which can never be mixed by any of the rotations or by any of the reflections; correspondingly, the reflections a_7, are divided into two distinct classes.

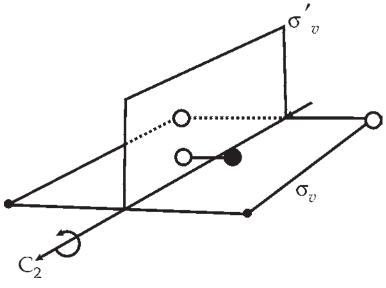


Fig. *cis* $C_2H_2C1_2$.

Examples:

(i) C_{1v} is the same group as $C_{1h} = C_s$ with just a single plane of symmetry.

(ii) C_{2v} has the elements E, C_2, σ_v, σ'_v, where σ_v and σ'_v are reflections in two mutually perpendicular planes intersecting along the twofold axis. This is the point group of molecules like H_2O, SO_2, or cis-$C_2H_2Cl_2$.

(iii) C_{3v} is the point group of NH_3, or any molecule with the symmetry of a trigonal pyramid.

(iv) C_{4v} is the point group for a pyramid with a square base. The two classes of reflections in C_{4v} arise from the pair of symmetry planes containing the diagonals of the square and the pair of planes passing through the midpoints of opposite sides of the square. A molecule with this point group is SF_5Cl.

Group D_n: We return now to the group C_n of rotations about the main axis and add a twofold symmetry axis perpendicular to the main axis. There will be altogether *n* such twofold axes intersecting at a point on the main axis. The angle between two adjacent twofold axes is π/n. The *n* rotations of C_n and *n* rotations C'_2 about these twofold axes together form the group D_n. By similar arguments to those used for C_{nv} we find that in D_n each rotation C_n^k and C_s^{-k} from a class of two elements; if *n* is odd, all the rotations about the twofold axes belong to the same class, but if *n* is even they divide into two distinct classes of rotations about two sets of alternate axes.

Examples:

(i) The group D_2 is that of rotations through 180 about three mutually perpendicular axes.

(ii) If the two CH_3 groups in C_2H_6 are in arbitrarily rotated positions, neither 'eclipsed' nor 'staggered', the molecule has the point group D_3.

Group D_{nh}: If the horizontal plane containing the twofold axes of D_n is also a plane of symmetry, then *n* vertical planes containing the main axis of symmetry and a twofold axis are necessarily also planes of symmetry. This system of axes and planes of symmetry gives rise to the group D_{nh} which, in addition to the elements of

D_n, contains n improper rotations $\sigma_h C_n^k$, and n reflections $\sigma_v = \sigma_h C_2'$. The pure rotations of D_{nh} divide into the same classes as those of D_n; correspondingly the improper rotations $\sigma_h C_n^k, \sigma_h C_n^{-k}$ pair off into classes, and the reflections a_v form one class if n is odd and two classes of reflections in alternate planes if n is even.

Another way of looking at D_{nh} is to say that it arises from C_{nv} by the addition of a horizontal plane of symmetry perpendicular to the main axis.

Examples:

(i) D_{2h} has three mutually perpendicular twofold axes. If these are the *x, y, z* axes, and we regard the *z* axis as the main axis, the elements of D_{2h} are: E; C_2 about the z axis; C'_2 about the *x* axis; C'_2 about the *y* axis; σ_c, reflection in the *xy* plane; $\sigma'_v = \sigma'_h C'_2{}'$ reflection in the *xz* plane; $v'' = \sigma_h C'_2$, reflection in the *yz* plane; and $i = \sigma_h C_2 = \sigma'_v C''_2 = \sigma''_v C'_2$, inversion in the origin. These elements all commute and each is in a separate class. An example of this point group is affected by C_2H_4.

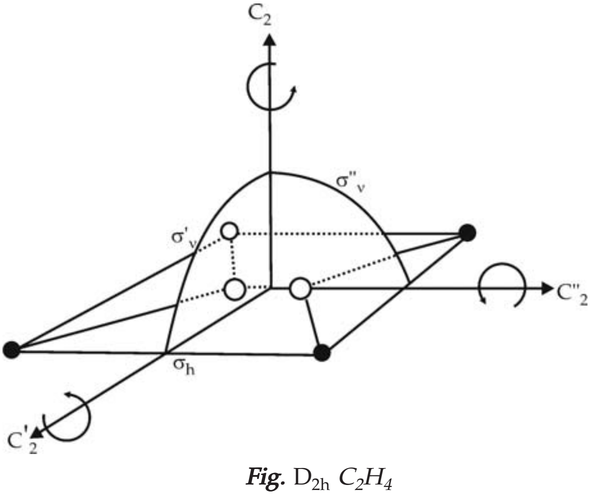


Fig. D_{2h} C_2H_4

(ii) D_{3h} is the point group of any molecule with the complete symmetry of an equilateral triangle, *e.g.*, CO_3^{2-}, $C(NH_2)_3^+$, PF_3Cl_2, *eclipsed-*C_2H_6.

(iii) D_{4h} is the point group of any molecule with the complete symmetry square, *e.g.*, $PtCl_4^{2-}$ phthalocyanine; octahedrally coordinated MX_4Y_2 where the X ligands are at the corners of a square.

(iv) D_{6h} has benzene as its best known example.

Group D_{nd}: Starting again from the system of axes of D_n one can add *n* vertical symmetry planes which contain the main axis and which bisect the angles between adjacent twofold axes. We denote a reflection in such a plane by σ_d. This system of planes and axes gives the group D_{nd} whose elements are the elements of D_n and in addition *n* reflections $\sigma._d$ and *n* elements of the form $\sigma_d C'_2$. These are improper rotations about the *n*-fold axis of the form S_{2n}^{2k+1}, $k = 0, 1, 2,.., n -1$.

By suitable reflections σ_d we can move any one of the twofold axes into the position of any other, and similarly any symmetry plane can be moved into the position of any other by suitable rotations C'_2. Thus the reflections σ_d all belong to one class whether *n* is even or odd; the rotations C'_2 all belong to one class; the rotations C_n^k, C_n^{-k} pair off in classes, as also do the improper rotations.

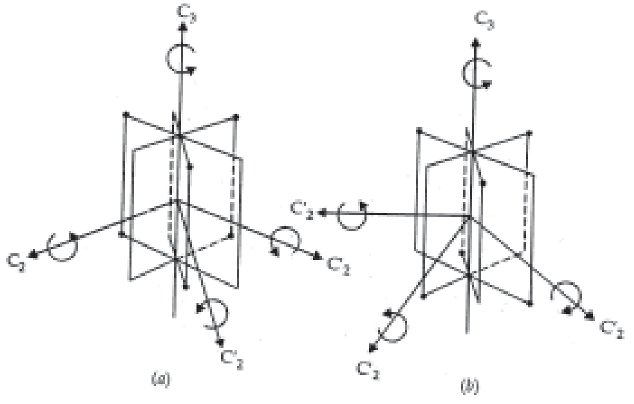


Fig. (a) eclipsed C_2H_6. (b) D_{3d} staggered C_2H_6.

We may note that if *n* is odd, each of the twofold axes is perpendicular to one of the symmetry planes and the corresponding operation $\sigma_d C'_2$ is the inversion *i.*

Examples:

The 'staggered' form of C_2H_6 has the point group D_{3d}. The elements of this group are the elements of D_3 namely E, the two rotations C_3 and C_3^{-1} about the threefold axis, and three rotations C'_2 about the three twofold axes. In addition, there are six elements obtained by multiplying the elements of D_5 by the inversion *i.* These are *i,* $S_6 = iC_3^{-1}, S_6^{-1} = iC_3$, and the three reflections $\sigma_d = iC'_2$.

Linear Molecules

These constitute a somewhat special case, although their point groups are closely related to the scheme just developed. Any linear molecule has an axis of symmetry coinciding with all the nuclei. The order of this axis is $\propto$, that is rotation by any and all angles about this axis constitute symmetry operations. Also, any plane containing the molecule is a plane of symmetry. There is an infinite number of such planes, all intersecting along the molecular axis. Proceeding from this, we have just two possibilities: (i) the molecule of the type of N_2, OCO, HCCH, and so on, such that it consists of two equivalent halves (or) its is of the type HCl, NHO, HCN and so on, and does not consist of two equivalent halves.

In the first case, the equivalence of the two halves mean that any line which is a perpendicular bisector of the molecular axis is a C_2 symmetry axis; there is an infinite number of such C_2 axes. The equivalence of the two halves of the molecule also means that there is a plane of symmetry perpendicular to the molecular axis, $C_\propto$, there is also an infinity of C_2 axes perpendicular to $C_\propto$, and there is a horizontal plane of symmetry. The group is, very reasonably designated $D_{\propto h}$.

For linear molecules which do not consist of equivalent halves, the only symmetry operation are the rotations about $C_\propto$ and reflections in the vertical planes. The group called $C_\propto v$.

Groups with More than One Main Axis

These groups are complex groups and find application in quantum chemistry or in Crystal Field theory and Ligand Field theory that too in a different format.

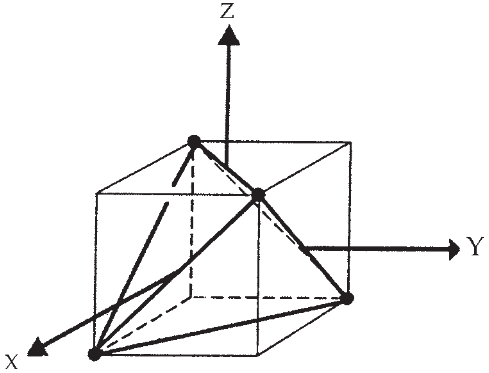


Fig. *A tetrahedron inscribed in a cube.*

If a molecule has several *n*-fold symmetry axes, these must intersect at a point and their spatial arrangement must be such that a rotation C_n about one of the axes results in an interchange of the other axes. This condition severely limits the number of possible groups containing more than one *n*-fold axis. We shall discuss the various values of *n* successively below.

(*a*) $n = 2$: *groups* D_2, D_{2h}, D_{2d}

If we have a set of intersecting twofold axes, there must be three of them, mutually perpendicular to each other. This is the set of axes of the group D_2 described above. There are only two different ways of adding planes of symmetry to this set of axes; these give rise to the groups D_{2h} and D_{2d}.

(b) $n = 3$: *groups* T, T_d, T_h

If we have a set of intersecting threefold axes it seems obvious (and can be rigorously proved) that there must be four such axes whose directions are those of the body diagonals of a cube, or, what is the same thing, whose directions lie along the lines joining the centre of a regular tetrahedron to its. The product of successive rotations C_3 about two of these threefold axes may be found by drawing diagrams, it is found that the product is either another rotation C_3 or a rotation C_2 about a line joining the midpoints of opposite faces of the cube. There are altogether three such lines so that the existence of the four threefold axes necessarily implies the existence of these three mutually perpendicular twofold axes. This set of threefold and twofold axes is complete: all the rotations associated with them together form a group called T, the group of rotations which move a regular tetrahedron into itself.

There are just two ways of enlarging this group by adding planes of symmetry (any such plane must, of course, reflect a threefold axis into a threefold axis and a twofold axis into a two fold axis). The first way is to introduce reflection planes which contain two of the threefold axes and one of the twofold axes and which bisect the angle between the other twofold axes. These are the six planes which pass through pairs of opposite edges of the cube and this system of axes and planes of symmetry gives rise to the complete point group of a regular tetrahedron. This group is called T_d.

The second way of adding planes of symmetry is to take three planes each of which contains two of the twofold axes and is perpendicular to the third twofold axis. This introduces inversion as a symmetry operation and gives rise to a group called T_h which does not appear to be of interest in chemistry.

It might seem possible to extend the group still further by having both sets of symmetry planes simultaneously present. In this case, however, one would have a set of planes intersecting along the C_2 axes at angles of 45 . The product of two reflections in adjacent planes would be a rotation C_4 about their line of intersection which would, therefore, be a symmetry axis with $n = 4$ and would belong to the next case to be described.

(c) $n = 4$*: groups O,* O_h

If we have intersecting fourfold axes, it seems obvious (and can be rigorously proved) that there must be three such axes, mutually perpendicular to each other. If one imagines these to be the axes passing through the midpoints of opposite faces of a cube in the following figure shows that the product of two rotations C_4 about different axes is a rotation C_3 about a body diagonal of the cube. There are four such diagonals and the existence of the three fourfold axes thus necessarily implies the existence of four threefold axes like those of T. Again, the reader may verify by adding a further rotation C_4 to the diagrams of the given figure that a rotation C_4 about one of the fourfold axes, followed by a rotation $C_4^2 = C_2$ about another, is a rotation C_2 about a line joining the midpoints of a pair of opposite edges of the cube. Thus the existence of the fourfold axes necessarily implies the existence of six twofold axes of this kind. The set of three fourfold axes, four threefold axes and six twofold axes is complete: all the rotations associated with them together form a group which is called O.

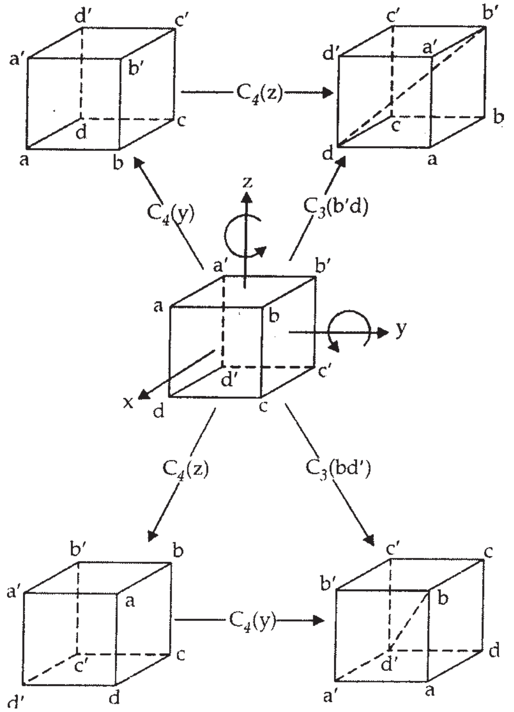


Fig. *Non-commuting rotations.*

$C_4(z)C_4(y) = C_3(b'd)$; $C_4(y)C_4(z) = C_3(bd')$.

It is the group of rotations that move a cube into itself. Since a regular octahedron can be symmetrically inscribed into a cube, with its vertices at the centre of the cube faces, O is also the group of rotations that move a regular octahedron into itself.

The only consistent way of adding planes of symmetry to the set of axes of O is simultaneously to introduce both the sets of planes described above for the case $n = 3$. The centre of the cube then becomes a centre of symmetry and one obtains the complete point group of a cube or a regular octahedron. It is called O_h

(d) $n = 5$: *groups I,* I_h

These groups contain twelve fivefold axes, twenty threefold axes and fifteen twofold axes. They are related to the symmetry of the icosahedron (a regular solid with twenty equilateral triangular faces) and the pentagonal dodecahedron (a regular solid with twelve regular pentagonal faces). They do not appear to have much chemical interest and we shall say nothing more about them.

The most important of the groups of type III are T_d and O_h. Their properties are summarised below.

T_d the point group of the regular tetrahedron

If the tetrahedron is inscribed with its vertices in alternate corners of a cube, there are three twofold axes joining midpoints of opposite faces of the cube; four threefold axes along the body diagonals of the cube; six symmetry planes through pairs of opposite edges of the cube.

The twenty-four elements of T_d divided into their classes are:

E; three rotations C_2 about the twofold axes; eight rotations C_3 C_3^{-1} about the body diagonals. This set of rotations by itself forms the group T.

The remaining twelve elements of T_d are a class of six reflections in the six symmetry planes and a class of six improper rotations S_4, S_4^{-2} about the twofold axes.

O_h, the point group of the regular octahedron or the cube

An octahedron may be inscribed into a cube with the vertices of the octahedron at the centres of the cube faces. There are three fourfold axes joining the midpoints of opposite faces of the cube; four threefold axes along the body diagonal: six twofold axes joining the midpoints of pairs of opposite edges; six symmetry planes through pairs of opposite edges; three symmetry planes though the centre of the cube parallel to its faces; a centre of inversion at the centre of the cube.

The forty-eight elements of O_h divided into their classes are:

E; six rotations C_4, C_4^{-1} about the fourfold axes; three rotations $C_4^2 = C_2$ about the fourfold axes; eight rotations C_3, C_3^{-1} about the threefold axes: six rotations C'_2 about the twofold-axes. This set of twenty-four rotations by itself forms the group O.

The remaining twenty-four elements of O_h, are obtained by multiplying each element of O by the inversion *i*. They are *i* itself;

six improper rotations S_4, S_4^{-1} about the fourfold axes; three reflections σh, in the planes parallel to the cube faces; eight improper rotations S_6, C_6^{-1} about the body diagonals; six reflections σ_d in the planes through opposite edges.

The systems of planes and axes of symmetry of the point groups are summarised in the table given below. The problem of finding the point group of a given molecule is one that must be solved by inspection and by trying to identify all the axes and planes and symmetry. The groups O_h and T_d are generally easy to recognise. If a molecule does not belong to these one should look for a main axis of symmetry.

If one can be found and if, further, there is a twofold axis perpendicular to it the point group will be of the D type. If there are no twofold axes perpendicular to the main axis, the point group will be of the C type. The final decision then rests on the identification of planes of symmetry. The reader will be well advised to examine models of molecules from this point of view and to work out the point groups of molecules, both planar and non-planar with which he is familiar.

***Table**: Molecular point groups*

Group	Axes and planes of symmetry
C_s	plane of symmetry
Ci	centre of symmetry
C_n	*n*-fold axis
S_{2n}	*2n*-fold alternating axis
C_{nh}	*n*-fold axis; horizontal plane
C_{nv}	*n*-fold axis; *n* vertical planes
D_n	*n*-fold axis; *n* horizontal twofold axes
D_{nh}	rotations as for D_n; one horizontal plane; *n* vertical planes containing the horizontal axes
D_{nd}	rotations as for D_n; *n* vertical planes bisecting angles between the horizontal axes
T_d	tetrahedron
O_h	octahedron or cube

Systematic procedure for deciding to what point group any molecule belongs can be carried out by any one of the two procedures. It is not necessary to commit to memory the symbols and symmetry elements for all the point groups.

Organisation of Symmetry

1. We determine whether the molecule belongs to one of the "special, groups, that is, $C_{\infty v}$ $D_{\infty h}$, or one of those with multiple high-order axes. Only linear molecules can belong to $C_{\infty v}$ or $D_{\infty h}$ so these cannot possibly involve any uncertainty. The specially high symmetry of the others is usually obvious. All of the cubic groups, T, T_h, T_d, O, and O_h, require four C_3 axes, while I and I_h require ten C_5's and six C_5's. These multiple C_3's and C_5's are the key things to look for. In practice only molecules built on a central tetrahedron, octahedron, cuboctahedron, cube, pentagonal dodecahedron, or icosahedron will qualify, and these figures are usually very conspicuous.
2. If the molecule belongs to none of the special groups, we search for proper or improper axes of rotation. If no axes of either type can be found, we look for a plane or centre of symmetry. If a plane only is found, the group 1 is C_s. If a centre only is found (this is *very* rare), the group is C_i. If no symmetry element at all is present, the group is the trivial one containing only the identity operation and designated C_1.
3. If an *even-order* improper axis (in practice only S_4 S_6 and S_8, are likely) is found but no planes of symmetry or any proper axis except a colinear one (or more), whose presence is automatically required by the improper axis, the group is S_4 S_6 S_8 . . . . An S_4 axis requires a C_2 axis; an S_6 axis requires a C_3 axis; an S_8 axis requires C_4 and C_2 axes. The important point here is that the S_{2n}, groups consist exclusively of the operations generated by the S_{2n} axis. If any additional operation is possible, we are dealing with a D_{nd} or D_{nh} type of group. Molecules belonging to these S_{2n} groups are relatively rare, and the conclusion that a molecule belongs to one of these groups should be checked thoroughly before it is accepted.

4. Once it is certain that the molecule belongs to none of the groups so far considered, we look for the highest-order proper axis. It is possible that there will be no one axis of uniquely high order but instead three C_2 axes. In such a case, we look to see whether one of them is geometrically unique in some sense, for example, in being colinear with a unique molecular axis. This occurs with the molecule allene, which is one of the examples to be worked through later. If all of the axes appear quite similar to one another, then any one may be selected at random as the axis to which the vertical or horizontal character of planes will be referred. Suppose that C_n is our reference or principal axis.

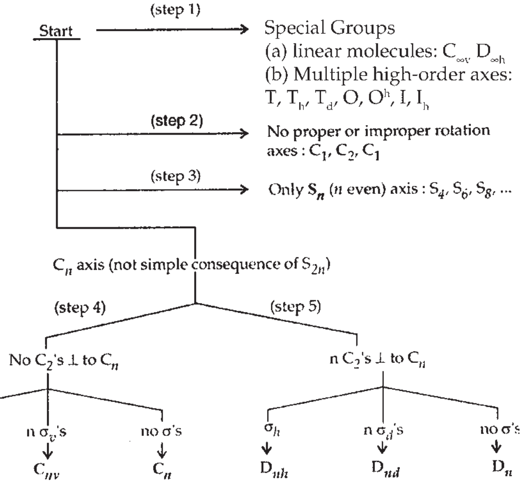


***Fig.** A five-stage procedure for the symmetry classification of molecules.*

The crucial question now is whether there exists a set of n C_2 axes perpendicular to the C_n axis. If so, we proceed to step 5. If not, the molecule belongs to one of the groups C_n, C_{nv}, and C_{nh}. If there are no symmetry elements except the C_n axis, the group is C_n. If there are n vertical planes, the group is C_{nv}. If there is a horizontal plane, the group is C_{nh}.

5. If in addition to the principal C_n axis there are n C_2 axes lying in a plane perpendicular to the C_n axis, the molecule belongs to one of the groups D_n, D_{nh}, and D_{nd}. If there are no symmetry elements besides C_n and the nC_2 axes, the group is D_n. If there is also a horizontal plane of symmetry, the group is

D_{nh}. AD_{nh}, group will also, necessarily, contain *n* vertical planes; these planes contain the C_2 axes. If there is no σ_h but there is a set of *n* vertical planes which pass between the C_2 axes, the group is D_{nd}.

Molecule Groups and Symmetry

A convenient procedure for determining the point group of a non-linear of non-cubic molecule is designed. The system requires finding out the axis of highest order, multiple axis of this order and additional twofold axis as prime step.

1. First, these symmetry elements must be found.
2. Look for the highest rotation axis.
3. Determine the symmetry planes σ_v σ_d or σ_h.
4. Determine the two fold axis at right angles to the highest rotation axis.

For example, the highest rotation axis in NH_3 is C_3 with three σ_v planes but no C_2 axis. This corresponds to the point group C_{3v}.

The following table does not indicate all the symmetry elements possessed by a molecule. Therefore one should consult the table of the chosen group and identify all the symmetry elements in turn, as these are deduced from the list of operations.

Point group for linear molecules will have rotation axis C_∞. If the molecule has a centre of symmetry, it corresponds to the point group $D_{\infty h}$, otherwise the $C_{\infty v}$.

Table: *Deduction of point group of any molecule from the knowledge of symmetry elements*

Point Group	D_n	D_{nd}	D_{nh}	C_n	C_{nv}	C_{nh}	C_s	C_i
symmetry elements								
σh			1			1	1	
σ_v or σ_d		n	n		n			
C_2	n	n	n					
i								1
C_n	1	1	1	1	1	1		

n in the point group symbols is the order of highest rotation axis.

If the highest axis of symmetry is four and the molecule has three more C_4 axes + $6\sigma_d + 3\sigma_h$, the molecule corresponds to point group O_h.

If the highest axis of symmetry is three and the molecule has $8C_3 + 6\sigma_d + i$, it belongs to point T_h If the centre of symmetry is not there it belongs to point group T_d.

Point Group	C^*_n	C_{nv}	C_{nh}	D_n	D_{nh}	D_{nh}
symmetry elements for						
n = 2	E, C_2	$2\sigma_v$	i, σ_h	C_2	$i, 3\sigma_v$	$2S_4, 2\sigma_d$
n = 3	$E, 2C_3$	$3\sigma_v$	$\sigma h, 2S_3$	c3, $2C'_2$	$3C'_2$, sh' $2S_3, 3\sigma_v$	$3C'2, i, 2S_6, 3\sigma_d$
n = 4	$E, 2C_4,$	$2\sigma_v, 2\sigma d$	$i_1, \sigma_h, 2S_4$	$2C'_2{}'$ $2C''_2$	$2C'_2, 2C''_2{}'$, $i, 2S_4, \sigma h'$ $2\sigma_v{}'2\sigma_d$	$4S_8, 4C'_2, 4\sigma_d$
n = 6	$E, 2C_6,$ $2C_3, C_2$	$3\sigma_v, 3\sigma_d$ $2S_6$	$i, \sigma_h, 2S_3,$ $2S'_6$	$3C'_2, 3C''_2,$	$3C'_2, 3C''_2,$ $i, 2S_3, 2S_6$ $\sigma_h, 3\sigma_d\ 3\sigma_v$	$4S_{12}, 2S_4$ $6C'_2, 6\sigma_d$

*Symmetry elements of this point group are common to all point groups in this row so have not been written, just to save space.

C_s, E, σ_h C_2 E, i

Pictorial Instances

The schemes just outlined for allocating molecules to their point groups will now be illustrated. We shall deal throughout with molecules that do not belong to any of the special groups, *i.e.*, point groups of Groups III.

Example: H_2O

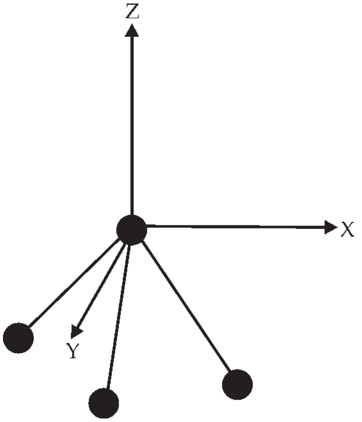
Selection of axis is carried out by the procedure:

1. Since there is only one rotational axis this is taken as Z-axis.
2. Since water is a planner molecule, X-axis is chosen to be normal to this plane.
3. An axis perpendicular to the X-Z plane is taken as Y-axis.
4. H_2O possesses no improper axis.
5. The highest-order proper axis is a C_2 axis passing through the oxygen atom and bisecting a line between the hydrogen

atoms. There are no other C_2 axes. Therefore H_2O must belong to C_2, C_{2v}, or C_{2h}. Since it has two vertical planes, one of which is the molecular plane, it belongs to the group C_{2v}.

Example: NH_3

1. Since there is only rotational axis this is chosen as Z-axis.
2. Since ammonia molecule is not planar, X-axis is chosen to be arbitrary and is taken perpendicular to Z-axis.
3. An axis perpendicular to X-Z axis is the Y-axis.
4. There is no improper axis.



5. The only proper axis is a C_3 axis; there are no C_2 axes at all. Hence, the point group must be C_3, C_{3v} or C_{3h}. There are three vertical planes, one passing through each hydrogen atom. The group is thus C_{3v}.

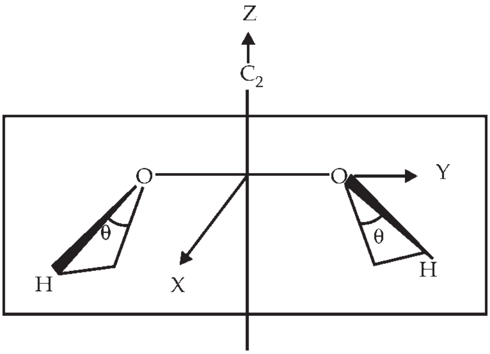


Fig. *The hydrogen peroxide molecule in its non-planar form.*

Example: H_2O_2.

A. *The non-planar equilibrium configuration*

1. There is no improper axis.
2. There is a C_2 axis and no other proper axis. There are no planes of symmetry. The group is therefore C_2. Note that the C_2 symmetry is in no way related to the value of the angle θ except when θ equals 0 or 90 , in which case the symmetry is higher. We shall next examine these two non-equilibrium configurations of the molecule.

B. *The cis-planar configuration* ($\theta = 0$)

1. Again there is no even-order S_n axis.
2. The C_2 axis, of course, remains. There are still no other proper axes. The molecule now lies in a plane, which is a plane of symmetry, and there is another plane of symmetry intersecting the molecular plane along the C_2 axis. The group is C_{2v}.

C. *The trans-planar configuration* ($\theta = 90$)

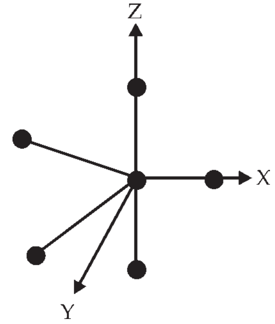
1. Again, there is no even-order S_n axis, (except $S_2 = i$).
2. The C_2 axis is still present, and there are no other proper axes. There is now a σ_h, which is the molecular plane. The group is C_{2v}.

Example: *Benzene*

1. Since benzene has several rotational axis, the one of highest order, perpendicular to benzene plane is chosen as Z-axis.
2. Since benzene is a planer molecule and Z-axis is perpendicular to this plane the X-axis is chosen to pass the largest number of atoms, *i.e.,* it pass through the centre of carbon-carbon atoms.
3. An axis perpendicular to XZ plane is assigned as Y-axis.
4. There is an S_6 axis, perpendicular to the ring plane, but there are also other symmetry elements independent of the S_6 axis.
5. There is a C_6 axis perpendicular to the ring plane and six C_2 axes lying in the ring plane. Hence the group is a D_6 type.
6. Since there is a σ_h, the group is D_{6h}. Note that there are vertical planes of symmetry, but they contain the C_2 axes.

Example: PF_5 (Trigonal Bipyramidal)

1. Since the molecule has several rotational axis, one of the highest order along F = P = F is chosen as Z-axis.



2. Since the molecule is non-planar an axis passing through the largest number of atoms is through P-F perpendicular to Z-axis is thus chosen as X-axis.
3. An axis perpendicular to XZ plane is assigned as Y-axis.
4. There is no even-order S_n axis.
5. There is a unique C_3 axis, and there are three C_2 axes perpendicular to it.
6. There is a σ_h; the group is D_{3h}.

Important Information from Point Groups of Molecules

As soon as the point group of a molecule is know, it is possible to state some consequences relating to its properties.

1. Molecules belonging to the groups C_n, C_{nv} and C_s may have an electric dipole moment and in the case of C_n and C_{nv} it must lie along the rotation axis. This can be understood as follows. If molecule has C_n symmetry it cannot possess a charge distribution corresponding to a dipole moment perpendicular to the axis. However, as the group makes reference to the symmetry of the molecule between top and bottom of the molecule, a charge distribution along the axis thus giving a dipole along the symmetry axis. The same remarks apply to C_{nV}. In all the other groups there are symmetry operations corresponding to turning the molecule upside down, therefore have no dipole moment.

2. A molecule can rotate the plane of polarised light only if it cannot be superimposed on its mirror image. The symmetry element to look for is an axis of improper rotation S_n if one is present the object can be superimposed on its mirror image, and therefore cannot be optically active. If S_n is absent, the superposition is impossible and molecule may be optically active.
3. One should be careful of any improper rotation axes that may be implied by the group rather than just written explicitly. For example, the group C_{nh} include s_n in a concealed form because they include C_n and σ_n. Any group containing the inversion as an element also possess at least the element S_2, because an inversion can be envisaged as a 180 rotation followed by a σ_h reflection. It follows that molecules with centres of inversion cannot be optically active. However, not all molecules without a centre of inversion are optically active. For instance, if their symmetry is S_4 they lack an *i* element but possess S_4 which implies inactivity.
4. Even for simple organic molecule it is generally difficult to calculate the energies of the molecular orbitals that might be involved in electronic transition. Symmetrical molecules with a high degree of symmetry have more restrictions on their electronic transitions than less symmetrical molecules. As for example, benzene is highly symmetrical having a large number of symmetry elements many restrictions apply to the electronic transitions of the benzene molecule and therefore its electronic absorption is simple. For a totally unsymmetrical molecules, no symmetrical restrictions apply to the electronic transitions so that transitions may be observed among all its unfilled molecular orbital and thus result in complex electronic spectra.
5. Symmetrical vibrations of a molecule with a centre of symmetry do not involve change in dipole moment hence are IR-inactive but are Raman active, while asymmetrical stretching vibrations with a centre of symmetry involve change of dipole moment and hence IR-active but are Raman inactive.
6. Again molecules with centre of symmetry have no dipole moment and thus do not show any pure rotational spectra.

5

The Polymers

Polymer have existed in natural form since life began and those such as DNA, RNA, proteins and polysaccharide play crucial roles in plant and animal life. From the earliest times man has exploited natural-occurring polymers as materials for providing clothing, decoration, shelter, tools, writing materials and other requirements. The situation that had been prevailing that everything that everyone is/was wearing or carrying in pockets and hands are/were made up of polymers.

Synthetic polymers started with phenol-formaldehyde resin in 1910. Within ten years polymer industry was firmly established, but its growth was restricted by the considerable lack of understanding of the nature of polymers. By 1920, the common belief was that they consisted of physically associated aggregates of small molecules. Few scientists gave credence to the viewpoint so passionately believed by Hermann Staudinger, that polymers were composed of very large molecules containing long sequences of simple chemical units linked together by covalent bonds. Staudinger introduced the word ‘macromolecule’ to describe polymers, and during the 1920s vigorously set about proving his hypothesis to be correct. Particularly important were his studies of the synthesis, structure and properties of polyoxymethylene and of polystyrene, the results from which left little doubt as to the validity of the macromolecular viewpoint. Staudinger’s hypothesis was further substantiated by the crystallographic studies of natural polymers reported by Herman Mark and Kurt Meyer, and by the classic work of Wallace Carothers on the preparation of polyamides and polyesters.

Thus by the early 1930s most scientists were convinced of the macromolecular structure of polymers. During the following 20 years, work on polymers increased enormously: the first journals devoted solely to their study were published and most of the fundamental principles of *Polymer Science* were established.

The theoretical and experimental work of Paul Flory was prominent in this period, and for his long and substantial contribution to Polymer Science he was awarded the Nobel Prize for Chemistry in 1974. In 1953, Staudinger had received the same accolade in recognition of his pioneering work.

Not surprisingly, as the science of macromolecules emerged, a large number of synthetic polymers went into commercial production for the first time. These include polystyrene, poly(methyl methacrylate), nylon 6.6, polyethylene, poly(vinyl chloride), styrene-butadiene rubber, silicones and polytetrafluoroethylene, as well as many other. From the 1950s onwards regular advances, too numerous to mention here, have continued to stimulate both scientific and industrial progress.

Whilst Polymer Science is now considered to be a mature subject, its breadth is ever increasing and there are many demanding challenges awaiting scientists who venture into this fascinating multidisciplinary science.

Fundamentals and System of Naming

Several important terms and concepts must be understood in order to discuss fully the synthesis, characterisation, structure and properties of polymers. However, some are of such fundamental importance that they must be defined at the outset.

In strict terms, a *polymer* is a substance composed of molecules which have long sequences of one or more species of atoms or groups of atoms linked to each other by primary, usually covalent, bonds. The emphasis upon substance in this definition is to highlight that although the words polymer and macromolecule are used interchangeably, the latter strictly defines the molecules of which the former is composed.

Macromolecules are formed by linking together monomer molecules through chemical reactions, the process by which this is achieved being known as *polymerisation.* For example, polymerisation of ethylene yields polyethylene, a typical sample of which may contain molecules with 50000 carbon atoms linked together in a chain. It is this long chain nature which sets polymers apart from other materials and gives rise to their characteristic properties.

Skeletal Structure

The definition of macromolecules presented up to this point implies that they have a linear skeletal structure which may be represented by a chain with two ends. Whilst this is true for many macromolecules, there are also many with *non-linear* skeletal structures of the type shown in the following figure:

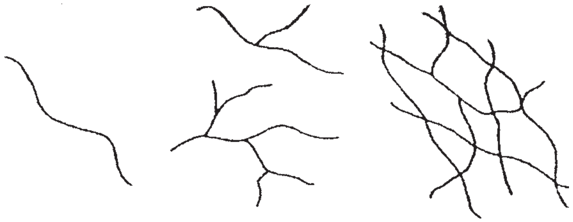


Fig. *Representive skeletal structures of linear and non-linear polymers.*

Branched polymers have side chains, or branches, of significant length which are bonded to the main chain at *branch points* (also known as *junction points),* and are characterised in terms of the number and size of the branches. *Network polymers* have three-dimensional structures in which each chain is connected to all others by a sequence of junction points and other chains. Such polymers are said to be crosslinked and are characterised by their crosslink density, or degree of crosslinking, which is related directly to the number of junction points per unit volume.

Non-linear polymers may be formed by polymerisation, or can be prepared by linking together *(i.e. crosslinking)* pre-existing chains.

Variations in skeletal structure give rise to major differences in properties. For example, linear polyethylene has a melting point about 20 C higher than that of branched polyethylene. Unlike linear and branched polymers, network polymers do not melt upon heating and will not dissolve, though they may swell considerably in compatible solvents.

The importance of crosslink density has already been encountered in terms of the vulcanisation (*i.e.* sulphur-crosslinking) of natural rubber. With low crosslink densities (i.e. low levels of sulphur) the product is a flexible elastomer, whereas it is a rigid material when the crosslink density is high.

Homopolymers

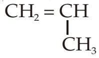
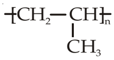
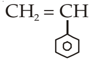
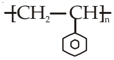
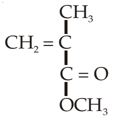
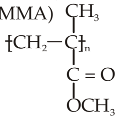
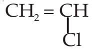
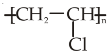
The formal definition of a homopolymer is a polymer derived from one species of monomer. However, the word *homopolymer* often is used more broadly to describe polymers whose structure can be represented by multiple repetition of a single type of repeat unit which may contain one or more species of monomer unit. The latter is sometimes referred to as a structural unit.

The chemical structure of a polymer usually is represented by that of the repeat unit enclosed by brackets. Thus the hypothetical homopolymer $\sim\sim\sim A—A—A—A— \;\; A—A—A—A\sim\sim\sim$ is represented by $-[A]-_n$ where *n* is the number of repeat, units linked together to form the macromolecule. Table given below shows the chemical structures of some common homopolymers together with the monomers from which they are derived and some comments upon their properties and uses. It should be evident that slight differences in chemical structure can lead to very significant differences in properties.

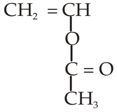
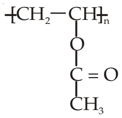
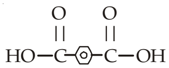
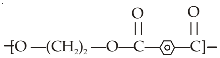
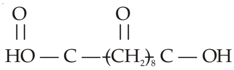
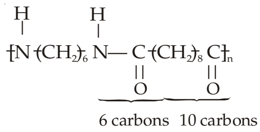
The naming of polymers or envisaging the chemical structure of a polymer from its name is often an area of difficulty. At least in part this is because most polymers have more than one correct name, the situation being further complicated by the variety of trade-names which also are used to describe certain polymers. The approach adopted here is to use names which most clearly and simply indicate the chemical structures of the polymers under discussion.

The names given to the polymers in the following table exemplify elementary aspects of nomenclature. Thus source-based nomenclature places the prefix 'poly' before the name of the monomer, the monomer's name being contained within parentheses unless it is a simple single word. In structure-based nomenclature the prefix poly is followed in parentheses by words which describe the chemical structure of the repeat unit.

Table: *Some common homopolymers*

Monomers	*Polymer*	*Comments*
(1) Ethylene $CH_2 = CH_2$	Polyethylene (PE) $\left[CH_2 - CH_2\right]_n$	Moulded objects, tubing, film, electrical insulation, *e.g.* ‘Alkathcne’, ‘Lupolen’.
(2) Propylene  $CH_2 = \underset{\underset{CH_3}{\vert}}{CH}$	Polypropylene(PP)  $\left[CH_2 - \underset{\underset{CH_3}{\vert}}{CH}\right]_n$	Similar uses to PE; lower density, stiffer, *e.g.,* ‘Propathene’, ‘Novolen’.
(3) Tetrafluor-oethylene $CF_2 = CF_2$	Polytetraflu-oroethylene (PTFE)$\left[CH_2 - CH\right]_n$	Mouldings, film, coatings; high temperature resistance, chemically inert, excellent electrical insulator, very low coefficient of friction; expensive, *e.g.,* ‘Teflon’,‘Fluon’.
(4) Styrene 	Polystyrene (PS) 	Cheap moulded objects, *e.g.,* ‘Styron’, ‘Hostyren’. Modified with rubbers to improve toughness, *e.g.,* high-impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene copolymer (ABS). Expanded by volatilisation of a blended blowing agent *(e.g.,* pentane) to produce polystyrene foam.
(5) Methyl methacrylate  $CH_2 = \overset{CH_3}{\overset{\vert}{\underset{\underset{\underset{\underset{OCH_3}{\vert}}{C=O}}{\vert}}{C}}}$	Poly(methyl methacrylate) (PMMA)  $\left[CH_2 - \overset{CH_3}{\overset{\vert}{\underset{\underset{\underset{\underset{OCH_3}{\vert}}{C=O}}{\vert}}{C}}}\right]_n$	Transparent sheets and mouldings; used for aeroplane windows; more expensive than PS, *e.g.,* ‘Perspex’. ‘Diakon’. ‘Lucite’, ‘Oroglass’, ‘Plexiglas’.
(6) Vinyl chloride  $CH_2 = \underset{\underset{Cl}{\vert}}{CH}$	Poly(vinyl chloride) (PVC)  $\left[CH_2 - \underset{\underset{Cl}{\vert}}{CH}\right]_n$	Water pipes and gutters, bottles, gramophone records; plasticised to make PVC lathercloth, raincoats, flexible pipe and hose, toys, sheathing on electrical cables, e.g., ‘Darvic’. ‘Welvic’, Vinoflex, ‘Hostalit’.

Contd...

Monomers	*Polymer*	*Comments*
(7) Vinyl acetate  $CH_2=CH-O-C(=O)-CH_3$	Poly(vinyl acetate) (PVA)  $-[CH_2-CH(-O-C(=O)-CH_3)]_n-$	Surface coatings, adhesive, chewing gum.
(8) Ethylene glycol $HO-CH_2-CH_2-OH$	Poly(ethylene glycol) (PEG) $-[CH_2-CH_2-O]_n-$	Water-soluble packaging films, textile sizes, thickeners, e.g., 'Carbowax'.
(9) Ethylene glycol $HO-CH_2-CH_2-OH$ and terephthalic acid 	Poly(ethylene terephthalate)(PET) 	Textile fibres, film, bottles, *e.g.,*'Terylene', 'Dacron', 'Melinex', 'Mylar'.
(10) Hexamethylene diamine $H_2N-(CH_2)_6-NH_2$ and sebacic acid  $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-OH$	Poly(hexamethylene sebacate) (nylon 6.10)*  $-[\overset{H}{\overset{\mid}{N}}-(CH_2)_6-\overset{H}{\overset{\mid}{N}}-\underset{O}{\underset{\|}{C}}-(CH_2)_8-\underset{O}{\underset{\|}{C}}]_n-$ 	Mouldings, fibres, *e.g.,* 'Ultramid 6.10'.

*The polymer has two monomer units in the repeat unit.

Copolymers

The formal definition of a *copolymer* is a polymer derived from more than one species of monomer. However, in accordance with use of the word homopolymer, it is common practice to use a structure-based definition. Thus the word copolymer more commonly is used to describe polymers whose molecules contain two or more different types of repeat unit. Hence, polymers nine and ten are considered to be homo-polymers rather than copolymers.

There are several categories of copolymer, each being characterised by a particular form of arrangement of the repeat units along the polymer chain. For simplicity, the representation of these categories will be illustrated by copolymers containing only two different types of repeat unit (A and B).

Statistical copolymers are copolymers in which the sequential distribution of the repeat units obeys known statistical laws *(e.g.,* Markovian).

Random copolymers are a special type of statistical copolymer in which the distribution of repeat units is truly random (some words of caution are necessary here because older textbooks and scientific papers often use the term random copolymer to describe both random and non-random statistical copolymers). A section of a truly random copolymer is represented below:

Alternating copolymers have only two different types of repeat unit and these are arranged alternately along the polymer chain

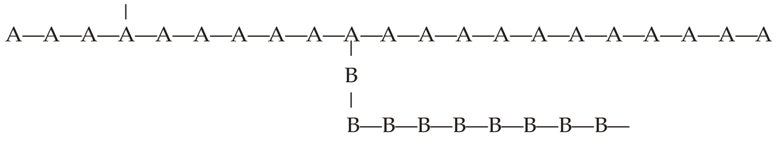
Statistical, random and alternating copolymers generally have properties which are intermediate to those of the corresponding homopolymers. Thus by preparing such copolymers it is possible to combine the desirable properties of the homopolymers into a single material. This is not normally possible by blending because most homopolymers are immiscible with each other.

Block copolymers are linear copolymers in which the repeat units exist only in long sequences, or blocks, of the same type. Two common block copolymer structures are represented below and usually are termed AB di-block and ABA tri-block copolymers

A—A—A—A—A—A—A—A—A—A—B—B—B—B—B—B—B—B—B—B—B

A—A—A—A—A—A—A—A—A—B—B—B—B—B—B—B—B—B—A—A—A—A—A—A—A—A

Graft copolymers are branched polymers in which the branches have a different chemical structure to that of the main chain. In their simplest form they consist of a main homopolymer chain with branches of a different homopolymer.



In distinct contrast to the types of copolymer described earlier, block and graft copolymers usually show properties characteristic of each of the constituent homopolymers. They also have some unique properties arising from the chemical linkage(s) between the homopolymer sequences preventing them from acting entirely independently of each other.

Table: *Principles of nomenclature for copolymers*

Type of copolymer	*Example of nomenclature*
Unspecified	Poly(A-co-B)
Statistical	Poly (A-stat-B)
Random	Poly(A-ran-B)
Alternating	Poly(A-alt-B)
Block	PolyA-block-polyB
Graft*	PolyA-graft-polyB

* The example is for polyB branches on a polyA main chain.

The current principles of nomenclature for copolymers are indicated in the following table where A and B represent source or structure-based names for these repeat units.

Thus a statistical copolymer of ethylene and propyiene is named poly(ethylene-stef-propylene), and an ABA tri-block copolymer of styrene (A) and isoprene (B) is named polystyrene-block-polyisoprene-block-polystyrene. In certain cases, additional square brackets are required. For example, an alternating, copolymer of styrene and maleic anhydride is named poly[styrene-*alt*-(maleic anhydride)].

Polymers and Stratification

The most common way of classifying polymers is outlined in the figure below where they are first separated into three groups: *thermoplastics, elastomers* and *thermosets.* Thermoplastics are then further separated into those which are *crystalline* and those which are *amorphous (i.e.,* non-crystalline).

This method of classification has an advantage in comparison to others since it is based essentially upon the underlying molecular structure of the polymers.

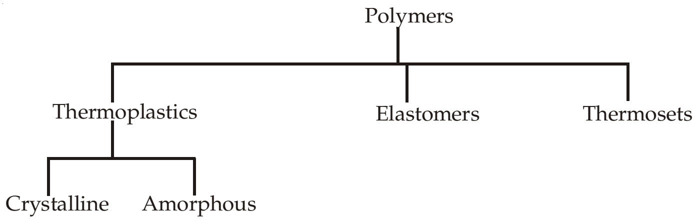


Fig. Classification of polymers.

Thermoplastics, often referred to just as plastics, are linear or branched polymers which can be melted upon the application of heat. They can be moulded (and remoulded) into virtually any shape using processing techniques such as injection moulding and extrusion, and now constitute by far the largest proportion of the polymers used in industry. Generally, thermoplastics do not crystallise easily upon cooling to the solid state because this requires considerable ordering of the highly coiled and entangled macromolecules present in the liquid state.

Those which do crystallise invariably do not form perfectly crystalline materials but instead are *semi-crystalline* with both crystalline and amorphous regions. The crystalline phases of such polymers are characterised by their melting temperature (T_m). Many thermoplastics are, however, completely amorphous and incapable of crystallisation, even upon annealing. Amorphous polymers (and amorphous phases of semi-crystalline polymers) are characterised by their glass transition temperature (T_g), the temperature at which they transform abruptly from the glassy state (hard) to the rubbery state (soft). This transition corresponds to the onset of chain motion; below T the polymer chains are unable to move and are 'frozen' in position. Both T_m and T_g increase with increasing chain stiffness and increasing forces of intermolecular attraction.

Elastomers are crosslinked rubbery polymers (*i.e.* rubbery networks) that can be stretched easily to high extensions (*e.g.* 3 to 10 their original dimensions) and which rapidly recover their original dimensions when the applied stress is released. This extremely important and useful property is a reflection of their molecular structure in which the network is of low crosslink density. The rubbery polymer chains become extended upon deformation but are prevented from permanent flow by the crosslinks, and driven by entropy, spring back to their original positions on removal of the stress. The word rubber, often used in place of elastomer, preferably should be used for describing rubbery polymers which are not crosslinked.

Thermosets normally are rigid materials and are network polymers in which chain motion is greatly restricted by a high degree of crosslinking. As for elastomers, they are intractable once formed and degrade rather than melt upon the application of heat.

Polymerisation and Molar Mass

Many properties of polymers show a strong dependence upon the size of the polymer chains, so that it is essential to characterise their dimensions. This normally is done by measuring the molar mass (M) of a polymer which is simply the mass of 1 mole of the polymer and usually is quoted in units of g mol^{-1} or kg mol^{-1}. The term 'molecular weight' is still often used instead of molar mass, but is not preferred because it can be somewhat misleading. It is really a dimensionless quantity, the relative molecular mass, rather than the weight of an individual molecule which is of course a very small quantity (*e.g.* $\sim 10^{-19} - \sim 10^{-18}$g for most polymers). By multiplying the numerical value of molecular weight by the specific units g mol^{-1} it can be converted into the equivalent value of molar mass. For example, a molecular weight of 1,00,000 is equivalent to a molar mass of 1,00,000 g mol^{-1} which in turn is equivalent to a molar mass of 100 kg mol^{-1}.

For network polymers the only meaningful molar mass is that of the polymer chains existing between junction points *(i.e. network chains),* since the molar mass of the network itself essentially is infinite.

The molar mass of a homopolymer is related to the *degree of polymerisation (x),* which is the number of repeat units in the polymer chain, by the simple relation

$$M = x M_0 \qquad ...(5.1)$$

where M_0 is the molar mass of the repeat unit. For copolymers the sum of the products xM_0 for each type of repeat unit is required to define the molar mass.

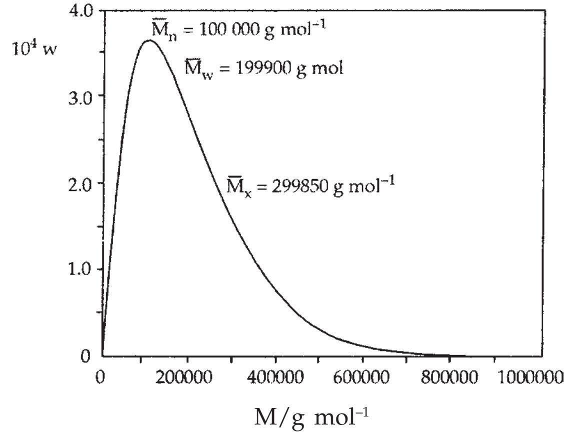


Fig. A typical molar mass distribution curve.

Molar Mass Distribution

With very few exceptions, polymers consist of macromolecules (or network chains) with a range of molar masses. Since the molar mass changes in intervals of M_0, the distribution of molar mass is discontinuous. However, for most polymers these intervals are extremely small in comparison to the total range of molar mass and the distribution can be assumed to be continuous, as exemplified in the figure above.

Molar Mass Averages

Whilst a knowledge of the complete molar mass distribution is essential in many uses of polymers, it is convenient to characterise the distribution in terms of molar mass averages. These usually are defined by considering the discontinuous nature of the distribution in which the macromolecuies exist in discrete fractions i containing N_i molecules of molar mass M_i.

The *number-average molar mass* $\left(\bar{M}_n\right)$ is defined as 'the sum of the products of the molar mass of each fraction multiplied by its mole fraction

i..e., $$\bar{M}_n = \sum X_i M_i \qquad ...(5.2)$$

where X_i is the mole fraction of molecules of molar mass M_i and is given by the ratio of N; to the total number of molecules. Therefore it follows that

$$\bar{M}_n = \sum N_i M_i / \sum N_i \qquad ...(5.3)$$

showing this average to be the arithmetic mean of the molar mass distribution. It is often more convenient to use weight fractions rather than numbers of molecules. The weight fraction w_i is defined as the mass of molecules of molar mass M_i, divided by the total mass of all the molecules present

i.e., $$w_i = N_i M_i / \sum N_i M_i \qquad ...(5.4)$$

from which it can be deduced that

$$\sum (w_i / M_i) = \sum N_i / \sum N_i M_i \qquad ...(5.5)$$

Combining Equations (5.3) and (5.5) gives $\bar{M}_n$ in terms of weight fractions

i.e., $$w_i = N_i M_i / \sum N_i M_i \qquad ...(5.6)$$

The *weight-average molar mass* $(\bar{M}_w)$ is defined as 'the sum of the products of the molar mass of each fraction multiplied by its weight fraction'

i.e., $$\bar{M}_w = \sum w_i M_i \qquad ...(5.7)$$

By combining this equation with Equation (5.4) $\bar{M}_w$, can be expressed in terms of the numbers of molecules

$$\bar{M}_w = \sum N_i M_i^2 / \sum N_i M_i \qquad ...(5.8)$$

The ratio $\bar{M}_w / \bar{M}_n$ must by definition be greater than unity for a *polydisperse* polymer and is known as the *polydispersity* or *heterogeneity index.* Its value often is used as a measure of the breadth of the molar mass distribution, though it is a poor substitute for knowledge of the complete distribution curve. Typically $\bar{M}_w / \bar{M}_n$ is in the range 1.5-2, though there are many polymers which have smaller or very much larger values of polydispersity index. A perfectly monodisperse polymer would have $\bar{M}_w / \bar{M}_n = 1.00$.

Higher molar mass averages sometimes are quoted. For example, certain methods of molar mass measurement *(e.g.,* sedimentation equilibrium) yield the z-average molar mass $(\bar{M}_z)$ which is defined as follows

$$\bar{M}_z = \sum N_i M_i^3 / \sum N_i M_i^2 = \sum w_i M_i^2 / \sum w_i M_i \qquad ...(5.9)$$

In addition, more complex exponent averages can be obtained *(e.g.,* by dilute Solution viscometry and sedimentation measurements).

Degree of polymerisation averages are of more importance than molar mass averages in the theoretical treatment of polymers and polymerisation. For homopolymers they may be obtained simply by dividing the corresponding molar mass average by M_0. Thus the *number-average* and *weight-average degrees of polymerisation* are given by

$$\bar{x}_n = \bar{M}_n / \bar{M}_0 \qquad ...(5.10)$$

and

$$\bar{x}_w = \bar{M}_n / \bar{M}_0 \qquad ...(5.11)$$

Molar Mass and Measurement

Molar mass of polymers may be established from appropriate physical measurements on very dilute solutions or, if circumstances permit, by chemical analysis for end groups. The former methods are applied with difficulty at molar mass below 5000 to 10000 where as the chemical methods generally are reliable only for molar mass below about 25000. Hence, neither physical nor chemical methods alone are sufficients in all situations, but physical methods are definitely indicated for the high molar mass polymers of general interest.

End Group Analysis

The non-thermodynamic methods for evaluation of M_n; have their basis in determination of the number of moles of end groups of a particular type in a given mass of polymer and therefore are methods of end group analysis. These are four essential requirements which must be satisfied for end group analysis to be applicable:

(i) The end group(s) on the polymer molecules must be amenable to quantitative analysis.

(ii) Other functional groups which interfere with end group analysis either must be absent or their effects must be capable of being corrected.

(iii) The concentration of end groups must be sufficient for accurate quantitative analysis.

(iv) Application of a chemical method requires that the structure of polymer as established from prior consideration, be such as to contain a known number of chemically determinable functional groups per molecule.

Suppose that the end group is a carboxyl group acidic enough to be titrated with NaOH. If N_i moles of NaOH is needed to titrate the i-molecules, then the total moles of NaOH required to titrate the mixture will be

$$n_i = \frac{\sum_{i=1}^{\infty} N_i}{N_A} = \frac{N}{N_A} \qquad \text{...(5.12)}$$

Since each mole of polymer require one mole of NaOH. The total mass of polymer in the sample is

$$w = \frac{\sum_{i-1}^{\infty} N_i M_i}{N_A} = \frac{N}{N_A} M_n \qquad \text{...(5.13)}$$

and the number average molar mass is

$$M_n = \frac{w}{n_i} \qquad \text{...(5.14)}$$

where both w, mass of polymer and n_i moles of polymer are measureable quantities.

End group analysis is most appropriate to polymers prepared by step polymerisation since they tend to be of relatively low molar mass and have characteristic end group suitable for analysis, *e.g.,* polyester (–OH and –COOH end groups), polyamides (–NH_2 and –COOH end groups) and polyurethanes (–OH and –NCO end groups). Low molar mass polyesters, polyamines and polyethers (–OH and group) prepared by ring opening polymerisation similarly are suitable for end group analysis.

Measuring by Physical Methods

All of the physical methods presently used for the determination of molar mass of polymers require the molecules contribute individually, *i.e.,* additively, to the property being measured, contribution due to interactions between pairs (or clusters) of molecules being negligible. The light-scattering method requires that the total turbidity consist of the sum of the turbidities due to the individual molecules, the osmotic method that the decrease in activity of the solvent be proportional to the number of solute particles, and viscosity method that the energy dissipated by each individual polymer molecule be uninfluenced by all others in the solution.

In all these cases the solution is sufficiently dilute to permit the polymer molecules to occupy separate portions of the volume, without appreciable overlapping two or more molecules. Thus working with dilute solution should give good results. Working with concentration below one per cent, and in many cases down to several tenths of a per cent, is apparent and the extapolation to infinite dilution is required.

Further, accurate measurement of the small physical effects observed at small concentration of polymer calls for sensitive experimental methods. An addition complication arises from the different types of molar mass averages obtained by different methods.

Determination of Viscosity

Of all the methods used for the determination of molar masses of macromolecules, the viscosity method, introduced by H. Staudinger, is the one most commonly employed in research. Accurate measurement of absolute viscosity being difficult, it is convenient to measure relative viscosity, η_{ret}, denned as

$$\eta_{ret} = \eta/\eta_0 \quad ...(5.15)$$

where η and η_0 are, respectively, the viscosity of the solution and the viscosity of the solvent. The relative viscosity is related to some other quantities as follows:

$$\eta_{sp} = \eta_{rel} - 1 \quad ...(5.16)$$

$$\eta_{red} = \eta_{sp} / c \quad ...(5.17)$$

$$[\eta] = \lim_{c \to 0} \left(\eta_{sp} / c\right) \quad ...(5.18)$$

where η_{sp} is specific viscosity, η_{red} is reduced viscosity and $[\eta]$ is intrinsic viscosity (also called the viscosity number or Staudioger index). In these equations, *c* is the concentration of the polymer. Note that none of these quantities has the units of viscosity.

The plots of η_{sp}/c and ln η_{red}/c versus c give straight lines which conform to the following equations:

Huggin's equation: $\eta_{sp}/c = [\eta] + k' [\eta]^2 C$ ..(5.19)

Kraemer's equation: $\text{In}\,\eta_{red}/c = [\eta] - k'' [\eta]^2 c$ ...(5.20)

Both these equations are applicable only in dilute solutions. For many polymers, $k' = 0.4 \pm 0.1$ and $k'' = 0.50 \pm 0.05$.

Fortunately, Staudinger found, in 1950, that for a series of samples of the same polymer in a given solvent and at a constant temperature, the intrinsic viscosity (or the viscosity number) is related to the molar mass of the polymer by the following equation, known as *Mark-Houwink equation or Staudinger equation:*

$$[\eta] = K \left(\bar{M}_{visc}\right)^a \qquad ...(5.21)$$

where $\bar{M}_{visc}$ is the viscosity-average molar mass of the polymer and K and *a* are constants, usually determined by intrinsic viscosity measurements on a series of polymer samples for which the molar mass has been determined by a different method, say, the light-scattering method. The value of the exponent *a* depends upon the geometry or shape of the macromolecule. The more elongated a molecule, the more effective are the higher molar mass fractions in reducing the viscosity of the solution. The values of *a* vary from 0.5 to 1. For polymers behaving as random coils, *a* is about 0.8 and for globular proteins possessing a compact structure, it is about 0.5. Note that [η] has the dimensions of reciprocal density and hence its units are $cm^3\,g^{-1}$. Typical values of K and *a* are summarised in table given below.

Table: *Parameters of the Mark-Houwink Equation*

Polymer	***Solvent***	***Temperature***	***Kx 10^5***	***a***
Polystyrene	Benzene	25	10.3	0.74
	Methyle ethyl ketone	25	39	0.58
Polyisobutylene	Cyclo hexane	30	26	0.70
	Benzene	25	107	0.51
Polyacrylonitrile	Dimethyl formamide	25	16.6	0.81
Natural rubber	Toluene	25	50	0.62
Polyisoprene	Cyclo hexane	27	30	0.70

Poly(vinyl methacrylate)	Benzene	25	5.7	0.76
Poly vinyl chloride	Tetrahydrofuran	20	3.6	0.92
Poly vinyl acetate	Acetone	25	17.6	0.68
Poly vinyl alcohol	Water	25	20	0.76
Poly vinyl pyrrolidone	Water	25	67.6	0.55
Polyethylene glycol	Water	25	156	0.50

The exponent *a* varies from about 0.5 for well coiled polymer in a poor solvent to as much as 1.7 for rigidly extended rod between polymer molecule. In rod like molecules that are oriented by the flow so that they slide past each other more freely. This is an example of non-newtonian behaviour where viscosity may decrease when the rate of flow of solution is increased.

Taking logs of both sides of Eq. 5.21, we have

$$\ln [\eta] = \ln K + a \ln \bar{M}_{visc} \qquad \text{....(5.22)}$$

Eq. 5.22 shows that a log-log plot of [η] versus $\bar{M}_{visc}$ gives a straight line with slope equal to *a* and intercept equal to ln K. Thus, the constants *a* and K can be easily determined.

Knowing the values of *a* and K, for a polymer-solvent system, the viscosity-average molar mass M_{vis} can be easily determined from intrinsic viscosity measurements.

Example: *Equal numbers of molecules with* M_1 *= 10000 and* $M_2 = 100000$ *of polystyrene with a = 0.74 are mixed. Calculate* M_n, M_w, M_z *and* M_{vis}.

Solution: Let $N_1 = N_2 = 10$ (say)

$$M_n = \frac{N_1M_1 + N_2M_2}{N_1 + N_2} = \frac{10\times10^4 + 10\times10^5}{10+10}$$

$$= \frac{10^5 + 10^6}{20} = \frac{11}{2}\times10^4 = 55000$$

$$M_w = \frac{N_1M_1^2 + N_2M_2^2}{N_1M_1 + N_2M_2} = \frac{10\times\left(10^4\right)^2 + 10\times\left(10^5\right)^2}{10+10}$$

$$= \frac{10^9 + 10^{11}}{10^5 + 10^6} = \frac{10^9(1+100)}{10^5(1+10)} = \frac{101}{11}\times10^4 = 9181.8$$

$$M_z = \frac{N_1M_1^3 + N_2M_2^3}{N_1M_1^2 + N_2M_2^2} = \frac{10\times\left(10^4\right)^3 + 10\times\left(10^5\right)^3}{10\times\left(10^4\right)^2 + 10\times\left(10^5\right)^2}$$

$$= \frac{1001}{101}\times 10^4 = 99109$$

$$M_{vis} = \left[\frac{N_1M_1^a + N_2M_2^a}{N_1 + N_2}\right]^{1/a}$$

$$= \left[\frac{10\times\left(10^4\right)^{0.74} + 10\times\left(10^5\right)^{0.74}}{10 + 10}\right]^{1/0.74}$$

$$= (2962)^{1/0.74} = 49384$$

Example: *Equal masses of polymer molecules with $M_1 = 10000$ and $M_2 = 100000$ are* mixed. Calculate M_n, M_w.

Solution: Let $m_1 = m_2 = 200000$ (say)

$$n_1 = \frac{\text{mass } m_1}{\text{molar mass } M_1} = \frac{200000}{10000} = 20$$

$$n_2 = \frac{\text{mass } m_2}{\text{molar mass } M_2} = \frac{200000}{100000} = 2$$

$$M_n = \frac{20\times 10^4 + 2\times 10^5}{20 + 2} = \frac{2}{11}\times 10^5 = 18182$$

$$M_w = \frac{20\times\left(10^4\right) + 2\times\left(10^5\right)}{20\times 10^4 + 2\times 10^5}$$

$$= \frac{20\times 10^9 + 2\times 10^{10}}{20\times 10^5 + 2\times 10^5} = \frac{11}{2}\times 10^4$$

$$= 55000$$

Example: The intrinsic viscosity of a solution of polyisobutylene at 20 C is 180 cm^3 per gram. If [η] is related to the visocisty-average molar mass $\bar{M}_{visc}$ by the expression

[η] = 3.6 $10^{-4}\left(\bar{M}_{visc}\right)^{0.64}$, calculate the molar mass of the polymer.

Solution: $[\eta] = 3.60 \quad 10^{-4} \left(\bar{M}_{visc}\right)^{0.64}$

or $180\ \text{cm}^3\ \text{g}^{-1} = 3.60 \quad 10^{-4} \left(\bar{M}_{visc}\right)^{0.64}$

$$\therefore \quad \left(\bar{M}_{visc}\right)^{0.64} = \frac{180 cm^{-1} g^{-1}}{3.60 \times 10^{-4}} = 5.0\ 10^{5}$$

Taking logs, 0.64 In $\bar{M}_{visc}$ = In (5.0 x 10^5)

$\bar{M}_{visc} = 6.0\ 10^5$ g mol^{-1}

Example: The viscosities of series of solution of polystyrene in toluene were measured at 25 C with the following results

c/(g dm^{-3})	0	2.0	4.0	6.0	8.0	10.0
$\eta/10^{-4}$ kg m^{-1}s^{-1}	5.58	6.15	6.74	7.35	7.98	8.64

Find the intrinsic viscosity and viscosity average molar mass on the basis that the viscosity of the system obeys $[\eta] = K\ M_{vis}^{\ a}$ with K = 3.80 10^{-5} dm^3 g^{-1} and a = 0.63.

Solution: Draw up the following table

c/(g dm^{-3})	0	2.0	4.0	6.0	8.0	10.0
η / η^0	1	1.102	1.208	1.317	1.43	1.549
$[\eta/\eta^0 - 1]/c$	—	0.0511	0.052	0.0528	0.0538	0.0549

Plot a graph between $[\eta/\eta_0 - l]/c$ vic as shown in the following figure.

The intercept at c = 0 is 0.0504 and so $[\eta]$ = 0.0504 dm^3 g^{-1}. Viscosity average molar mass.

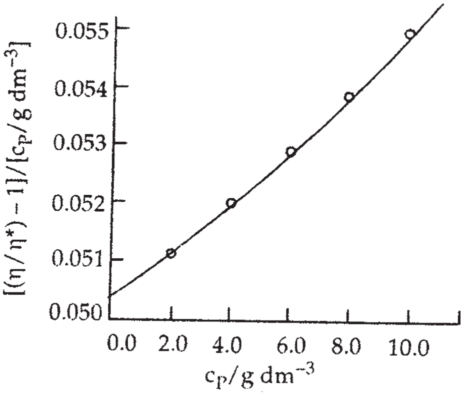


Fig. *Determination of the Intrinsic viscosity.*

$$M_{vis} = ([\eta]/K)^{1/a} = (0.0504\ \mathrm{dm^3 g^{-1}}/3.8\ \ 10^{-5}\ \mathrm{dm^{-3}\ g^{-1}})^{1/0.63}$$
$$= 1326^{1.59} = 90450$$

Example: The following data were obtained for the intrinsic viscosity of poly isobutylene in CCl_4 solution at 30 C as a function of viscosity average molar mass

$[\eta]/\mathrm{cm^3g^{-1}}$	430	206	78	73	43	15.1	13.1	11.5
Mois g $\mathrm{mol^{-1}}$	1260000	463000	110000	927000	48000	10000	9550	7080

Determine the constants K and a for the system

Solution: Since $[\eta] = K(M_{vis})^a$

$$\ln [\eta] = \ln K + a \ln M_{vis}$$

Plot a graph between ln [η] versus ln M_{vis} a straight line will be obtained, slope of this line $a = 0.70$ and intercept = ln K = – 8.245 from where $K = 2.6\ \ 10^{-4}$.

We shall now comment on the viscosity-average molar mass, $\bar{M}_{visc}$. If the exponent a in the Mark-Houwink equation, we, $[\eta] = K\left(\bar{M}_{visc}\right)^a$, has the value = 1 and c→0, then the viscosity-average molar mass can be written

as $$\bar{M}_{visc} = [\eta]/K = (\eta_{rel} - 1)/Kc \qquad \text{...(5.23)}$$

The $(\eta_{rel} - 1)$ values of the individual fractions can then be added to yield the total $(\eta_{rel} - 1)$ Thus,

$$\eta_{rel} - 1 = (\eta_{rel} - 1)_1 + (\eta_{rel} - 1)_2 + (\eta_{rel} - 1)^3 + \ldots\ldots\ldots.$$
$$= Kc_1M_1 + Kc_2M_2 + Kc_3M_3 + \ldots\ldots\ldots$$

Therefore, the viscosity-average molar mass can be written as

$$\bar{M}_{visc} = \frac{K\left(c_1M_1 + c_2M_2 + c_{3+}M_3 + \ldots..\right)}{K\left(c_1 + c_2 + c_3 + \ldots\ldots\right)}$$

$$= \bar{M}_M \qquad \text{...(5.24)}$$

We see that when the Mark-Houwink constant $a = 1$, the viscosity-average molar mass yields the mass-average molar mass.

If $a \neq 1$ then, according to Eqs. 5.21 and 5.23

$$\left(\bar{M}_{visc}\right)^a = (\eta_{rel} - 1)/Kc \qquad \text{...(5.25)}$$

$$= \frac{K\left(c_1 M_1^a + c_2 M_2^a + c_3 M_3^a + ...\right)}{K\left(c_1 + c_2 + c_{3+.....}\right)} = \sum c_1 M_1^a / \sum c_1$$

....(5.26)

Hence, $\bar{M}_{visc} = \left[\sum c_i M_i^a / \sum c_i\right]^{1/a}$ ....(5.27)

As a →1, $\bar{M}_{visc} \rightarrow \bar{M}_M$

Significance of Osmometry

Osmotic pressure is the only colligative property that is useful for investigating macromolecules. It is not a useful technique for studying solutes of low molar mass, primarily because it is difficult to find membranes that are impermeable to such solutes. Osmotic pressure measurements are used for studying macromolecules because osmotic changes are larger than the changes in boiling point elevation, freezing point depression and vapour pressure lowering. For instance, an order-of-magnitude calculation shows that for an aqueous solution containing 10 g dm^{-3} of a polymer having molar mass 20,000, the boiling point elevation and freezing point depression are 0.0025 C and 0.00093 C, respectively. Evidently, these values are too low to be measured.

If Π is the osmotic pressure of a solution in which the mole fraction of the solvent is or x_1 then, the condition for equilibrium for the chemical potential of the solvent on both sides of the osmometer membrane gives

$$RT \text{ In } \gamma_1 x_1, + \Pi \ \bar{V}_1 = 0 \qquad ...(5.28)$$

where g is the activity coefficient of the solvent and $\bar{V}_1$ is the partial molar-volume of the solvent in the solution. For a dilute solution, $\gamma_1 \rightarrow 1$ and $\bar{V}_1 \rightarrow V_1^0$, the molar volume of the pure solvent. If we replace x_1 by $(1 - x_2)$, where x_2 is the mole fraction of the solute, then the expansion of the logarithm gives

$$\Pi \ V_1^0 = RT\left(x_2 + \frac{x_2^2}{2} + \frac{x_2^3}{3} + ...\right) \qquad ...(5.29)$$

For a polymer solution of concentration c, x_2 is given by

$$x_2 = \frac{c/M}{1/V_1^0 + c/M} \qquad ...(5.30)$$

$$\approx \frac{V_1^0 c}{M} \text{ for a dilute solution}$$

Here M is the molar mass of the polymer.

Substituting Eq. 5.30 in Eq. 5.29, we obtain, for an ideal solution,

$$\frac{\Pi}{c} = \frac{RT}{M}\left[1+\frac{1}{2}\left(\frac{V_1^0}{M}\right)c+\frac{1}{3}\left(\frac{V_1^0}{M}\right)^2 c^2+....\right] \qquad ....(5.31)$$

which is the virial expression of the form

$$\frac{\Pi}{c} = \frac{RT}{M}(1+ A_2c + A_3c^2 +........) \qquad ...(5.32)$$

Eq. 5.32 is often written in the form

$$\frac{\Pi}{c} = \text{RT}\left[\frac{1}{M}+B_2c+B_3c^2+.....\right] \qquad ...(5.33)$$

where B_2, B_3, etc., are the second, third, etc., virial coefficients. Eq. 5.33 is the van't Hoff equation relating the osmotic pressure of a polymer solution with the molar mass of the polymer. The quantity Π/c is called *reduced osmotic pressure.* We see that if the third term is neglected, a graph of Π/c versus *c,* extrapolated to c = 0, gives the intercept on the Π/c axis as R T/M, that is,

$$\lim_{c\to 0} (\Pi/c) = RT/M$$

From the intercept, the molar mass M can be easily calculated.

Example: The following data were obtained on the osmotic pressure of solutions of γ-globulin in 0.15 M NaCl at 37 C:

C, g/100 ml	19.27	12.53	5.81
Π, mm H_2O	453	253	112

Calculate the molar mass of the polymer.

Solution: 100 ml = 0.1 litre = 0.1 dm^3

$$\frac{\Pi}{c} = \frac{453\,\text{mm}\,H_2O}{192.7\,\text{g}\,\text{dm}^{-3}} = 2.35 \text{ mm } H_2O \text{ dm}^3 \text{ g}^{-1}$$

Construct the following table:

c(g dm^{-3})	192.7	125.3	58.1
Π/c (mm H_2O dm^3 g^{-1})	2.35	2.05	1.93

Plot Π/c versus c to obtain a straight line. It will be seen from the plot that

$$\lim_{c\to 0} (\Pi/c) = 18.6 \text{ mm } H_2O \text{ dm}^3 \text{ g}^{-1}$$

$$= RT/M$$

$$M = \frac{RT}{\lim\limits_{c\to 0}(\Pi/c)} - \frac{RT}{18.6 \text{ mm} H_2O \text{dm}^3 g^{-1}}$$

$$R = 0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

$$= 0.08206 \quad 760 \quad 13.56 \text{ mm } H_2O \text{ dm}^3 \text{ K–1 mol}^{-1}$$

(1 atm=760 mm Hg; 1 mm Hg=13.56 mm H_2O)

$$= 845.67 \text{ mm } H_2O \text{ dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

$$M = \frac{(845.67 \text{mm} H_2O \text{dm}^3 \text{K}^{-1} \text{mol}^{-1})(310\text{K})}{1.86 \text{mm} H_2O \text{dm}^3 \text{g}^{-1}}$$

$$= 1.49 \quad 10^5 \text{ g mol}^{-1}$$

The osmotic pressure measurement leads to number-average molar mass since this method is also a means for counting the number of molecules as each molecule contributes equivalently to the measured effect. This can be shown mathematically by remembering that the osmotic pressure Π consists additively of the partial pressures Π_1, Π_2, Π_3,..... for the molecules of different degrees of polymerisation, 1, 2, 3, etc. Thus,

$$\Pi = \Pi_1 + \Pi_2 + \Pi_3 + ... = \frac{c_1 RT}{M_1} + \frac{c_2 RT}{M_2} + \frac{c_3 RT}{M_3} + ... \qquad ...(5.34)$$

The same holds for the total concentration:

$$c = c_1 + c_2 + c_3 \qquad ...(5.35)$$

Thus, the osmotic-average molar mass can be written as

$$\bar{M}_{osmotic} = \frac{(c_1 + c_2 + c_3 + ...)RT}{\Pi_1 + \Pi_2 + \Pi_3 + ...}$$

$$= \frac{(C_1 + C_2 + C_3 + ...)\text{RT}}{RT(c_1/M_1 + c_2/M_2 + c_3/M_3 + ...)} \qquad ...(5.36)$$

The presence of charge introduce complication on some type of macromolecules. Some polymers are strings of acid groups (as in polyacrylic acid—($(CH_2CHCOOH)n$— or stringls of base (such as nylon - $[NH(CH_2)_6NHCO(CH_2)_4CO]_n$— and proteins have acid and base groups. Polymers may therefore be polyelctrolytes and depending upon their state of ionisation, polyanions, polycations and polyampholytes molar mass will change.

One consequence of dealing with polyelectrolytes and naturally occurring ionisable macromolcules is that it is necessary to know the extent of ionisation before osmotic data can be interpreted. For example, suppose the sodium salt of a polyelectrolyte dissociates into u sodium ions and the single polyanion P^{v-}, then the van't Hoff equation read

$$\frac{\Pi}{c} = (v + 1)RT/M \qquad ...(5.37)$$

where c is the mass concentration of the added Na_vP. If we get that $v = 1$ when in fact $v = 10$ the estimate of the molar mass will be seriously wrong. The way out of this difficulty can be found by considering the other consequence of dealing with charged macromolecules.

Donnan Membrane Equilibria

Suppose that the solution of the protein or polymer contains additional salt (so that solution Na_vP also contain added NaCl, for example) and that it is in contact through a membrane such as cellophane (or a cell wall) with another salt solution, and that the membrane is permeable to the solvent and the salt ions but not to the polyelectrolyte ion itself. This arrangement, which is referred to as dialysis, is one that actually occurs in living systems, where osmosis is an important feature of cell operation. What effect does the salt have on osmotic pressure? We shall see that answering this question leads to a resolution of laboratory problem of coping with the extent of ionisation of the macromolecule. The reason why we anticipate an effect to arise from the presence of the added salt is that the anions and cations cannot migrate through the membrane in arbitrary amount because electrical neutrality has to be preserved on both sides; if an anion migrates in one direction, a cation must accompany it and *vice versa*. The general term of the effect of added salt on dialysis equilibria is the Donnan effect.

Consider what happens when polyelectrolyte $(Na^+)_v$ is at concentration [P] on one side of a membrane and NaCl is added to both sides

Initial state

Na^+	$P^{\upsilon-}$		Na^+	Cl^-
c_1	c_1		c_2	c_2

Equilibrium state

Na^+	$P^{\upsilon-}$	Cl^-	Na^+	Cl^-
$c_1 + x$	c_1	x	$c_2 - x$	$c_2 - x$

On the left there are P^{v-}, Na^+Cl^- ions and on the right there are Na^+ and Cl^-. The condition for equilibrium is the chemical potential of NaCl should be same on both sides of the membrane, and so a net flow of Na^+ and Cl^- ions occurs will be the condition μ(NaCl, left) = μ(NaCl, right) is established. This requires

$$\mu\ (NaCl) + RT \ln [a(Na^+)\ a(Cl^-)]_{left} = \mu\ (NaCl) + RT \ln [a(Na^+)\ a\ (Cl^-)]_{Right}$$

If activity coefficients are disregarded, and if it is assumed that the standard values μ (NaCl) are same on both sides of the barrier, then this is equivalent to requiring that

$$[[Na^+][Cl^-]]_{left} = [[Na^+][Cl^-]]_{Right}$$

The sodium ions are supplied by the polyelectrolyte as well as the added salt. Furthermore, if a sodium ion migrates through the membrane it has to be accompanied by chloride ion in order to maintain electrical neutrality on both sides of the membrane. It follows that, at equilibrium

$$[Na^+]_{left} = [Cl^-]_{left} + v\ [P] \qquad ...(5.38)$$

$$[Na^+]_{right} = [Cl^-]_{right}$$

These constraint equations can be combined (to obtain expressions for the differences in ion concentration across the membrane):

$$[Na^+]_{left} - [Na^+]_{right} = \frac{v[P][Na^+]_{left}}{[Na^+]_{left} + [Na^+]_{right}} = \frac{v[P][Na^+]_{left}}{2[Cl^-] + v[P]} \qquad ...5.39$$

$$[Cl^-]_{left} - [Cl^-]_{right} = -\frac{v[P][Cl^-]_{left}}{[Cl^-]_{left} + [Cl^-]_{right}} = \frac{v[P][Cl^-]_{left}}{2[Cl^-]} \qquad ...(5.40)$$

In obtaining these expressions use has been made of the relations

$$[\mathrm{Cl}]^{\mathrm{def}} = \frac{1}{2}\{[\mathrm{Cl}^-]_{\mathrm{left}} - [\mathrm{Cl}^-]_{\mathrm{right}}\}$$

$$= \frac{1}{2}\{[\mathrm{Na}^+]_{\mathrm{left}} + [\mathrm{Na}^+]_{\mathrm{right}} - v[\mathrm{Pl}]\} \qquad \ldots(5.41)$$

the first being a definition of [Cl], which can be measured by analysing the two solutions, and the second coming from the first electroneutrality equation. The final step is to note that the osmotic pressure depends on the difference of the numbers of particles on either side of the membrane at equilibrium and so the van't Hoff equation Π = RT [solute] becomes

$$\Pi = \mathrm{RT}\{[\mathrm{P}] + [\mathrm{Na}^+]_{\mathrm{left}} - [\mathrm{Na+}]_{\mathrm{right}} + [\mathrm{Cl}^-]_{left} - [\mathrm{Cl}^-]_{\mathrm{right}}]\}$$

$$= \mathrm{RT}[\mathrm{P}]\left[1 + \frac{v^2[P]}{\left[4\left[Cl^-\right] + v\left[P\right]\right]}\right] \qquad \ldots(5.42)$$

The second line comes from algebraic manipulation of the result outlined above. There are several points that can be made. First, when the amount of salt that has been added is so great that condition 4 $[\mathrm{Cl}^-] >> \nu$ [P] is satisfied, Eq. 5.42 simplified

$$\Pi \approx \mathrm{RT}[\mathrm{P}]\left[1 + \frac{v^2[P]}{4\left[Cl^-\right]}\right] \qquad \ldots(5.43)$$

and the presence of the salt contributes to a kind of virial coefficient. When the salt is at such a high concentraton that the ratio v^2 [P]/4 $[\mathrm{Cl}^-]$ much smaller than unity the last equation reduces to $\Pi \approx$ RT [P] and osmotic pressure is independent of the value *v*. This is the first principal result we have been seeking: it means if that osmotic pressures are measured in the presence of high concentrations of salt (as is commonly the case for naturally occurring macromolecules) the molar mass may be obtained unambiguously. The underlying reason for this simplification is that when there is a great deal of salt present the fact that the polyelectrolyte provided additional cations (or anions if it is a polycation) is barely noticeable. In passing you should also notice that if no salt is added, so that [Cl] = 0 Eq., reduces to n = (1 + *v*) [P]RT the form encountered originally in equation 5.37.

Scattering of Light

When a beam of light is passed through a colloidal solution or a macromolecular solution, it suffers scattering. This phenomenon is called *Tyndall effect,* having been first observed by Tyndall in 1871. In the same year, Lord Rayleigh gave a theory of the scattering of light by isotropic particles with dimensions less than one-tenth of the wave length of the light. He found that the ratio of the intensity I_θ scattered at an angle θ from the direction of the transmitted beam, to the intensity I_0 of incident unpolarised, monochromatic light, is given by

$$\frac{I_\theta}{I_0} = \frac{8\pi^4 a\alpha^2}{\lambda^4 r^2}\left(1+\cos^2\theta\right) \qquad \text{...(5.44)}$$

where r is the distance of the observer from the sample, a is the number of scattering particles per unit volume and α is the electrical polarizability of the particle. Notice that in Rayleigh equation, the *scattered intensity is proportional to the inverse fourth power of wave length.* Thus, blue light is scattered much more than the red light. This accounts for the blue colour of the sky when viewed in any direction except towards the sun. The existence of polarziability, α, in Rayleigh equation arises from the fact that the incident light induces vibrating dipoles in the particle which, in turn, act as sources and radiate light in all directions. The mole polarisable a particle, the greater is the magnitude of the vibrating (oscillating) dipoles.

It is customary to use the refractive index n of the scattering particles as a measure of their polarizability. It is known from optics that specific refraction, *i.e.,* refraction per unit volume, is given by

$$\frac{n^2-1}{n^2+2} = \frac{4}{3}\pi a\alpha \qquad \text{...(5.45)}$$

Assuming that $n \approx 1$ so that $n^2 + 2 \approx 3$, this equation reduces to

$$\alpha = \frac{n^2-1}{4\pi a} \qquad \text{...(5.46)}$$

In the case of a solution we are interested in knowing the difference between the polarizability a of the solution and the polarizability α_0 of the solvent so that

$$\alpha - \alpha_0 = \frac{n^2 - n_o^2}{4\pi a} \qquad ...(5.47)$$

where the subscript zero denotes the solvent. For a solution having concentration *c,* the refractive index can be written as a Taylor's series, *viz,*

$$n = n_0 + c(dn/dc) + ... \qquad ....(5.48)$$

where n_0 is the refractive, index when the concentration *c* (in mass per unit volume) is zero.

Squaring both sides of this equation, we get

$$n^2 = n_0^2 + 2n_0 c\frac{dn}{dc} + c^2\left(\frac{dn}{dc}\right)^2 + ... \qquad ...(5.49)$$

The last term, being small, can be neglected, giving

$$n^2 - n_0^2 = 2n_0 c + \frac{dn}{dc} \qquad ...(5.50)$$

Since the light scattering method yields the mass-average molar mass, hence *a* may be written as $cN_A\sqrt{M_m}$. Combining Eqs. 5.47 and 5.50 and assuming that the polarisability of the solvent, α_0 is negligible, we obtain

$$\alpha = \frac{n_0(dn/dc)\overline{M}_m}{2\pi N_A} \qquad ...(5.51)$$

Squaring both sides of this equation and substituting for α^2 in the Rayleigh equation 5.44, we obtain

$$\frac{I_\theta}{I_0} = \left(\frac{2\pi^2 n_0^2 (dn/dc)^2}{N_A \lambda^4}\right)\left(\frac{1+\cos^2\theta}{r^2}\right)\overline{M}_m c \qquad ...(5.52)$$

which may be rewritten as

$$R_\theta = K\overline{M}_M c \qquad ....(5.53)$$

where $$R_\theta = \left(\frac{I_\theta}{I_0}\right)\left(\frac{r^2}{1+\cos^2\theta}\right) \qquad ....(5.54)$$

and $$K = \frac{2\pi^2 n_0^2 (dn/dc)^2}{N_A \lambda^4} \qquad ...(5.55)$$

R_θ is called Rayieigh ratio; it represents the intensity ratio corrected for the geometry of the system; K is the optical constant;

it contains the wave length of the light and information about the refractive index. P_θ is independent of the value of θ. Eq. 5.53 can be used to calculate the molar mass of the polymer. Light-scattering measurements give mass-average molar mass, as already stated. Lord Rayleigh, the versatile British physicist, was awarded the 1904 Physics Nobel prize for his contributions to mathematical physics and the discovery of argon in the atmosphere.

For non-ideal polymer solutions where there are interactions between the polymer molecules, Einstein and Debye showed independently that if the solute is uniformly distributed throughout the solution, no light is scattered by the solution because light scattered by one particle will interfere destructively with light scattered by the neighbouring particle. Random Brownian motion causes fluctuations in concentration, the extent of fluctuations is inversely proportional to the osmotic pressure developed by the concentration difference. It is found that

$$\frac{K_c}{R_0} = \frac{1}{RT}\cdot\frac{d\Pi}{dc} \qquad \text{...(5.56)}$$

where Π is the osmotic pressure. It may be recalled that for an ideal solution, $\Pi = cRT/\ \overline{M}_M$. For a non-ideal solution,

$$\frac{\Pi}{c} = RT\left(\frac{1}{\overline{M}_m}+2B_2\right) \qquad \text{...(5.57)}$$

where B_2 is the second virial coefficient, From Eqs. 5.55 and 5.56,

$$\frac{K_c}{R_\theta} = \frac{1}{\overline{M}_m}+2B_{2c} \qquad \text{...(5.58)}$$

A graph of Kc/Rθ versus *c* gives a straightline with slope 2 B_2 and intercept = $1/M_m$. This permits determination of M_m, the mass-average molar mass of the polymer.

In deriving equation (5.58) it was assumed that the solvent and solute molecules act as point scatterners, *i.e.,* their dimensions are very much smaller than λ. Whilst in general this assumption is satisfactory for the solvent molecule, it is often inappropriate for polymer solute molecules.

The theory for R_θ begins to fail when the solute molecules have dimensions of the order of λ′/20, where λ′ is the wavelength of the light in the medium ($\approx \lambda/n_0$). Thus the limiting dimensions when using He-Ne laser light (λ = 632.8 nm) are typically about 20 nm. Most polymer molecules of interest have dimensions which either are close to or exceed $\lambda'/20$.

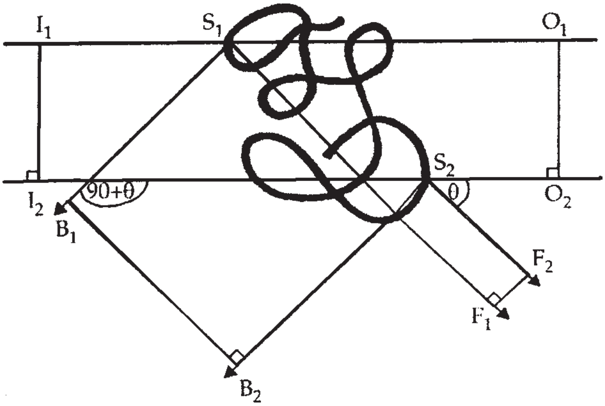


Fig. *Schematic illustration of the origin of the interference effects which occur between light scattered by two different segments.* S_1 *and* S_2 *in the same molecule. The path-length difference* ($I_2S_2B_2 - I_1S_1B_1$) *in the backward direction is greater than the path-length difference* ($I_1S_1F_1 - I_2S_2F_2$) *in the forward direction. The path-length difference is zero at* $\theta = 0$, ($I_1S_1O_1 = I_2S_2F_2$).

The consequence of this is that interference occurs between light scattered from different parts of the same molecule, and so R_0 is reduced. This effect is illustrated schematically in the figure above which also shows that the path-length *(i.e.,* phase) difference increases with θ and is zero only for θ = 0. Thus the scattering envelope is unsymmetrical with I_θ greater for forward scattering than for backward scattering. In order to account for such interference effects, a *particle scattering factor* P(θ) is introduced and is given by the ratio

$$P(\theta) = \frac{R_\theta}{R_{\theta=0}} \qquad \text{....(5.59)}$$

where R_θ is the measured value of R at the scattering angle θ *(i.e.,* including the effects of interference) and $R_{\theta = 0}$ is the values of R in the be absence of interference effects. For small molecules P(θ) = 1 for all values of θ, whereas for large molecule P(θ) can be very much smaller than unity but increases as θ decreases and at θ = 0 become equal to unity. By combining eqn. 5.58 and 5.59 a more general expression is obtained

$$\frac{K_c}{R_\theta} = \frac{1}{P(\theta)}\left[\frac{1}{M_w} + 2B_2c\right] \qquad ...(5.60)$$

Details of analytical form derivation of P(θ) can not be given in a book of this type, however, we quote the final result hare as

$$\frac{K_c}{R_\theta} = \left[\frac{1}{M_w} + 2B_2C\right]\left[1 + \left(\frac{16\pi^2 n_0^2 \sin^2(\theta/2)}{3\lambda^2}\right)\right] < S^2 >_z \; ...(5.61)$$

which is applicable at low solute concentration and enables M_W, B_2 and for polymer molecules of sufficient size, $<S^2>$ to be determined from the measurement of R_θ at different angles for each of several polymer solutions with different concentration c.

Although Equation 5.61 describes a three-dimensional surface for the variation of Kc/R_θ with c and θ, it is usual to plot the experimental data in two dimensional using an elegant technique devised by Zimm. In the Zimm plot, Kc/R_θ is plotted against the composite quantity $\sin^2(\theta/2) + k'c$ where k' is an arbitrary constant the value of which is chosen so as to give a clear separation of the data points (usually k' is taken as 0.1 when the units of c are g dm^{-3}).

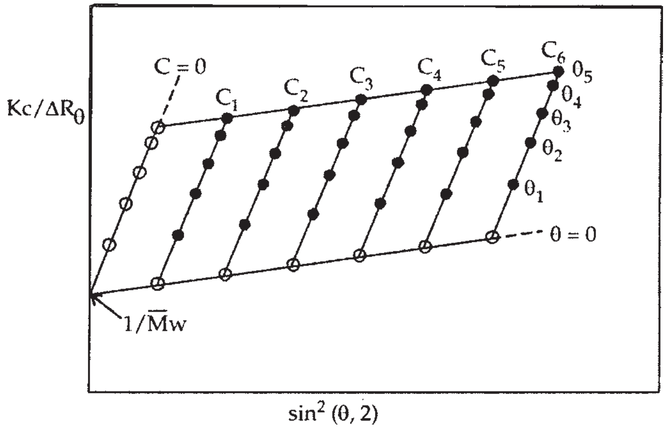


Fig. Schematic illustration of Zimm plot for analysing light-scattering data. The solid points (•) represent experimental measurements the open circles (O) are extrapolated points.

A grid-like graph is obtained, such as that shown schematically in the following figure and consists of two sets of lines one set joining points of constant c and the other joining points with the same value of θ. In order to evaluate B_2, each of the lines at constant c is extrapolated to θ = 0 (i.e., to *k′c)* and the limiting points thus obtained further extrapolated to c = 0. The initial linear slope of this limiting extrapolation then gives B_2 from

$$B_2 = \left(\frac{k'}{2}\right)\left[d\left[K_c / R_\theta\right]_{\theta=0}\, d(k'c)\right]_{c\to 0} \qquad \text{...(5.62)}$$

Similarly, each of the lines at constant θ are extrapolated to c = 0, *{i.e.,* to $\sin^2(\theta/2)$} and the limiting points obtained extrapolated to θ = 0. In this case the initial linear slope gives $<s^2>_z$ in terms of $\overline{M}_w$ and n_0

$$\left\langle \overline{s^2} \right\rangle_z = \left(\frac{3\lambda^2 \overline{M}_w}{16\pi^2 n_0^2}\right)\left[d\left[Kc/R_\theta\right]_{c=\theta} / d\left[\sin^2(\theta/2)\right]\right]_{a\to 0}$$

...(5.63)

The common intercept of the two limiting extrapolations allows $\overline{M}_W$ to he evaluated

$$\left(\frac{K_c}{R_\theta}\right)_{\substack{c\to 0\\ \theta\to 0}} = \frac{1}{M_w} \qquad \text{...(5.64)}$$

and hence $\left\langle \overline{s^2} \right\rangle_z$ from Equation (5.63). Thus static light scattering measurements yield *absolute values* for $\overline{M}_w$, B_2, and $\left\langle \overline{s^2} \right\rangle_z$, the latter without reference to molecular shape.

The basic features of a light-scattering instrument are evident from the following figure namely a light source and a thermostated (± 0.01 C) sample cell positioned on a precision goniometer which enables a photomultiplier detector to be moved accurately to a wide range of scattering angles. Since $I_0 \propto I_0\lambda^{-4}$ greatest sensitivity is achieved by using high-intensity visible radiation ideally of short wavelength. Modern instruments use monochromatic laser radiation *(e.g.* He-Ne: λ = 632.8 nm, and Ar ion; λ = 488.0 nm or 514.5 nm) and are able to measure I_θ for θ from about 10 to 160 . It is usual practice to record I_θ as the photomultiplier voltage output, and to evaluate the Rayleigh ratios of the solvent and the solutions from the ratios of their photomultiplier voltage outputs to that of a standard *(e.g.* benzene) for which the Rayleigh ratio and refractive index are accurately known for the incident radiation at the temperature of measurement. In this way the need to determine I_θ and to measure absolute values of I_θ are avoided. The Rayleigh ratios thus obtained then are corrected for the effects of refraction and for the variation of the scattering volume with θ.

In addition to the nature of the light source, the sensitivity of the measurements depends strongly upon the refractive index increment, *dn/dc,* which should be as large as possible. Thus solvents which have refractive indices substantially different from that of the polymer should be chosen (typically to give *dn/dc* of about 0.0001 dm^3g^{-1}). The value of *dn/dc* at the wavelength of the incident radiation must be accurately known in order to perform the calculations of $\overline{M}_w$, B_2 and $\left\langle \overline{s^2} \right\rangle_z$, and if not available in the published literature, can be determined using a differential refractometer.

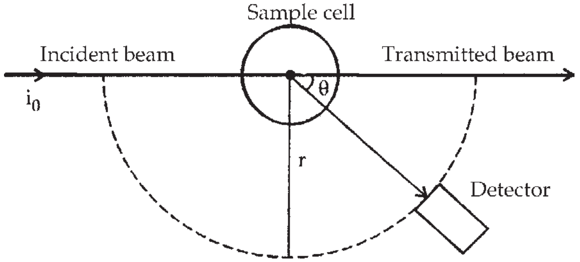


***Fig.** Main features of apparatus required to measure the light scattered from a polymer solution.*

A further consideration which is of great practical importance is the need to ensure that all of the samples analysed are completely dust-free, otherwise the dust particles would contribute to the scattering intensity and lead to erroneous results. Thus the standard, solvent and solutions analysed must he clarified just prior to use, usually by micropore *(e.g.,* 0.2-0.5 μm porosity) pressure filtration or by high-speed centrifugation.

Light scattering measurements have the potential to be accurate over a broad range of $\overline{M}_w$ typically 2 10^4 to 5 10^6 mol^{-1}. The lower limit of $\overline{M}_w$ is determined by the ability to detect small values of i_θ and by the variation of *dn/dc* with molar mass at very low molar masses. The upper limit corresponds to the molecule dimension approaching $\lambda/2$ when complete destructive interference of light scattered from different parts of the same molecule occurs.

Effects of Ultra Centrifugation

Measurements of sedimentation behaviour of polymer molecule in solution can provide a consideratble amount of information, *e.g.,* hydrodynamic volume, average molar masses and even some indication of molar mass distribution. Such measurements have been extensively used to characterise biologically-active polymers which often exist in solution as compact spheroids or rigid rods. However, sedimentation methods are rarely used to study synthetic polymers and so will be given only brief non-theoretical consideration here.

The normal gravitational force acting upon a polymer molecule in solution is insufficient to overcome its Brownian motion and does not cause sedimentation. Thus in order to make measurements of sedimentation it is necessary to subject the polymer solutions to much higher gravitational fields. This is achieved using *ultracentrifuges* which can attain rotation speeds of up to about 70,000 revolutions per minute (rpm) and generate centrifugal fields up to about 4,00,000 g where g is the acceleration due to gravity. The polymer solution is placed in a cell which fits into the rotor of the ultracentrifuge and has windows on other side. The cell is in the form of a truncated cone and is positioned so that its peak would be located at the axis of the rotor. This design ensures that sedimentation in radial directions is not restricted.

The sedimentation process gives rise to a solvent phase and a concentrated polymer solution phase which are separated by a boundary layer in which the polymer concentration varies. There is, therefore, a natural tendency for backward diffusion of the molecules in order to equalise the chemical potentials of the components in the different regions of the cell, and this causes broadening of the boundary layer. The breadth of the boundary layer also increases with the degree of polydispersity because molecules of higher molar mass sediment at faster rates. The windows in the cell enable the radial variation in polymer concentration to be measured during ultracentrifugation typically by monitoring refractive index differences (cf. light scattering). There are two general methods by which sedimentation experiments can be performed and they will now be briefly described.

In a *sedimentation equilibrium experiment* the cell is rotated at a relatively low speed (typically 5000-10000 rpm) until an equilibrium is attained whereby the centrifugal force just balances the tendency of the molecules to diffuse back against the concentration gradient developed. Measurements are made of the equilibrium concentration profiles for a series of solutions with different initial polymer concentrations so that the results can be extrapolated to c = 0. A rigorous thermodynamic treatment is possible and enables absolute values of $\overline{M}_w$ and $\overline{M}_z$, to be determined. The principal restriction to the use of sedimentation equilibrium measurements is the long time required to reach equilibrium, since this is at least a few hours and more usually is a few days.

The *sedimentation velocity method* involves rotating the solution cell at very high speeds (typically 60,000-70,000 rpm) and gives results in much shorter time scales than sedimentation equilibrium measurements. The movement of the boundary layer is monitored as a function of time and its steady-state velocity used to calculate the mean sedimentation coefficient, S, for the polymer in solution. Measurements are made for a series of solution concentrations and enable the limiting sedimentation coefficient. S_0, to be obtained by extrapolation to c = 0. In order to calculate an average molar mass, it is necessary either to know the limiting diffusion coefficient of the polymer in the solvent or to calibrate the system by measuring S_0 for a series of similar polymers but which have narrow molar mass distributions and known molar masses. The latter procedure is more common and an equation similar in form to the Mark-Houwink Equation (5.21) is used to correlate S_0 data with molar mass for each specific polymer/solvent/temperature system. The resulting average molar mass usually is close to $\overline{M}_w$.

Conducting Polymers: the Concept

Until about 30 years ago all carbon based polymers were rigidly regarded as insulators. The idea that plastics could be made to conduct electricity would have been considered to be absurd. Indeed, plastics have been extensively used by the electronics industry because of this very property. They were utilised as inactive packaging and insulating material. This very narrow perspective is rapidly changing as a new class of polymer known as *intrinsically conducting polymer* or e*lectroactive polymers* are being discovered. Although this class is in its infancy, much like the plastic industry was in the 30's and 50's, the potential uses of these are quite significant.

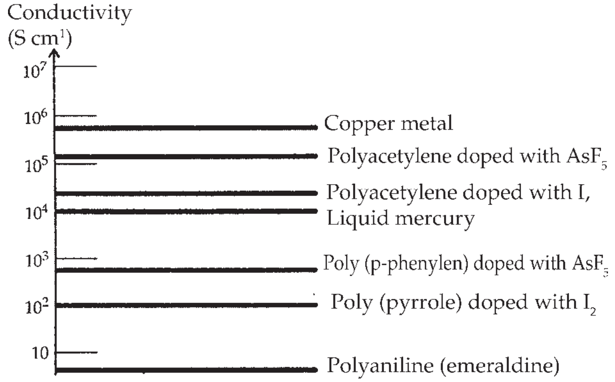


Fig. Logarithmic conductivity ladder locating some metals and conducting polymers.

In 1958, polyacetylene was first synthesised by Natta et al. as a black powder. This was found to be a semi-conductor with a conductivity between 7 10^{-11} to 7 10^{-3} Sm^{-1}, depending upon how the polymer was processed and manipulated. This compound remained a scientific curiosity until 1967, when a post-graduate student of Hideki Shirakawa at the Tokyo Institute of Technology was attempting to synthesise polyacetylene and a silvery thin film was produced as a result of a mistake.

It was found that 1000 times more of the Ziegler-Natta catalyst, $Ti(O\text{-}n\text{-}Bu^1)_4 - Et_3AI$, had been used. When this film was investigated it was found to be semi-conducting, with a similar level of conductivity to the best of the conducting black powders. Further investigations, showed that exposure of this form of polyacetylene to halogens increased its conductivity a billion fold. Undoped polymer was silvery, insoluble and intractable, with a conductivity similar to that of semi-conductors. When it was weakly oxidised by compounds such as iodine it turned a golden colour and its conductivity increased to about 10^4 Sm^{-1}. In the 1980's, polyheterocycles were first developed. Polyheterocycles were found to be much more air stable than polyacetylene, although their conductivities were not so high, typically about 10^3 Sm^{-1}. By adding various side groups to the polymer backbone, derivatives which were soluble in various solvents were prepared. Other side groups affected properties such as their colour and their reactivity to oxidising and reducing agents. A Logarithmic conductivity ladder of some of these polymers are shown in the figure above.

Since then it has been found that about a dozen different polymers and polymer derivatives undergo this transition when doped with a weak oxidation agent or reducing agent. They are all various conjugated polymers. This early work has led to an understanding of the mechanisms of charge storage and charge transfer in these system. All have a highly conjugated electronic state. This also causes the main problems with the use of these systems, that of processibility and stability. Most early conjugated polymers were unstable in air and were not capable of being processed. The most recent research in this has been the development of highly conducting polymers with good stability and acceptable processing attributes.

Charge Storage

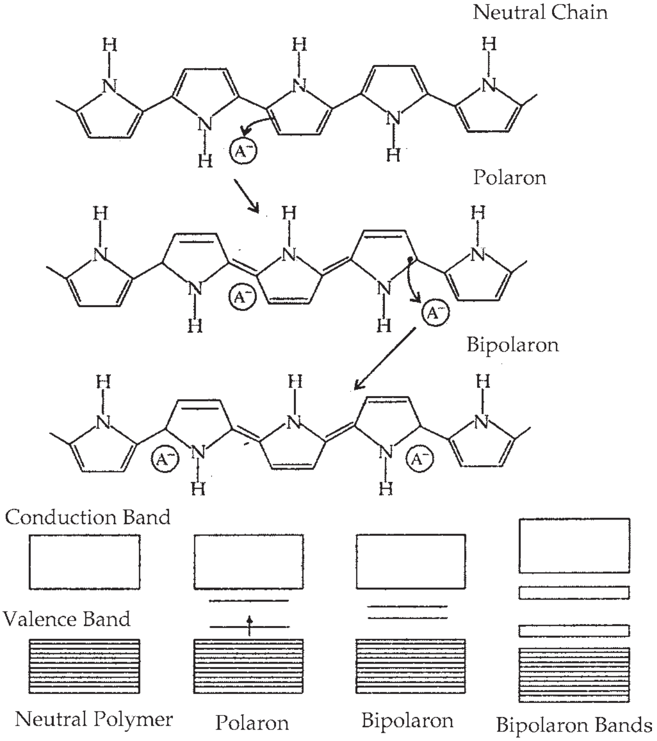
One early explanation of conducting polymers used band theory as a method of conduction. This said that a half filled valence band would be formed from a continuous delocalised π -system. This would be an ideal condition for conduction of electricity. However, it turns out that the polymer can more efficiently lower its energy by bond alteration (alternating short and long bonds), which, introduces a band width of 1.5 eV making it a high energy gap semi-conductor. The polymer is transformed into a conductor by doping it with either an electron donator or an electron acceptor. This is reminiscent of doping of silicon based semi-conductors where silicon is doped with either arsenic or boron. However, while the doping of silicon produces a donor energy level close to the conduction band or a acceptor level close to the valence band, this is not the case with conducting polymers. The evidence for this is that the resulting polymers do not have a high concentration of free spins, as determined by electron spin spectroscopy. Initially the free spins concentration increases with concentration of dopant. At larger concentrations, however, the concentration of free spins levels attain a maximum. To understand this it is necessary to examine the way in which charge is stored along the polymer chain and its effect.

The polymer may store charge in two ways. In an oxidation process it could either lose an electron from one of the bands or it could localise the charge over a small section of the chain. Localising the charge causes a local distortion due to a change in geometry, which costs the polymer some energy. However, the generation of this local geometry decreases the ionisation energy of the polymer chain and increases its electron affinity making it more able to accommodate the newly formed charges. This method increases the energy of the polymer less than it would if the charge was delocalised and, hence, takes place in preference of charge delocalisation. This is consistent with an increase in disorder detected after doping by Raman spectroscopy. A similar scenario occurs for a reductive process.

Typical oxidising dopants used include iodine, arsenic pentachloride, iron(III) chloride and $NOPF_6$. A typical reductive dopant is sodium naphthalide. The main criteria is its ability to oxidise or reduce the polymer without lowering its stability or whether or not they are capable of initiating side reactions that inhibit the polymers ability to conduct electricity. An example of the latter is the doping of a conjugated polymer with bromine. Bromine it too powerful an oxidant and adds across the double bonds to form sp^3 carbons. The same reaction may occur with $NOPF_6$ but at a lower rate.

The oxidative doping of polypyrrole proceeds in the following way. An electron is removed from the π-system of the backbone producing free radical and a spinless positive charge. The radical and cation are coupled to each other via local resonance of the charge and the radical. In this case, a sequence of quinoid-like rings is used. The distortion produced by this is of higher energy than the remaining portion of the chain. The creation and separation of these defects costs a considerable amount of energy. This limits the number of quinoid-like rings that can link these two bound species together. In the case of polypyrrole it is believed that the lattice distortion extends over four pyrrole rings. This combination of a charge site and a radical is called a polaron. This could be either a radical cation or radical anion. This creates a new localised electronic states in the gap, with the lower energy stales being occupied by a single unpaired electrons. The polaron state of polypryyole are symmetrically located about 0.5 eV from the band edges.

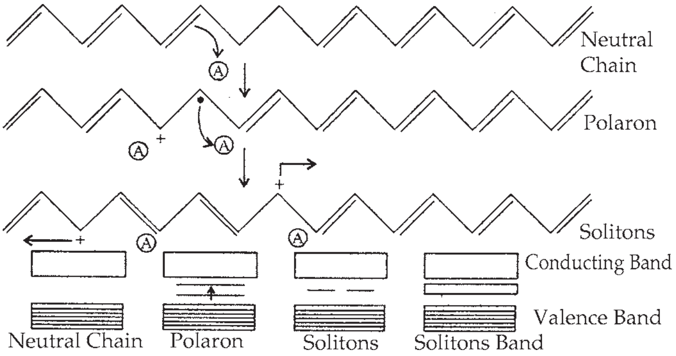
Upon further oxidation the free radical of the polaron is removed, creating a new spinless defect called a bipolaron. This is of lower energy than the creation of two distinct polarons. At higher doping levels it become possible that two polarons combine to form a bipolaron. Thus at higher doping levels the polarons are replaced with bipolarons. The bipolarons are located symmetrically with a band gap of 0.75 eV for polypryyole. This eventually, with continued doping, forms into a continuous bipolaron bands. Their band gap also increases as newly formed bipolarons are made at the expense of the band edges. For a very heavily dope polymer it is conceivable that the upper and the lower bipolaron bands will merge with the conduction and the valence bands respectively to produce partially filled bands to produce metal like conductivity. This is shown in the following figure:



Conjugated polymers with a degenerate ground slate have a slightly different mechanism. As with polypyrrole, polarons and bipolarons are produced upon oxidation. However, because the ground state structure of such polymers are twofold degenerate, the charged cation are not bound to each other by a higher energy bonding configuration and can freely separate along the chain.

The effect of this is that the charged defects are independent of one another and can form domain walls that separate two phases of opposite orientation and identical energy. These are called solitons and can sometimes be neutral. Solitons produced in polyacetylene are believed to be delocalised over about 12 CH units with the maximum charge density next to the dopant counterion. The bonds closer to the defect show less amount of bond alternation than the bonds away from the centre.

Soliton formation results in the creation of new localised electronic states that appear in the middle of the energy gap. At high doping levels, the charged solitons interact with each other to form a soliton band which can eventually merge with the band edges to create true metallic conductivity. This is shown in the figure given below:



Charge Transport

Although solitons and bipolarons are known to be the main source of charge carriers, the precise mechanism is not yet fully understood. The problem lies in attempting to trace the path of the charge carriers through the polymer. All of these polymers are highly disordered, containing a mixture of crystalline and amorphous regions. It is necessary to consider the transport along and between the polymer chains and also the complex boundaries established by the multiple number of phases. This has been studied by examining the effect of doping, of temperature, of magnetism and the frequency of the current used.

These test show that a variety of conduction mechanisms are used. The main mechanism used is by movement of charge carriers between localised sites or between soliton, polaron or bipolaron states. Alternatively, where inhomogeneous doping produces metallic island dispersed in an insulating matrix, conduction is by movement of charge carriers between highly conducting domains. Charge transfer between these conducting domains also occurs by thermally activated hopping or tunnelling. This is consistent with conductivity being proportional to temperature.

Stability

There are two distinct types of stability. Extrinsic stability is related to vulnerability to external environmental agent such as oxygen, water, peroxides. This is determined by the polymers susceptibility of charged sites to attack by nucleophiles, electrophiles and free radicals. If a conducting polymer is extrinsic unstable then it must be protected by a stable coating.

Many conducting polymers, however, degrade over time even in dry, oxygen free environment. This intrinsic instability is thermodynamic in origin. It is likely to be caused by irreversible chemical reaction between charged sites of polymer and either the dopant counter ion or the π-system of an adjacent neutral chain, which produces an sp^3 carbon, breaking the conjugation. Intrinsic instability can also come from a thermally driven mechanism which causes the polymer to lose its dopant. This happens when the charge sites become unstable due to conformational changes in the polymer backbone. This has been observed in alkyl substituted polythiophenes.

Processibility

Conjugated polymers may be made by a variety of techniques, including cationic, anionic, radical chain growth, coordination polymerisation, step growth polymerisation or electrochemical polymerisation. Electrochemical polymerisation occurs by suitable monomers which are electrochemically oxidised to create an active monomeric and dimeric species which react to form a conjugated polymer backbone. The main problem with electrically conductive plastics stems from the very property that gives it its conductivity, namely the conjugated backbone.

This causes many such polymers to be intractable, insoluble films or powders that cannot melt. There are two main strategies to overcoming these problems. These are to either modify the polymer so that it may be more easily processed, or to manufacture the polymer in its desired shape and form. There are four main methods used to achieve these aims.

The first method is to manufacture a malleable polymer that can be easily converted into a conjugated polymer. This is done when the initial polymer is in the desired form and then, after conversion, is treated so that it becomes a conductor. The treatment used is most often thermal treatment. The precursor polymer used is often made to produce highly aligned polymer chain which are retained upon conversion. These are used for highly orientated thin films and fibres. Such films and fibres are highly anisotropic, with maximum conductivity along the stretch direction.

The second method is the synthesis of copolymers or derivatives of a parent conjugated polymer with more desirable properties. This method is the more traditional one for making improvements to a polymer. It modifies the structure of the polymer to increase its processibility without compromising its conductivity or its optical properties. All attempts to do this on polyacetylene have failed as they always significantly reduced its conductivity. However, such attempts on polythiophenes and polypyrroles proved more fruitful.

The hydrogen on carbon 3 on the thiophene or the pyrrole ring was replaced with an alkyl group with at least four carbon atoms in it. The resulting polymer, when doped, has a comparable conductivity to its parent polymer whilst be able to melt and it is soluble. A water soluble version of these polymers has been produced by placing carboxylic acid group or sulphonic acid group on the alkyl chains.

If sulphonic acid groups are used along with built-in ionisable groups, then such system can maintain charge neutrality in its oxidised state and so they effectively dope themselves. Such polymers are referred to as "self-doped" polymers. One of the most highly conductive derivative of polythiophene is made by replacing the hydrogen on carbon three with a $-CH_2-O-CH_2CH_2-O-CH_2CH_2-O-CH_3$. This soluble polymer shows a conductivity of about 1000 Scm^{-1} upon doping.

The third method is to grow the polymer into its desired shape and form. An insulating polymer impregnated with a catalyst system is fabricated into its desired form. This is then exposed to the monomer, usually a gas or a vapour. The monomer then polymerises on the surface of the insulating plaslic producing a thin film or a fibre. This is then doped in the usual manner. A variation of this technique is electrochemical polymerisation with the conducting polymer deposited on an electrode either at the polymerisation stage or before the electrochemical polymerisation.

This cast may be used for further processing of the conducting polymer. For instance, by stretching aligned bends of polyacetylene/porybutadiene the conductivity increase 10 fold, due to the higher state of order produced by this deformation.

The fourth method use the Laingmuir-Blodgett trough to manipulate the surface active molecules into a highly ordered thin films whose structure and thickness are controllable at the molecular layer level. Amphiphilic molecules with hydrophilic and hydrophobic groups produces monolayers at the air-water interface of a Langmuir-Blodgett trough.

This is then transferred to a substrate creating a multilayer structure comprised of molecular stacks which are normally about 2.5 run thick. The main advantage of this technique is its unique ability to allow control over the molecular architecture of the conducting films produced. It can be used to create complex multilayer structures of functionally different molecular layers as determined by the chemist. By producing alternating layers of conductor and insulator it is possible to produce highly anisotropic film which is conducting within the plane of the film, but insulating across it.

Table: *Stability and Processing Attributes of Some Conducting Polymers*

Polymer	Conductivity $\left(\Omega^{-1} cm^{-1}\right)$	Stability (doped state)	Processing ***Possibilities***
Polyacetylene	10^3-10^5	poor	limited
Polyphony lone	1000	poor	limited
PPS	100	poor	excellent
PPV	1000	poor	limited
Polypyrroles	100	good	good
Polythiophenes	100	good	excellent
Polyaniline	10	good	good

Applications

The extended π-systems of conjugated polymer are highly susceptible to chemical or electrochemical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to precisely control these properties. Since these reactions are often reversible, it is possible to systematically control the electrical and optical properties with a great deal of precision. It is even possible to switch from a conducting state to an insulating slate.

There are two main groups of applications for these polymers. The first group utilises their conductivity as its main property. The second group utilises this electroactivity. They are shown below:

Group 1	Group 2
Electrostatic materials	Molecular electronics
Conducting adhesives	Electrical displays
Electromagnetic shielding	Chemical biochemical and thermal sensors
Printed circuit boards	Rechargeable batteries and solid electrolytes
Artificial nerves	Drug release systems
Antistatic clothing	Optical computers
Piczoceramics	Ion exchange membranes
Active electronics (diodes transistors)	Electromechanical actuators
Aircraft structures	'Smart' structures
	Switches

Much research will be needed before many of the above applications could become a reality. The stability and processibility, both need to be substantially improved if they are to be used in the market place. The cost of such polymers has to be substantially lowered. However, one must consider that, although conventional polymers were synthesised and studied in laboratories around the world, they did not become widespread until years of research and development had been done.

In a way, conducting polymers are at the same stage of development as their insulating brothers were some 50 years ago. Regardless of the practical application that are eventually developed for them, they will certainly be challenge to researchers with new and unexpected phenomena. Only time will tell whether the impact of these novel plastics will be as large as their insulating relatives or more.

6

Surface Chemistry

Concept of Surface Chemistry

As is well known, unbalanced or residual forces act along the surface of a liquid giving rise to surface tension. Such forces also exist on the surface of a solid. As a result of these residual forces, the surface of a solid has a tendency to attract and retain molecules of other species with which it is brought into contact. As these molecules remain only at the surface and do not go deeper into the bulk, their concentration is more at the surface than in the bulk of the solid.

Whenever we have an interface between a solid and a gas or vapour, the concentration of the gas is higher in the immediate vanity of the solid than it is in the free space beyond. The gas is said to be 'adsorbed' on the solid. The amount of adsorption is defined as the mass of the gas that is actually present within the sphere of action of the solid, less the mass which would be present if the solid exerted no action. This amount is usually referred to 1 gram of the adsorbent, and may be expressed in any convenient units. The commonest being gram-molecules, milligrams, or the volume in cc of the gas would occupy at NTP. The adsorbed substance is called *adsorbate* and the adsorbing solid the *adsorbent.*

When a quantity of gas is admitted to a sample of solid adsorbent in a closed system previously evacuate equilibrium is not in general attained instantaneous owing to gradual adsorption the pressure of the gas continues to fall for a period which may be anything from some minutes to many weeks, depending on the state and nature of the system under consideration but usually it eventually becomes sensibly constant. The pressure then prevailing is said to be the "equilibrium pressure" and is an important quantity in adsorption work.

The quantity x adsorbed per unit weight of adsorbent is found to depend to a marked degree upon this equilibrium pressure p.

The quantity of a gas adsorbed by a given weight of adsorbent varies greatly from one adsorbent to another. This variation in adsorption must be due to the operation of at least two factors; the area of the interface and the specific adsorbing properties of the substance per unit area. However, it is not in general possible to determine precisely the relative importance of these two factors.

Various Adsorbents

Some of adsorbents may be classified as follows:

1. Active charcoal, graphite and Carbon
2. Silica gel and other gels
3. Chabasite and other zeolites
4. Glass
5. Metals
6. Surfaces of crystals

Adsorption by Active Charcoal: Charcoal as ordinary prepared by the charring of wood, bones, sugar, and carbon has a low adsorbing capacity. It can be raised to a useful figure by activating it either chemically or by heat treatments. Chemical activation is carried out by soaking the starting material *(e.g.,* wood) in one of a number of inorganic solutions, a common one being zinc chloride on subsequent charring the products is active in an adsorption sense. For the heat treatment the starting substance is charred in the ordinary way and the inactive charcoal thus obtained is heated in an atmosphere of air, oxygen-nitrogen mixture, carbon dioxide, nitrogen, or steam (800 - 1000 C). Heating above 1100-1200 C appears to have a great deactivation effect.

Three factors may be distinguished to the contribution to the activation (a) cleansing the charcoal surface of the adsorbed hydrocarbons, tarry matter and carbon (b) increasing the surface area of charcoal by oxidation (c) increasing the degree of chemical unsaturation of the surface carbon atoms. A very good method of creating a high vacuum is to connect a bulb of charcoal cooled in liquid air to a vessel which has already been exhausted as far as possible by a vacuum pump. Since the magnitude of adsorption at such low temperature is quite high the remaining trace of air in spite of the low pressure are adsorbed by charcoal almost completely.

Activated charcoal is used in gas masks in which all toxic gases are adsorbed by charcoal while pure air passes through its pores practically unchanged. Animal charcoal is used as decolouriser in the manufacture of cane sugar.

Adsorption by Silica Gel and other Gels

The commonest gel for adsorption purposes is silica gel but measurement have also been carried out on ferric oxide, aluminium oxide, stannous oxide and titanium oxide. The characteristics of adsorption on silica gel differ somewhat from those for charcoal, particularly with respective Freundlich isotherm which holds fairly accurately. Moreover, deviation from Henry’s Law even, seems to be much less than for charcoal. Water is somewhat exceptional. Silica and alumina gels are used as adsorbents for removing moisture and for controlling humidities of rooms.

Adsorption by Chabasite and other Zeolites

Zeolites are hydrated calcium aluminium silicates, one of the commonest being $CaAl_2Si_4O_{12}6H_2O$, unlike ordinary crystals containing water of crystallisation, they can be dehydrated without any change in the form of their crystal lattice. X-ray radiograms show that removal of water from cabasite change the intensities and not the position of lines. From this, it would appear that the water is present in a loosely bound condition and not in any chemical combine. The places vacated by the water molecules are capable of occupation by then molecules, of other substances, for the zeolites, especially in the dehydrated form are good adsorbents. A very significant fact in connection with cliabasite is that whereas it rapidly takes up the vapours having small molecules, such as water, ethyl or methyl alcohol but larger molecules like ether or benzene are largely excluded. Thus partially dehydrated chabasite seems to be able to act as a molecules shieve or semi-permeable membrane of a regular structure.

Adsorption by Glass

The rate of adsorption of certain gases on glass follow a simple exponential law. The adsorption on glass is often troublesome in sealing off evacuated glass apparatus, for the pressure always increases somewhat during the operation, due to the gas which is liberated. Thus vacuum in a glass apparatus deteriorates with time, the difficulty can be minimised though not entirely removed by baking out the vessel under high vacuum, prior to sealing off at as high a temperature as is consistent with avoiding collapse of the walls.

Adsorption by Impermeable Crystals

Measurement of the adsorption of gases on crystals are less numerous than on most other adsorbents because of the difficulty of securing a reasonably large surface area per unit weight. A few experiments have been performed for monolayer adsorption of methane, carbon monoxide on mica and adsorption of water vapours on finely powdered quartz and anthronite (a calcium aluminium silicate).

Adsorption by Metals

The system gas + metals is complicated by the occurrence of solubility of the gas is metals or by forming surface chemical compounds. It is probable that in the absence of these complicating effects adsorption on metals in quite analogous to that on the adsorbents, where it form monomolecular layer. Gas-metal complicated by solubility are hydrogen adsorption on copper (above 400), iron (400 - 600), nickel (above 200), platinum (580 - 1340) tungsten (1500), solubility of oxygen in silver, nitrogen-iron. Metals like Pd, Pt, Ni, Cu are good adsorbent and are being used for contact catalysis. Role of finely divided iron on the manufacture of ammonia and that of finely divided Nickel in the hydrogenation of oils is well known.

Adsorption by Metal Oxides

Many oxides of metals such as NiO, ZnO, Cr_2O_3, MnO_2, CuO posses marked adsorbing properties as indeed is only to be expected from their porous nature. Often however, the straight forward adsorption is complicated by the simultaneous occurrence of other effects, notably termed 'activated adsorption'.

It is customary to divide adsorption into two broad classes, namely, physical adsorption and chemisorption. Physical adsorption equilibrium is very rapid in attainment and is reversible, the adsorbate being removable without change by lowering the pressure. It is supposed that this type of adsorption occurs as a result of the same type of relatively non-specific intermolecular forces that are responsible for condensation of a vapour to liquid. Heat of physical adsorption should be in the range of heats of condensation. It is important for gases below their critical temperature.

Chemisorption may be rapid or slow and may occur above or below the critical temperature of the adsorbate. Its chemical specificity is higher and that energy of adsorption is large enough to suggest that full bonding has occurred. Gas that is chemisorbed may be difficult to remove. For example oxygen adsorbed on charcoal at room temperature is held very strongly; on heating it comes off in the form of carbon monoxide.

Causes of Adsorption

(i) *Nature of Adsorbent and its State of Subdivision*: The absorption is a surface phenomenon. Hence extent of adsorption depends on the surface area of adsorbent. Active adsorbent have very high surface area hence the magnitude of adsorption increase. This is why finely divided metals like Pt, Ni and porous substances like charcoal, silica gel provide very high surface area and hence are very good adsorbents.

(ii) *Nature of Adsorbents*: The amount of gas adsorbed by solid adsorbent also depends on the nature of the gas. The gases which liquify more easily are adsorbed readily than those gases which do not liquify easily. The reason is that easily liquifiable gases have greater van der Waals forces of attraction and thus higher initial temperature.

(iii) *Effect of Temperature:* Adsorption is accompanied by evolution of heat an exothermic process hence according to Le Chatelier principle, the rate of adsorption should increase with decrease in temperature.

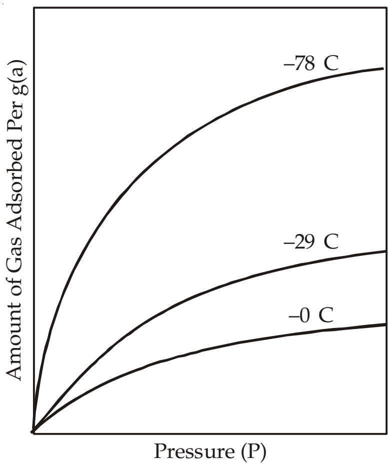


Fig. *Adsorption isotherms.*

(iv) *Effect of Pressure:* For a given gas and a given adsorbent, the magnitude of adsorption depends on the partial pressure of the gas. Adsorption of gas leads to decrease of pressure hence according to Le Chatelier principle magnitude of adsorption will increase with increase in pressure and *vice versa*.

The variation of adsorption with pressure at a given constant temperature is generally expressed graphically as shown in the figure given above. Each curve is known as adsorption isotherm for a particular temperature. The relation ship between the magnitude of adsorption and pressure can be expressed mathematically by a empirically equation commonly known as Freundlich adsorption isotherm, viz.

$$\frac{x}{m} = kp^n \qquad \text{...(6.1)}$$

where *x* is mass of gas absorbed on *m* grams of adsorbent at a pressure *p, k* and *n* are constants depending upon the nature of the gas and the nature of adsorbent. As the values of *n* is always less than one, hence *x/m* does not increase as rapidly as pressure.

Time of Adsorption

A useful approach to the phenomenon of adsorption is from the point of view of the adsorption time. Consider a molecule in the gas phase that is approaching the surface of the solid. If there were no attractive forces at all between the molecule and the solid, then the time of stay of the molecule in the vicinity of the surface would be of the order of a molecular vibration time/or about 10^{-13} sec which means that molecule retains its original energy. A "hot" molecule striking a cold surface should then rebound with its original energy and its reflection from the surface would be specular.

If however, there are some attractive forces present then the average time of stay τ of the molecule on the surface will be

$$\tau = \tau_0 \, e^{(E/RT)} \qquad \text{...(6.2)}$$

where τ_0 is about 10^{-12} to 10^{-13} sec and E is interaction energy, *i.e.,* the energy of adsorption. If τ is as large as several vibration periods, it becomes reasonable to consider that adsorption has occurred; temperature equilibrium between the molecule and the surface is approached and on desorption the molecule leaves the surface in a direction that is independence of that of its arrival.

In addition to E and τ, a quantity of interest is surface concentration Γ, where

$$\Gamma = Z\tau \qquad \text{...(6.3)}$$

Here if Z is expressed in moles of collision per square centimetre per second, then Γ is in moles per square centimetre. We assume the condensation coefficient to be unit, *i.e.,* that all the molecule that hit the surface stick to it. At very low E values, Γ as given by equation 6.3 is of the order expected just on the basis that the gas phase continues uniformly upto the surface so that surface concentration is essentially zero. This is the situation prevailing in the first two rows of the following table:

***Table**: The Absorption Spectrum*

[illegible]	[illegible]	Γ [illegible]	Comments
0.42	10^{-13}	0	Adsorption nil, specular reflection
6.3	10^{-12}	0	Region of physical adsorption
14.7	$4 \quad 10^{-11}$	0	
38.0	$4 \quad 10^{-7}$	10^{-}	
84	100		
168	10^{17}		Region of chemisorption

Above table summarises the spectrum of adsorption behaviour shows that with intermediate E values of the order of ten kilojoules, Γ rise to a level comparable to that of complete monolayer. Qualitatively, this intermediate region corresponds to the physical adsorption.

The third region is one for which the E values are of the order of chemical bond energies; the τ values become preposterously large. Such values are evidently meaningless and the difficulty lies in the assumption embodied in Eq. 6.3 that the collision frequency gives the number of molecules hitting and sticking to the surface.

As monolayer coverage is approached, it is to be expected that more and more impinging molecules will hit occupied areas and rebound without experiencing the full E value.

Concept of Langmuir

The following are the postulates on which Langmuir Theory is based:

1. Adsorbed gas behaves ideally in the vapour phase.
2. Only a monolayer is formed by the adsorbed gas. This implies that once surface sites are covered by gas molecules, no further adherence of gas molecules would occur.
3. The surface of the solid is homogenous so that each binding site has he same affinity for the gas molecules.
4. There is no lateral interactions between the adsorbent molecules.
5. The adsorbed gas molecules are localised, i.e., they do hot move around on the surface.
6. A dynamic equilibrium exists between the adsorbed molecules and the free molecules.

If G is the gas molecule and S is the surface site, then

$$\mathrm{G(g)} + \mathrm{S(surface)} \underset{K_b}{\overset{k_a}{\rightleftarrows}} \mathrm{GS}$$

where k_a and k_b are the rate constants for adsorption and desorption, respectively.

The surface is assumed to consists of a certain number of sites S of which S_1 are occupied and $S_0 = S - S_1$ are free. The rate of desorption is taken to be proportional to S_1 or equal to k_b S_1 and rate of condensation, proportional to the bare surface S_0 and to the gas pressure, or equal to $k_a p_G S_0$. At equilibrium

$$k_b S_1 = k_a p_G S_0 = k_a p_G\ (S - S1) \qquad ...(6.4)$$

Since S_1/S equals θ the fraction of surface covered. Eq. 6.4 can be written in the form

$$k_a p_G\ (1 - \theta) = k_b\ \theta$$

$$K p_G\ (1 - \theta) = \theta \qquad ...(6.5)$$

where $K = k_a/k_b$ Equation 6.5 may be written as

$$\frac{1-\theta}{\theta} = \frac{1}{kp_G}$$

or

$$\frac{1}{\theta} = \frac{1+kp_G}{kp_G}$$

$$\theta = \frac{kp_G}{1+kp_G} \qquad ...(6.6)$$

Alternatively θ can be replaced by v/v_m where v_m denotes the cc STP/g adsorbed at monolayer point. Thus

$$v = \frac{v_m\, kp_G}{1+kp_G} \qquad ...(6.6a)$$

For convenience in testing data equation (6.6a) may be put in linear form

$$\frac{p_G}{v} = \frac{1}{Kv_m} + \frac{P_G}{v_m} \qquad ...(6.7)$$

A plot of p_G/v *vs* p_G should give a straight line and the two constants v_m and K may be evaluated from the slope and intercept. Eq. 6.6 and 6.7 are called Langmuir Adsorption Isotherm as shown in the following figure:

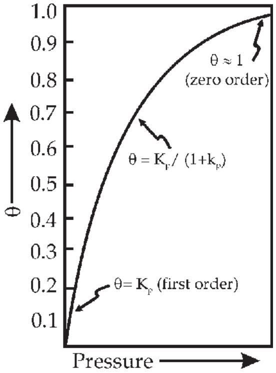


Fig. *The Langmuir plot. The kinetics of a gaseous reaction on solid surface.*

Limitation of Langmuir Adsorption Isotherm:

1. The first assumption holds at low pressure.
2. The second assumption breaks down when the pressure is increased.
3. The third assumption is not strictly true because the real surfaces are quite heterogeneous so that affinity for gas molecules is different at different sites. Crystal imperfections and cracks lead to the creation of different sites on the surface.
4. The fourth and fifth assumptions too are not strictly valid.

Consider equations 6.6 at low pressures $kp_G << 1$ so that

$$\theta = kp_G$$

i.e., the fraction of the surface covered is directly proportional to the partial pressure of the gas molecules. This behaviour corresponds to first order reaction and is depicted by the initial steep rise of the isotherm.

At high pressure $Kp_G >> 1$ so that Eq. 6.6 reduces to

$$\theta = 1$$

Thus at high pressures, the value of θ tends to become unity, *i.e.,* the entire surface gets covered by a monomolecular layer of the gas thereby making the reaction rate independence of the pressure. In other words the reaction becomes zero order.

Combining these results of Eq. 6.6 it is evident that according to this theory, the magnitude of adsorption at a given temperature should first increase in proportion to increase of pressure and finally tend to attain a certain limiting value.

The result can also be looked at in another way. Since at low pressures, adsorption is proportional to pressure

$$\theta = K(p_G)^1$$

and at high pressures

$$\theta = K = (p_G)^0$$

From equation 6.6 and figure it follows that at intermediate pressures the following expresses hold good

$$\theta = K\,(p_G)^n \qquad \text{....(6.8)}$$

where n lies between 0 and 1.

Since, according to Langmuir theory only a single layer of molecules is adsorbed on the surface of the adsorbent, the fraction θ gives a measure of the amount of the gas adsorbed per unit mass of the adsorbent, that is $\frac{x}{m} \alpha\ \theta$ or $\frac{x}{m} = k_1\theta$ where k_1 is another proportionality constant

$$\text{Thus } \frac{x}{m} = k_1\theta = k_1K\,(p_G)^n = kp_G{}^n \qquad \text{...(6.9)}$$

Equation 6.9 is the same as the Freundlich empirical equation 6.1. This agreement was taken as a proof for the theory of monomolecular adsorption advanced by Langmuir.

In turn v_m evaluated by Eq. 6.7 plot may be related to the surface area of the solid

$$v_m = \Sigma\, v_0/N\sigma_0 \qquad \text{...(6.10)}$$

where Σ denotes the specific surface area of solid, σ_0 is the area of a site and v_0 is just STP number, 22400 cc/mole. Thus if σ_0 can some how be evaluated Σ can be calculated from the experimental v_m.

The rate constants k_a and k_b may be related to the concepts of the preceding section as follow, first k_a is simply the reciprocal of the adsorption time, *i.e.,*

$$k_a = \frac{1}{\tau_0} e^{-E/RT} \qquad \text{...(6.11)}$$

In evaluated k_b, if a site can be regarded as a two dimensional potential box, then the rate of adsorption will be given by the rate of molecules impinging on the site area σ_0. Then from kinetic theory of gases

$$k_b = \frac{N\sigma_0}{(2\pi \mathrm{MRT})^{1/2}} \qquad \text{...(6.12)}$$

and the Langmuir constant K then becomes

$$K = N\sigma_0 \tau_0 e^{E/RT}/2(2\pi\ \mathrm{MRT})^{1/2} \qquad \text{...(6.13)}$$

It will be convenient to write K as

$$K = K_0 e^{E/RT} \quad K_0 = N\sigma_0 \tau_o/(2\pi\ \mathrm{MRT})^{1/2} \qquad \text{...(6.14)}$$

where K_o is now of the nature of a frequency factor.

Thus for nitrogen at its normal boiling point of 77 K, K_0 is 9.2 10^{-4}, with pressure in atmospheres, σ_0 taken to be 16.2 A^2 pressure (actually, this is the estimated molecular area of Nitrogen) and τ_0 as 10^{-12} sec.

The specific surface area can be obtained from Eq. 6.8 provided σ_0 is known. There is some ambiguity at this point. A widely used practice is to take σ_0 to be the molecular area of the adsorbate, estimated from liquid or solid densities. On the other hand, Langmuir models, is cast around the concept of adsorption sites, whose spacing one would suppose to be characteristic of adsorbent. However, to obtain site spacing requires much more knowledge about the surface structure than normally has been available, and actually the wide spread use of an adsorbate based value of σ_0 has mainly been faute demieux. No doubt other reinterpretations of σ_0 values will come.

The area of cross section σ_0 can be determined from the density of the liquified or solidified adsorbate. Thus if ρ is the density then volume occupied by a single molecule, assuming the adsorbate to be closely packed with void volume, is obtained as follows:

$$\rho = M_m/V = M_m/(N_A v) \qquad \text{...(6.15)}$$

$$v = M_m (NA\ \rho) \qquad \text{...(6.16)}$$

Assuming the molecule to be spherical with radius *r*, we have

$$v = \frac{4}{3}\pi r^3 = M_m(N_A\rho)$$

$$r = \left[\frac{3M_m}{4\pi N_A \rho}\right]^{1/3} \qquad \text{...(6.17)}$$

Hence $$\sigma_0 = \pi r^2 = \pi \left[\frac{3M_m}{4\pi N_A \rho} \right]^{2/3} \qquad ...(6.18)$$

Eq. 6.18 is only approximate for calculating the area of cross-section of a molecule for it does not take into account the nature of packing at the surface of the adsorbent. Also the presence of void volumes in the crystal lattice has been ignored. The areas of cross section of some common molecules are given in the following table:

Table: *Cross-section area of some common molecules*

Adsorbate	*Temperature*	*Liquid density* $\rho/g\,cm^{-3}$	$\sigma_o(nm^2)$
Ar	–18.3	1.374	0.144
N_2	–195.8	0.808	0.162
O_2	–183	1.140	0.141
CO	–183	0.763	0.168
CO_2	–56.6	1.179	0.170
CH_4	–140	0.392	0.181
NH_3	–36	0.688	0.129

Some kinds of Adsorption

A large number of adsorption isotherms of gases on a variety of adsorbents at different temperatures have now been determined, but by no means all adsorption isotherms are of Langmuir type in shape. It has been possible to divide them broadly into five different types as shown in the following figure. In each case, p_0 represent the saturation pressure of the gas.

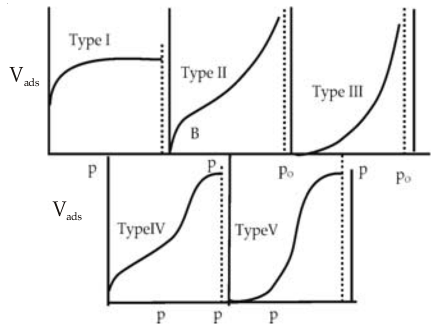


Fig. *Brunauer's five types of adsorption isotherms*

Type I*:* Correspond to monomolecular adsorption postulated by Langmuir. The volume of the gas adsorbed approaches a limiting value, just enough to complete a mono molecular layer even when the gas pressure is rather low. Further increase in pressure hardly produce any further rise in the amount of adsorption. The examples are furnished by adsorption of nitrogen or hydrogen on charcoal at temperatures close to –180 C.

Type II and III: Shows large deviation from Langmuir model. The model of adsorption keeps on rising in each case with increase in pressure.

This is attributed to the formation of additional layers of physically adsorbed gas molecules. It is postulated that gas molecules adsorbed in the first layer may hold by van der Waals forces a second layer of gas molecules which, in turn may hold a third layer and so on.

The type II is very common in the case of physical adsorption and undoubtedly corresponds to multilayer formation. For many years it was the practice to take point B at the knee of the curve, as the point of completion of mono layer consistent with those found using adsorbate that give type I isotherms.

Type III is relatively rare—a recent example of nitrogen on ice and seems to be characterised by a heat of adsorption equal to or less than heat of liquifaction of the adsorbate. The example of Type II isotherms are furnished by adsorption of nitrogen on an iron or a platinum catalyst at –195 C and those Type III by adsorption of bromine on silica or alumina gas at 80 C.

Types IV and V: They are considered to reflect capillary condensation phenomena, *i.e.,* possibility of condensation of gases in minute pores of the adsorbent at pressures even below the saturation pressures of p_0 of the gas and may show hysteresis effect. An example of type IV is furnished by adsorption of benzene on silica gel at 50 C and that of type V by adsorption of water vapour on activated charcoal at 100 C.

It may again be noted that in the case of adsorption isotherm of type IV and V there is formation of multimolecular adsorbed layer of the gas molecules within the narrow capillary pores of the adsorbent also. This latter phenomenon is known as capillary condensation of the gas.

Adsorption and BET Theory

The Langmuir theory of adsorption is restricted to the formation of a monomolecular layer of the gas molecules on the solid surface and disregards the possibility of multi layer adsorption may also take place. The theory of adsorption proposed in 1983 by Brunauer, Emmett and Teller (known as the BET theory after the initials of these scientists) assumes that physical adsorption resulting in the formation of multilayers is the true pictures of adsorption. In the BET theory, it is assumed that the solid surface possess uniform, localised sites and that adsorption at one site does not affect adsorption at neighbouring sites as was assumed in Langmuir theory it is further assumed that molecules can be adsorbed in second, third,.... and nth layers, the surface area available for the nth layer being equal to the coverage of the $(n - 1)$th layer. The energy of adsorption in the first layer, E_1 is assume to be constant and energy of adsorption in succeeding layer, is assumed to be the same as E_1, the energy of liquifaction of the gas. Based on the above assumption Brunauer, Emmett and Teller derived the following equation known after them as BET equation.

$$\frac{p}{v_T \cdot (p_0 - p)} = \frac{1}{v_m C} + \frac{c-1}{v_m C}(p/p_0) \qquad ...(6.19)$$

Which may be written as

$$\frac{x}{v_T(1-x)} = \frac{1}{v_m C} + (c-1)\, x / c v_m \qquad ...(6.20)$$

where $x = p/p_0$, v_T is total volume of gas adsorbed at the pressure p, v_m is the volume adsorbed when the surface of the solid is covered completely with a monolayer of the adsorbed molecules of the gas, c is a constant depending upon the nature of the gas. Its numerical value is given approximately by the expression $c = \exp(E_1 - E_L)/RT$ in which E_1 is heat of adsorption of first layer and E_L is heat of liquefaction of the gas.

v_m and c can be obtained from the slope and intercept the straight line best fitting the plot of $x/v_T(1 - x)$ vs x. The specific surface area can then be obtained through Eq. 6.10.

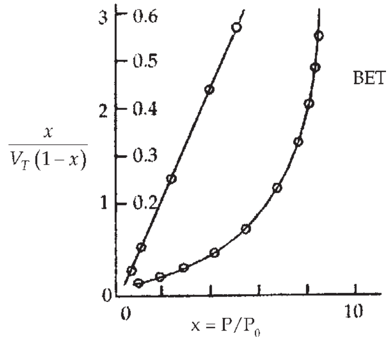


Fig. *Adsorption of nitrogen on potassium chloride at 79 K, plotted according BET equation.*

From experimental point of view, BET equation is easy to apply and the surface area so obtained are reasonably consistent. The equation in fact has become the standard one for practical surface area determinations usually with nitrogen at *77 K* as the adsorbate but in general with any system giving type II isotherms.

On the other hand, the region of fit usually is not vary great the linear region of a plot according Eq. 6.20 typically lies between p/p_0 of 0.05 and 0.3 as illustrated in the figure given above. The typical deviation is such that best fitting BET equation predicts too little adsorption at too low pressures and too much at high pressures.

The BET equation also seems to cover three of the five isotherms types of described in the figure above. Thus for *c* layer, *i.e.* $E_1 >> E_L$ it reduces to Langmuir equation and for small *c* values type III isotherm result/while for larger values of *c* it follows Type II. However, adsorption of relatively inert gases such as nitrogen argon, etc. on polar surfaces generally gives *c* value around 100 corresponding to type II isotherm. For such systems the approximate form of equation is

$$v_T/v_m = 1/1 - x \qquad ...(6.21)$$

works quite well in the usual region of fit of the BET equation.

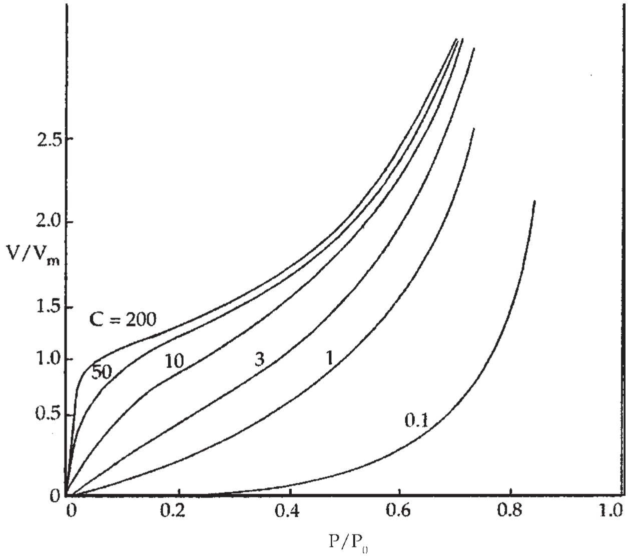


Fig. *For small* c *values type III BET isotherms.*

Non-electrolytes and Adsorption

The adsorption of non-electrolytes at the solid-solution interface may be viewed in terms of two somewhat difference physical pictures. The first is that the adsorption is essentially confirmed to a monolayer next to the surface, with the implication that succeeding layers are virtually normal bulk solution. The picture is similar to that for the chemisorption of gases and similarly carries with it assumption that solute solid interactions decay very rapidly with distance unlike the chemisorption of gases, however, the heat of adsorption from solution is usually fairly small and is more comparable with heats of solution than with chemical bond energies.

The second picture is that of an interfacial layer or region, multimolecular in depth (perhaps even 10 nm deep), over which a more slowly decaying interaction potential with the solid is present. The situation would be the more like that in the physical adsorption of vaporous which become multilayer near the saturation vapour pressure. Adsorption from solution, from this point of view, correspond to a partition between a bulk and an interfacial phase. While both models find some experimental support the monolayer one has been much more amenable to simple analysis and Langmuir adsorption equation holds good where pressure is replaced by concentration term Langmuir model assumes the surface to consists of adsorption sites, the area per site being σ_0, all adsorbed species interact only with a site and not with each other and adsorption is thus limited to a monolayer. In the case of adsorption from solution, however, it seems more plausible to consider an alternative phrasing of the model. Adsorption is still limited to a monolayer, but this layer is now regarded as an ideal two dimensional solution of equal size solute and solvent molecules of area σ_0. Thus, lateral interactions, absent in the site picture, cancel out in the ideal solution layer picture because of being independent of composition. However, in the first version, σ_0 is a property of the solid lattice, while in the second, it is properly of the adsorbed species; both versions attribute differences in adsorption behaviour entirely to differences in absorbate-solid interaction. Both present adsorption as a competition between solute and solvent and both version lead to same algebraic formulation

$$\theta = \mathrm{Kc}/l + \mathrm{Kc} \qquad \text{...(6.22)}$$

where c = concentration of solute, $\theta = S_1/S = n_2^s/n^s$ fraction of surface occupied n_S is the number of moles of adsorption sites per gram

Also

$$n^s = \Sigma\ /N\sigma^0 \qquad \text{...(6.23)}$$

where Σ denotes the surface area per gram. At low concentration n_2^S will be proportional to c with a slope n_SK. At sufficient high concentration n_2^S approaches the limiting value n^s. Thus, n^s is a measure of the capacity of the adsorbent and K, of the intensity of adsorption. In terms of ideal model, n^s should not depend on temperature, while K should show an exponential dependence.

For most surfaces are heterogeneous so that K in Eq. 6.22 will vary with θ and may be attributed entirely to the variation in the heat of adsorption. Which taken into account reduces to Freundlich adsorption isotherm

$$\frac{x}{m} = Kc^n \qquad \text{...(6.24)}$$

The Freundlich equation, unlike the Langmuir one, does not become linear at low concentration but remains concave to the concentration axis, nor does it show a saturation or limiting value. Roughly speaking kn^s gives a measure of the adsorbent capacity and slope n, of intensity of adsorption. The shape of isotherm is such that n is less than unity.

There is no assurance that above conclusions of the Freundlich equation is unique; consequently, if data fit the equation it is only likely but not proven, that surface is heterogeneous. Basically the equation is an empirical one, limited in its usefulness to its ability to fit data.

Chromatography of Adsorption

It has been found that closely related substances with almost similar physical and chemical properties which cannot be separated from one another by ordinary means, are adsorbed to different extents on the surface of adsorbents. This facilitates their separation and purification. If a solution containing different solutes is poured down a column filled with a finely divided adsorbent, the solute most readily absorbed is retained on the top layer along with smaller amounts of the other constituent; while the less readily adsorbed constituents are held on lower portions of the column. A partial separation of the constituents of the mixture is thus easily achieved. A fuller separation is possible by repeating and modifying the process.

This process of separation, also known as *column chromatography*, was first developed in 1900 by Day, an American petroleum chemist. However, a more extensive study was made in 1906 by Tswett, a Polish botanist. He observed that when a solution of plant pigments in petroleum ether is passed slowly through a column packed with alumina, a number of horizontal bands of different colours are produced in the column. This is, evidently, due to the fact that different constituents of the mixture are adsorbed to different extents. The most readily adsorbed constituent is held at the top. The others with decreasing order of adsorbabilities are held up in different zones down the column in the same order. This, of course, gives only a partial separation of the various constituents as some of the less readily adsorbed constituents are still present mixed up with the more readily adsorbed constituents and so on. The initial separation of the various coloured constituents can be improved by passing either the original or some other suitable solvent slowly through the column. The solvent used is called eluent.

The various coloured zones then become more sharply defined. Therefore, the name *chromatography*, which implies colour, was given to this technique. The banded column of the adsorbed constituents is called a chromatogram. The process of improving the separation by passing the original solvent or some other suitable solvent, is known as *development of the chromatogram*. The process of separation of a mixture of two components A and B is represented in the following figure.

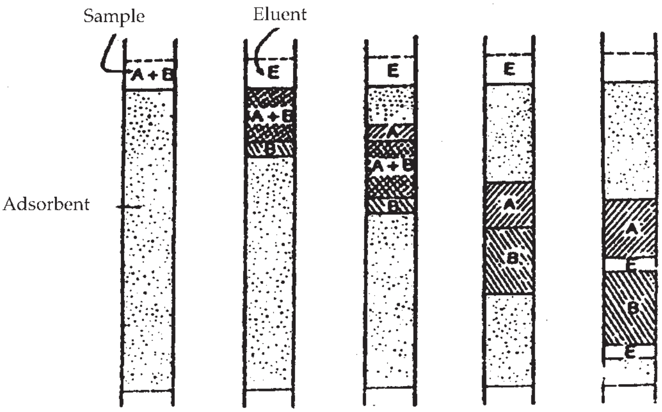


Fig. *Elution development of two solutes A and B. A is more strongly adsorbed than B. E is the eluent.*

In order to separate or to estimate the various constituents, the chromatogram, after development, is pushed out of the glass tube and the various zones are cut with a knife at the boundaries. The coloured components are dissolved separately in suitable solvents. This process of recovery of constituents from the chromatogram is known as *elution*. Since 1930 column chromatography has been used extensively in the separation and purification of plant pigments and other natural products. It is now frequently used in a number of laboratory processes for purification of several other compounds as well. The substance to be purified need not be necessarily coloured. However, a coloured substance is generally adsorbed more readily than a colourless one. If a substance, for example, contains a coloured impurity which cannot be removed even on treatment with active carbon, the same is readily got rid off on passing the substance through a chromatographic column.

As already mentioned, when a solution containing various constituents is passed through an adsorbent column, the separation is only partial. The separation is improved in several ways (development of chromatogram). The usual procedure is to allow some of the pure solvent to flow slowly through the column. The comparatively less readily adsorbed solutes which are retained in the upper parts pass into solution and are readsorbed in lower parts of the column. By repeating the process, we get, ultimately, a number of distinct bands (or layers) containing individual solutes in the order of decreasing ease of adsorption, down the column.

The compounds to be separated from one another in chromatography need not always be coloured. Colourless substances can also be separated by this technique. Advantage, in some cases, is taken of the fact that certain colourless compounds show a bright fluorescence when exposed to ultraviolet light. The position of such a substance in the column can thus be followed with the help of a mercury vapour lamp.

However, there are very few substances which show fluorescence in ultraviolet light. Therefore, other methods have to be used. These are based, generally, on the use of a chemical reagent which gives coloured product on reacting with the colourless compound in question. For example, the colourless carbonyl compounds are converted into their 2:4 dinitrophenyl hydrazones which are coloured. Similarly, hydrocarbons are identified through the formation of their coloured picrates and alcohols through their coloured 3:5 dinitrobenzoates.

Adsorption chromatography finds application in many processes, more important of which are:

1. Quantitative separation of two or more components of a mixture.
2. Purification of substances from their contaminants.
3. Concentration of solutes from dilute solutions.
4. Identification of technical products.

The apparatus essentially consists of a long narrow glass tube about 20-30 cm long and 2-3 cm in diameter. This can hold 60-70 g of absorbent. The absorbent column is supported on a plug of glass wool. If the tube is wider, a perforated disc covered by a pad of cotton is often used. The tube is provided with a tap at the bottom. The removal of the column from the tube is a simple process.

Al_2O_3 activated by heating to about 200 C in a current of air or carbon dioxide, is the most, widely used absorbent. Other adsorbents used are: silica gel (activated in the same manner as alumina), magnesium oxide, magnesium carbonate, calcium carbonate, calcium sulphate, barium carbonate, charocal, sucrose, talc, starch, cellulose and Fuller's earth. The inorganic adsorbents are usually heated to 200-220 C before use.

The glass wool or cotton plug which serves as a support for the column is placed first in position in the tube. The tube is then clamped vertically. It is important that the tube is packed uniformly with the adsorbent. For this purpose the adsorbent is added in portions. Each portion when added is pressed from above with a flattened glass rod before adding the next portion. This is continued till nearly two-thirds of it is filled.

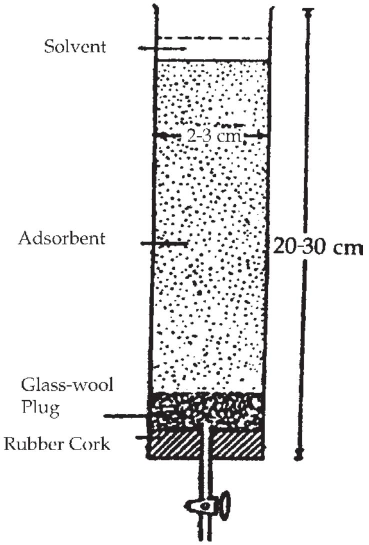


Fig. *Apparatus for Column Chromatography*

An alternative method is to prepare slurry of adsorbent in a suitable liquid medium. The liquid used is petroleum ether or sometimes the same as the solvent to be used in the chromatographic process. The slurry is poured into the tube gradually, a little at a time. It is better to connect the tube to a suction pump through the stopcock. Suction is applied after each addition. This is continued till a column of the desired height is obtained. The surface of the column should remain covered with petroleum ether all along.

The selection of solvent depends, in the first place, on its dissolving power. Subject to this primary requirement, the solvent should have boiling point between 60 and 85 C. For most purposes, petroleum ether boiling around 80 C is used. Other suitable solvents are: benzene, cyclohexane, chloroform, carbon tetrachloride, carbon disulphide, ethyl alcohol, acetic acid and ethyl acetate.

The solvents used in chromatography have three functions to perform:

1. *They dissolve the mixture of various constituents and introduce them into the column.* The solvents used for this purpose are generally non-polar (such as benzene and petroleum ether) since adsorption takes place more readily from such solvents.
2. They are passed into the column *for the development of the chromatogram.* In this process, the various zones of the chromatogram get separated sharply from one another.

   The solvents when used for this purpose are termed as developers. The developer is generally a solvent in which the components of a mixture are not highly soluble. It is usually a liquid of low molar mass. Attempt is often made to use the same solvent which is used for introducing the mixture, as a developer. But it is not always possible. Hence, other suitable solvents are used quite often.
3. They are also used *for removing the various constituents of a mixture from the chromatogram after it is properly developed.* The solvents used for this purpose are called *eluents*. A good eluent must be a liquid which can dissolve readily the various components. It must also get adsorbed itself to some extent. This helps in displacing the components from the column.

> Further, the eluent should be a low boiling liquid so that it can easily be removed from the recovered component. Sometimes it is desirable to use two eluents one after the other. If one eluent can desorb only a portion of an adsorbate, the second, a more powerful eluent, may be used to desorb the remaining portion of the adsorbate. Thus, if benzene is used as the first eluent, ether may be used at the second eluent or if ether is used as the first eluent, acetone may be used as the second eluent and so on.

The top of the column is covered by a plug of cotton wool. Some pure solvent is poured over it through a funnel. The rate of flow of the solvent through the column should be controlled under slight suction. It should be within 4–10 ml per minute. The solution is then added into the column and it is made to percolate at the same rate as the pure solvent before.

It is important to see that the top of the column remains covered by the solution throughout the operation. If this precaution is not taken, the column may dry up quietly and shrink. Too much suction should be avoided to prevent evaporation. After the entire portion of the solution has passed through, the developing liquid is led into the column slowly in a similar manner. After this liquid has also passed through and the various zones become well-defined, the system is allowed to dry in air.

The adsorbent is then pushed out of the tube with the help of a wooden pestle and the zones are cut by a knife. Each one is then dropped immediately into the eluent and the suspension is filtered on a sintered glass funnel to get rid of the adsorbent.

In some cases, it is not necessary to push out the adsorbent from the tube. A single solvent (eluent) or a succession of solvents having increasing eluent-actions are passed through the developed chromatogram. The various portions of the column are thus washed out one by one and collected in different receivers. If the separation is not complete, the extracts are passed again through the adsorbent column.

7

Photochemistry

Photochemistry concerns itself with the study of the effect of visible and near ultraviolet radiation on chemical reactions, the rates and mechanisms by which reactions initiated by light proceed.

Ordinary or thermal reactions are initiated by activation brought about through molecular collisions. It is characteristics of all such reactions that they can occur only when the reactions are accompanied by a free energy decrease. If a free energy increase is involved, no reaction is possible. However, thermal activation is not the only means by which the energy of atoms and molecules can be raised sufficiently to cause reaction. We have seen that atoms and molecules can absorb radiation. In fact, with the absorption of a sufficiently large quantum of radiant energy a molecule may be ruptured. Such absorption of light by an atom or molecule leads to its excitation; and if the activation is sufficiently great, chemical reaction may result. It is in this manner that absorbed light can affect the rate of a chemical reaction and frequently bring about chemical changes under conditions where thermal activation alone would not be effective.

The rate of thermal uncatalysed reactions at any fixed concentration can be varied only by change of temperature. With photochemical reactions, however, the rate can be controlled also by varying the intensity of the light used for irradiation. In the latter reactions the number of molecules activated, depends on intensity of the light and hence the concentration of activated molecules will be proportional to the light intensity to which the reactant is exposed. With sufficiently intense light sources it is thus possible to attain reactions at ordinary temperatures, which would not result thermally except at considerably elevated temperatures.

Again, since photochemical activation does not depend to any degree on temperature, the rate of activation is usually temperature independent. Any increase in the rate of a photochemical reaction with temperature is due to primarily to thermal reactions, which follow the activation process.

Further, not only spontaneous reactions can be made to proceed photochemical, but also many reactions attended by a free energy increase. In the spontaneous reactions the light acts to speed up the thermal reactions, on the other hand, the radiant energy supplied to the system may increase the free energy of the reactants sufficiently to make the ΔG negative.

An outstanding example of such a process is photosynthesis. Under the action of sun light and promoted by chlorophyll, carbon dioxide and water are combined in plants into complex carbohydrate and oxygen. On removal of the light products oxidise slowly back to carbon dioxide and water, releasing at the same time the energy accumulated from the sun's radiation.

Law of Beer-Lamberts

Beer-Lambert's Laws give the variation of intensity of light absorbed by molecules at a particular wavelength

$$\text{Absorbance} = A = \log I_o/I = \varepsilon c l \qquad ...(7.1)$$

where I_o = intensity of light of wavelength X incident on the front of a column of length *l* in cm of a single absorbing species of concentration c in moles per litre, I is intensity of the light transmitted through the column of material, ε is called molar extinction coefficient in *l* mole^{-1}. It is constant for a given species at wavelength; λ, log $1_o/I$ is called the absorbance (or molar absorbance) to the base 10. Equation (7.1) can also be written in terms of the natural logarithms.

$$\text{In } I_o/I = \alpha cl \qquad ...(7.2)$$

where $\alpha = 2.303\varepsilon$. Unfortunately, in literature the symbol ε and α often appear without specifying that they are to the base 10 or ε. The fraction of light absorbed I_a/I_o is given by

$$\frac{I_a}{I}=1-\frac{I}{I_0}=1-10^{-\varepsilon cl} \qquad ...(7.3)$$

which hold good for all concentrations. At low concentrations of absorber the fraction is directly proportional to concentrations of absorbing species since $e^y = 1 - y$, *i.e.,*

$$\frac{I_a}{I} = 1-10^{-\varepsilon cl} = 1-\exp(-2.303\,\varepsilon \mathrm{cl})$$

$$\approx 2.303 \qquad ...(7.4)$$

This relationships cannot hold at higher concentrations when it approaches *l*, indicating that at high concentrations all of the light is absorbed independent of absorber concentrations.

The most common units used in gas phase photochemistry for concentration are number of molecules cm^{-3} symbolised by N with natural logarithms. The gas phase absorption coefficient designated, σ, is then in units of cm^2 $molecule^{-1}$, σ is also known as absorption cross-section. The Beer-Lambert law becomes

$$\text{In } I_o/I = \sigma N l \qquad ...(7.5)$$

A second widely used set of unit for gaseous species is concentrations as pressure, in atmosphere, so that

$$\text{In } I_o/I = kpl \qquad ...(7.6)$$

Since pressure depends upon temperature, a reference temperature 270 or 298 K must be specified.

For a mixture of absorbing molecules, where each molecule has an extinction coefficient ε at concentration c_i $(i = 1, 2..)$ the Beer Lambert Law becomes

$$\frac{I}{I_o} = 10^{-(\varepsilon_1 c_1+\varepsilon_2 c_2+\varepsilon_3 c_3 .....)l} \qquad ...(7.7)$$

Example: A substance was dissolved in water at 10^{-3} M concentration absorbs 10 per cent of an incident radiation in a path of 1 cm length. What should be the concentration of the solution in order to absorb 90 per cent of the same radiation?

Solution: $A = \log I_o/I = \varepsilon bc$

In the first case

$A = 10\%$ so that $T = I/I_o = 90\%$

$b = 1$ cm $c_1 = 10^{-3}$ mol dm^{-3}

$\log 100/90 = \varepsilon bc_1$ ....(*i*)

In the second case

$A = 90\%$ so that $T = I/I_o$ - 10% $b = 1$ cm

$\log 100/10 = \varepsilon bc_2$ ...(*ii*)

From eqn (*i*) and (*ii*)

$$\frac{\log 100/90}{\log 10} = \frac{c_1}{c_2} = \frac{0.001}{c_2} \text{mol dm}^{-3}$$

$$= c_2\, 0.218 \text{ mol dm}^{-3}$$

Example: In a Beer-Lambert law cell, the aqueous solution of a substance of known concentration absorbs 10 per cent of the incident light. What fraction of the incident light will be absorbed by the same solution in a cell five times as long?

Solution:

In the first case $A_1 = \log (I_0/I)_1 = \varepsilon b_1 c$

In the second case $A_2 = \log (I_o/I)_2 = \varepsilon (5 b_1)c$

$A_2/A_1 = 5$

or $A_2 = 5 A_1 = 5 \log I_o/I = 5 \log (100/90)$

$= 5 (2.00 - 1.9542) = 0.2290$

i.e., $\log (I_o/I)_2 = 0.2290$

Taking antilogs $(I_o/I)_2 = 1.694$

$$T = (I/I_o)_2 = \frac{1}{1.694} = 0.59$$

Hence, fraction of light absorbed = 1 – 0.59 = 0.41

Photochemistry Rules

Grottus Draper Law

The first law of photochemistry, called the Grottus Draper law, states: Only the light, which is absorbed by a molecule, can be effective in producing photochemical changes in the molecule.

When light falls over a system one of the following three changes may happen.

1. The system is perfectly transparent to light of wavelength λ, means this light does not interact with molecules and cannot lead to a photochemical reaction.
2. The system is translucent to the light of wavelength λ, means this light cannot pass through the medium, rather it is scattered thus interaction between light and molecules is quite week so photochemical reactions may not be possible.
3. The system absorbs the light of wavelength λ, means this light interacts with molecules and thus a photochemical reaction may take place. Therefore, to assess the potential for photochemically induced changes, it is essential to know the absorption spectra of reactants. In order in fully characterise the reaction mechanism, one must also know the absorption spectra of the intermediate reaction products.

Stark-Einstein Law

A second important law of photochemistry, known as the Stark-Einstein Law, follows directly from the particle behaviour of electromagnetic radiations.

"Absorption of radiation is a one photon process. Absorption of one photon excites one atom or molecule in primary (initiating) step and all subsequent physical and chemical reactions follow from this excited species

i.e., $$\in = h\upsilon = \frac{hc}{\lambda}$$

when $h\upsilon$ is a quantum of light called photon and h is Planck's constant 6.62 10^{-34} Js. Since chemists generally deal experimentally with moles of material, a convenient unit is a mole of photons defined as 1 Einstein. The energy of Einstein of wavelength λ in nm is

$$E = 6.02 \quad 10^{23}\ h\upsilon = \frac{1.196 \times 10^{6}}{\lambda} \text{ kJ einstein}$$

If λ is in angstrom $$E = \frac{1.196 \times 10^{6}}{\lambda} \text{ kJ einstein}$$

Another unit used in photochemistry to express the energy is electron volt; 1eV = 96.46 kJ mole^{-1} and λ nm thus

$$E = \frac{1.24 \times 10^3}{\lambda} \text{eV}$$

Since absorption of photon of wavelength λ leads to dissociation, the bond dissociation energy may correspond to absorption peaks. Consider NO molecule, which show absorption peak at 191 nm, and has bond dissociation energy of 6.496 eV. This corresponds to a wavelength λ, *i.e.*

$$6.496 = \frac{1.24 \times 10^3}{\lambda} \qquad \text{or} \qquad \lambda = 191 \text{ nm}$$

Thus absorption of one photon of light of wavelength 191 nm by one molecule of nitric oxide will give it sufficient energy to dissociate. In other words NO molecule will be photochemically active to light of wavelength 191 nm.

Light Absorption: Some Effects

Absorption of radiation energy may lead to dissociation of the absorbing molecule. In fact, in most of photochemical reactions involving molecules, the primary step is usually dissociation of some molecules into atoms, simple molecules or free radicals, which by further interaction either with each other or with different molecules continue the reaction sequence. The primary photochemical stage is dissociation. The secondary reaction proceeds by thermal means.

Consider oxygen molecule, which show absorption, known as Herzberg continuum or Schumann Range lies in the range 147-130 nm. With the absorption of radiation of this wavelength, oxygen molecule dissociates to give oxygen atoms. Thus the primary photochemical reaction is

$$O_2 \xrightarrow{h\nu} O + O$$

These oxygen atoms so formed, react with other molecules to give products through thermal reactions. These are secondary effect

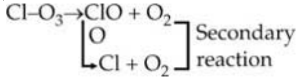
$$O_2 + O \longrightarrow O_3 \text{(secondary effect)}$$

Since UV radiation of wavelength 147-130 nm is absent in sunlight available on the earth's surface, hence no formation of ozone takes place. However, at a height of 32 km, this UV radiation is available that lead to formation of ozone. The ozone molecules so formed absorbs this UV radiation and thus is not available on the surface of earth.

Another example is that of chlorofluorocarbons (CFC). All chlorofluorocarbons show absorption in the range 160-280 nm. This UV radiation is available near ozone layer of earth atmosphere. Light spectrum available on the surface of earth is perfectly transparent to chlorofluorocarbons and thus behaves as photochemically inert. These do not dissolve in water and thus are not removed by rain. Slowly these molecules rise and reach the ozone layer. Their photons of 160-280 nm are available absorption of which lead to primary photochemical reaction

$$\mathrm{CFC-Cl} \xrightarrow{h\nu} \mathrm{CFC+Cl}$$

This chlorine atom reacts with ozone molecule as follow:



The net reaction $O_3 + O \xrightarrow{Cl} 2O_2$

one atom of chlorine decomposes 10,000 ozone molecules that lead to ozone hole formation. Why in CFC, chlorine is removed and not fluorine. The C-Cl bond length = 18 nm. C-F bond length= 12-14 nm. Larger the bond length lesser is dissociation energy. Since C-Cl bond energy is less than C-F bond energy thus C-Cl bond breaks.

The atmosphere becomes thinner and colder with increasing altitudes for the first nine to sixteen km above ground. Almost all of the water vapours are removed at lower attitudes. The gases undergo rapid vertical mixing and are periodically cleaned by rains including removal of all oxides of nitrogen. However, as a result of denitrification of chemical fertilizers a small amount of N_2O formation takes place. N_2O molecule is not a very reactive molecule, neither it is removed from atmosphere by rains. Hence it can survive unchanged in the atmosphere for decades till it reaches near ozone layer.

N_2O is a linear asymmetrical molecule. It shows absorption starting at 306 run with flat maxima near 290 nm. It is followed by second and third continuum in 280-260 nm. The photons of this wavelength are available near ozone layer and thus N_2O become photochemically active. Absorption of photons of this wavelength triggers the primary photochemical process

$$N_2O \xrightarrow{h\nu} N_2 + O \qquad (95\%)$$

$$\longrightarrow NO + N \qquad (5\%)$$

Primary photochemical reactions converts most of N_2O to Nitrogen but about 5 per cent becomes NO. These NO molecules so formed attacks the ozone molecule very efficiently to produce molecular oxygen and NO_2 which then reacts with atomic oxygen to form NO again, *i.e.*

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO_2 + O \longrightarrow NO + O_2 \text{ Secondary reaction}$$

Both reactions have occurred but NO molecule is still there. This cycle continue till NO molecule is removed photochemically by a photon of wavelength 191 nm.

Another interesting molecule is NO_2. Ignition of petrol to run vehicles also produces NO_2 as pollutant. Presence of even a small amount of NO_2 in atmosphere is sufficient to trigger the complex series of reactions to produce photochemical smog through the visible light in the wavelength 300-420 nm. NO_2 is a light brown gas and the primary photochemical reaction that takes place is

$$NO_2 \xrightarrow[\lambda<420\,nm]{h\nu} NO + O$$

The oxygen atom so formed reacts with oxygen molecule

$$O + O_2 \longrightarrow O_3 \text{ Secondary Reaction}$$

Rate of formation of ozone is widely used as a measure of smog formation. A fraction of the NO emitted in the air parcel reacts with ozone to regenerate NO_2

$$O_3 + NO \longrightarrow NO_2 + O_2$$

As a consequence of photochemical reaction peak value of ozone is reached in the early afternoon. As ozone is a very reactive molecule, it reacts with many other pollutants producing a variety of eye and throat irritants, aerosols. These molecules reduce visibility by producing smog and other irritating or destructive molecules. Pollution of atmosphere with NO_2 has now spread to all metropolitan cities like Delhi and Mumbai. However, if near the exhaust of vehicles, if catalytic converter is fixed NO_2 gets reduced to nitrogen and oxygen and thus removed from the exhaust gases.

Until now we had been talking of gas reactions. Many substances undergo photochemical reactions in liquid state. Again the reaction in initiated by Stark-Einstein law by direct light absorption on the part of reactants. However, it may be anticipated that quantum efficiency of these reactions will be less than for the same reaction in the gas phase. The reason for this is that in the liquid state an active molecule may readily be deactivated by frequent collisions with other molecules. Furthermore, because of the very short mean free path in the liquid phase free radicals or atoms when formed photochemically will tend to recombine before they have a chance to get very far from each other. The net effect of these processes will be to keep the quantum yield relatively low. In fact, only those reactions may be expected to proceed to any extent for which the primary products of the photochemical act are relatively stable particles. Otherwise the active intermediates will tend to recombine with the solvent and thereby keep the yield low.

Significance of Quantum Efficiency

The photochemical equivalence law applies only to the absorption of primary photochemical process. As a result of the primary absorption only one molecule decomposes, and the products enter no further reaction, the number of molecules reacting will be equal to the number of photons absorbed. More frequently, however, a molecule-activated photochemically initiates a sequence of thermal reactions as a result of which several or many reactant molecules may undergo chemical change. Under such conditions there will be no reaction between reacting molecules and the number of energy quanta absorbed. To express the relation between the number of molecules entering reaction and the number of quanta absorbed, the quantum yield or efficiency of a process ϕ is introduced. Quantum yield, ϕ is

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

$$= \frac{\text{Number of molecules reacting in a given time}}{\text{Number of Einstein's of light absorbed in the same}}$$

This gives the number of molecules observed to undergo chemical transformation per quantum of absorbed energy. The quantum efficiency of a reaction may vary from almost zero to about 10^6. Nevertheless, no matter how large or small ϕ may be, the Einstein equivalence law holds good.

Testing of Photochemical Reaction

To measure, the rate of a photochemical reaction it is necessary to irradiate a reaction mixture with light of a selected wavelength and to observe the manner in which the concentration of reactants or products varies with time. For this purpose some arrangement such as that shown in the following figure is required. In this diagram A is a light source emitting radiation of suitable intensity in the desired spectral range.

To select radiation of only a single wavelength or to confine the radiation to a narrow band, the light is passed through the lens B into a monochromator or filter at C. From C the light enters the cell D immersed in a thermostat and containing the reaction mixture. Finally, the light transmitted through D falls on some suitable recorder E, where its intensity is determined.

The light sources used depend on the spectral range in which radiation is desired and include filament lamps, carbon and metal arcs, and various gas discharge tubes. The reaction cells may be glass or quartz vessels usually with optically plane windows for entrance and exit of light. In some instances, metal cells have been used with windows cemented to the ends. Glass can be used only in the visible spectral range. Below 350 nm not only the cells but also any other optical part through which the light passes must be of quartz. With gases no provision need be made for stirring; solutions, however, must be agitated.

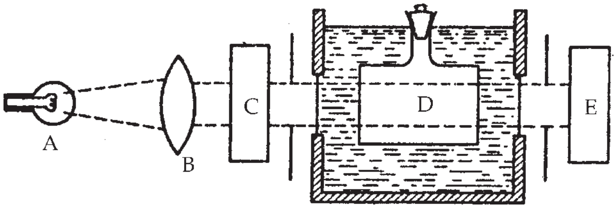


Fig. *Apparatus for study of photochemical reactions (schematic)*

The radiant energy is measured with some form of thermopile or actinometer. The thermopile is essentially a multi junction thermocouple consisting usually of silver and bismuth soldered to metal strips blackened with lamp, platinum or bismuth black. The radiation falling on the blackened strips is absorbed almost completely and non-selective, and is converted into heat. The heat thus generated raises the temperature of the hot junctions above the cold, and the current generated thereby is measured. The current produced is proportional to the energy absorbed and this, in turn, depends on the intensity of the incident light and the area exposed to it. Thermopiles are calibrated with standard light sources.

Photocells may be used in place of thermopiles. Still other devices are chemical actinometers, which are merely gas mixtures or solutions sensitive to light. When radiation impinges upon these, a chemical reaction ensures whose extent is determined by the amount of energy absorbed. The most common of these is the uranyl oxalate actinometer, consisting of 0.05 molar oxalic acid and 0.01 molar uranyl sulphate ($UO_2\ SO_4$) in water. Under the action of light following reaction take place:

$$UO_2^{2+} + h\nu \longrightarrow \left[UO_2^{2+}\right]^*$$

Uranyl ion

$$\left[UO_2^{2+}\right]^* + \begin{array}{c}\text{COOH}\\ | \\ \text{COOH}\end{array} \longrightarrow \left[UO_2^{2+}\right] + H_2O + CO_2 + CO$$

Extent of reaction can be ascertained by titrating the remaining oxalic acid with permanganate solution. For best results this actinometer should be calibrated against a thermopile in the spectral range in which it is to be employed. When this is not possible, the quantum yields recorded in the literature may be utilised. This actinometer is applicable to radiations lying between 200 and 500 nm.

To obtain the total radiant energy in unit time the procedure is as follow. First the empty cell or the cell filled with solvent alone in the case of solutions, is interposed in the light beam, and a reading is taken. This gives the total energy incident in a given time upon the system. Next the cell with the reactants is substituted and the reading is again taken, which gives now the total energy transmitted. The difference between these readings is the total energy absorbed by the reacting mixture in the given time.

The rate of the chemical reaction taking place in the system is ascertained in the usual manner. For this purpose the change in some physical property can be followed or samples can be removed periodically from the cell and analysed. It is thus possible to collect data on the rate of the chemical reaction and the light intensity, from which the rate law and quantum yield may be deduced.

Example: The quantum efficiency after the decomposition of uranyl oxalate in an experiment was found to be 0.570 at 300 nm. When light was passed through an empty cell, decomposition of $6.201\ \ 10^{-3}$ mole of the oxalate took place in 2 hours. When the cell contained acetone and irradiation continued for 10 hours, $1.4\ \ 10^{-3}$ mole of acetone were decomposed and light not absorbed by acetone decomposed $2.631\ \ 10^{-2}$ mole of the oxalate. What is the Quantum efficiency for the acetone decomposition?

Solution: Amount of oxalate decomposed in 2 hr in the empty cell = $6.201\ \ 10^{-3}$ mole

Amount of oxalate decomposed in 10 hr in the empty cell

$$= 5\ \ 6.201\ \ 10^{-3} = 3.1005\ \ 10^{-2} \text{ mole.}$$

The number of photons incident in 10 hrs,

$$= \frac{\left(3.1005\ \ 10^{-2}\,\text{mole}\right)\left(6.02\times10^{23}\,\text{mol}^{-1}\right)}{0.570} = 3.276\times10^{22}$$

Amount of oxalate decomposed after decomposing acetone = $2.631\ \ 10^{-2}$ mole Number of photons not absorbed by acetone in 10 hours

$$= \frac{\left(2.631 \times 10^{-2}\right)\left(6.02 \times 10^{23}\right)}{0.570} = 2.78 \quad 10^{22}$$

Hence, number of photons absorbed by acetone

$$= 3.276 \quad 10^{22} - 2.78 \quad 10^{22} = 4.96 \quad 10^{21}$$

Number of molecules of acetone decomposed

$$= (1.4 \quad 10\text{-}^{3} \text{ mole})\ (6.022 \quad 10^{23} \text{ mole}^{-1}) = 8.43 \quad 10^{20}$$

Hence, the quantum efficiency $= \phi = \dfrac{8.43 \times 10^{20}}{4.91 \times 10^{21}} = 0.17$

Example: Radiation of wavelength 250 nm was passed through a cell containing 10 ml of a solution which was 0.05 molar in oxalic acid and 0.01 molar in uranyle sulphate. After absorption of 80 joules of radiation energy, the concentration of oxalic acid was reduced to 0.04 molar. Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wavelength.

Solution: The energy of einstein associated with radiation of wavelength 2500 A is given by

$$E = \frac{Nhc}{\lambda} = \frac{6.022 \times 10^{23}\ \text{mol}^{-1} \times 6.626 \times 10^{-34}\ \text{Js} \ \ 3 \ \ 10^{8}\text{ms}^{-1}}{25000 \ \ 10^{-10}\text{m}}$$

$$= \frac{11.97 \times 10^{8}}{2500}\text{J}$$

∴ Number of einsteins corresponding to 80 J of radiation energy absorbed

$$= \frac{80\text{J} \ \ 2500}{11.97 \ \ 10^{8}} = 0.000167$$

Decrease in concentration of oxalic acid = 0.05 – 0.04 = 0.01 mole

Quantity of oxalic acid decomposed in 10 ml of the solution

$$= \frac{0.01 \times 10}{1000} = 0.0001 \text{ mole}$$

$$\phi = \frac{\text{No. of moles decomposed}}{\text{No. of einstein absorbed}}$$

$$= \frac{0.0001}{0.000167} = 0.598$$

Example: Photobromination of cinnamic acid to dibromocinnamic acid was carried out in blue light of wavelength 440 nm at 310 K using light intensity of $1.5 \quad 10^{-3}$ J per second. An exposure of 20 minutes produced a decrease of 0.075 millimole of bromine. The solution absorbed 80 per cent of the light passing through it. Calculate the quantum yield of the reaction.

Solution: Energy associated with a quantum of light of wavelength 440 nm

$$= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\,\text{Js} \;\; 3 \;\; 10^{8}\,\text{ms}^{-1}}{440 \times 10^{-9}\,\text{m}} = 4051 \quad 10^{-19}\ \text{J}$$

Intensity of light $= 1.5 \quad 10^{-3}\ \text{Js}^{-1}$

∴ Radiation energy absorbed in 20 minutes with 80 per cent absorption

$$= 1.5 \quad 10^{-3}\ \text{Js}^{-1} \quad 1200\text{s} \quad \frac{80}{100} = 1.44\ \text{J}$$

Number of Quanta absorbed $= \dfrac{1.44}{4.51 \times 10^{-19}\,\text{J}} = 3.19 \quad 10^{18}$

Amount of bromine that has reacted = (0.075/1000) mol

No. of Molecules of Bromine that reacted

$$= \frac{0.075}{1000}\,\text{mol} \quad 6.02 \quad 10^{23} = 45.15 \quad 10^{18}$$

$$\phi = 45.15 \quad 10^{18}/3.19 \quad 10^{18} = 14.15$$

Example: Calculate the number of moles of HCl (g) produced by the absorption of one joule of radiant energy of wavelength 480 nm in the reaction $H_2(g) + Cl_2(g) = 2HCl\ (g)$ if the quantum yield of the photochemical reaction is $1.0 \quad 10^{6}$.

Solution: The energy of einstein associated with radiation of wavelength 480 nm is given by

$$E = \frac{N_A hc}{\lambda}$$

$$= \frac{\left(6.022 \times 10^{23}\,\text{mol}^{-1}\right)\left(6.626 \times 10^{-34}\,\text{Js}\right)\left(3 \times 10^{8}\,\text{ms}^{-1}\right)}{480 \;\; 10^{-9}\,\text{m}}$$

$$= 2.492 \quad 10^{5}\ \text{J}$$

∴ Number of einstein corresponding to one joule of radiation energy absorbed

$$= \frac{1}{2.492 \times 10^5 \,\text{J}} = 0.40 \quad 10^{-5}$$

$$\phi = 1 \quad 10^6 \text{ (given)}$$

Number of moles of HCl (g) produced = $1\ 10^6\ 0.40\ 10^{-5} = 4$

Various Quantum Yields

Case I High Quantum Efficiency, $\phi > 1$: In reactions where number of reactant molecules undergoing chemical change per photon of radiation absorbed is more than one, extra energy absorbed by the reactant molecules is transferred to its product, which may take part in secondary reactions.

For example, decomposition of two molecules of HI by absorption of only one photon of light has the mechanism as follow:

$$\begin{array}{lll} \text{HI} + h\nu \longrightarrow \text{H} + \text{I} & (i) & \text{Primary Reeaction} \\ \text{H} + \text{HI} \longrightarrow \text{H}_2 + \text{I} & (ii) & \multirow{2}{*}{Secondary Reaction} \\ \text{I} + \text{I} \longrightarrow \text{I}_2 & (iii) & \end{array}$$

$$\text{or} \quad 2\text{HI} + h\nu \longrightarrow \text{H}_2 + \text{I}_2$$

In the primary process, only one molecule of HI is decomposed to its elements by absorbing one photon of light and this is in accordance to Einstein Law of Photochemical Equivalence. Subsequently, the obtained H atom reacts with another HI molecule yielding an atom of iodine. The iodine atoms obtained in steps (*i*) and (*ii*) combine to give a molecule of iodine. Thus the overall effect is that 2 molecules of HI undergo chemical change by absorption of one photon of light, Hence $\phi = 2$

There are many photochemical reactions in which a large number of molecules may undergo chemical change by the absorption of one photon of light. In such reaction, the quantum yield has been found to vary from 10^4 to 10^5. At moderate gas pressures and with comparable proportion of chlorine and hydrogen photochemical reaction takes place.

$$\begin{array}{rcll} Cl_2 + h\nu & \longrightarrow & 2Cl & \text{Primary Reaction} \\ Cl + H_2 & \longrightarrow & HCl + H & \\ H + Cl_2 & \longrightarrow & HCl + Cl & \text{Secondary Reactions} \\ Cl\ (\text{at walls}) & \longrightarrow & 1/2\ Cl_2 & \end{array}$$

Here the chains acquire great length and as many as 10^6 molecules of hydrogen chloride are obtained per quanta of light. In all combinations of atoms to form stable molecules considerable energy is evolved. Unless this energy is removed, the resulting molecule cannot be stable. Consequently in all such reactions it is necessary to assume either that a third body is involved in the collisions which carries off the energy, or that the reaction occurs at the walls. The third body may be a molecule of the reactants, the products, or some other neutral impurity present in the system that does this job.

Case II Low Quantum Efficiency, $\phi < 1$: In cases when $\phi < 1$

(*i*) The primary products may combine to form the reactants.

(*ii*) The activated molecules may be deactivated by collisions, by fluorescence or by internal rearrangement before they start to react.

(*iii*) Some of the activated molecules may not acquire sufficient energy for the chemical change.

For example, in the formation of HBr from H_2 and Br_2, the quantum efficiency is 0.02 only. The accepted mechanism of this reaction is as follows:

$$\begin{array}{rcll} Br_2 + h\nu & \longrightarrow & 2Br & \text{Primary Reaction} \\ Br + H_2 & \longrightarrow & HBr + H & \\ H + Br2 & \longrightarrow & HBr + Br & \text{Secondary} \\ H + HBr & \longrightarrow & H_2 + Br & \text{Reactions} \\ Br + Br & \longrightarrow & Br_2 & \end{array}$$

Such reactions show the variation of the quantum yield with temperature and are accountable by changes in the magnitude of reaction rate constants of secondary reaction with temperature. The quantum yield increased with temperature upto 2 near 200 C, and was still higher at higher temperatures.

The photochemical decomposition of ammonia proceeds quantitatively according to reaction.

$$2NH_3\,(g) \longrightarrow N_2\,(g) + 3H_2(g)$$

With an average quantum yield of 0.25. The following mechanism has been proposed to explain this result

$$\begin{array}{rcll} NH_3 + h\nu & \longrightarrow & NH_2 + H & \text{Primary Reaction} \\ NH_2 + H & \longrightarrow & NH_3 & \\ H + H & \longrightarrow & H_2 & \text{Secondary} \\ NH_2 + NH_2 & \longrightarrow & N_2H_4 & \text{Reactions} \\ N_2H_4 + H & \longrightarrow & NH_3 + NH_2 & \\ NH_3 + NH_3 & \longrightarrow & N_2 + 3H_2 & \end{array}$$

From this mechanism it can be shown that quantum yield should be small and that it should vary with pressure.

Example: A sample of gaseous HI was irradiated by light of wavelength 253.7 mm when 307 J of energy was found to decompose 1.30 I0^{-3} mole of HI. Calculate the quantum yield for the dissociation of HI.

Solution:

The energy possessed by a photon of radiation of wavelength 253.7 nm

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-23}\,\text{Js})(3 \times 10^{8}\,\text{ms}^{-1})}{253.7 \times 10^{-9}\,\text{m}} = 7.835 \quad 10^{-19}\,\text{J}$$

∴ Number of quanta absorbed by

$$HI = \frac{307\,J}{7.835 \times 10^{-19}}$$

$$= 3.92 \quad 10^{20}$$

Number of molecules of HI decomposed

$$= 1.3 \quad 10^{-3}\ \text{mol} \quad 6.022 \quad 10^{23}\ \text{mol}^{-1}$$

$$= 7.83 \quad 10^{20}$$

Quantum yield, $\phi = \dfrac{7.83 \times 10^{20}}{3.92 \times 10^{20}} = 1.997 \approx 2.00$

Transfer of Energy: Non-radiative

An understanding of the ways in which molecules can come together and exchange energy is important for the study of a number of chemical phenomena. For example, if a gas or liquid is suddenly compressed, and thereby heated, it is of interest to know how rapidly the various types of energy level available to the molecules become populated in accordance with the Boltzmann distribution for the new temperature. We shall not attempt here to approach such general problems, and it will be enough for our purpose to provide a background against which the more spectroscopically interesting phenomenon of radiative energy dissipation can be understood.

An initial understanding of how long an excited gas molecule might retain its excess energy before it passes this energy, or part of it, on to another molecule of the gas can be reached by calculating the average time that a gas molecule has between collisions with other molecules. This quantity is the number of collisions that gas molecules make per second, is obtained from the kinetic theory of gases. However, it will be sufficient here to mention the pertinent results. For relatively small molecules one calculates that, at 1-atm pressure, a molecule suffers a collision after about every 10^{-10} sec. This length of time between collisions increases, as would be expected, as the pressure is reduced; and furthermore, in the region of very low pressures, collisions with the walls of the container also become important and affect the calculation.

In the liquid state the concept of molecular collisions is less straightforward. It has been estimated, however, that a molecule in a liquid collides with a neighbouring molecules about 10^{-13} times per sec. This leads to a time between collisions of about 10^{-13} sec, and this value, in view of the greater proximity of the molecules in a liquid than in a gas at 1 atm, seems reasonable.

These values, 10^{-10} and 10^{-13} sec, give an idea of the shortest times in which the transfer of energy from an average excited molecule could occur. In fact, there is no reason to expect that all collisions will be effective in transferring energy; and, moreover, it should not be expected that rotational, vibrational, and electronic energies should be equally transferable.

It is a matter of some difficulty, and current research interest, to determine the probability that a collision will result in the transfer of excess molecular energy. Some qualitative ideas have, however, been developed.

It appears, for example, that rotational energy is relatively easily transferred and that most collisions are in fact effective in the exchange of such energy. Frequencies associated with typical molecular rotations are of the order of 10^{11} or 10^{12} cycles, or rotations, per second. Alternatively, we say that it takes about 10^{-11} or 10^{-12} sec for one rotation of a molecule. We see, therefore, that in gases at pressures lower than 1 atm many rotations occur between collisions, and deactivation, but that in liquids the molecules generally will not be able to complete a rotation in the short time of 10^{-13} sec that exists on the average between collisions. We conclude, therefore, that in liquids the molecules are not free to rotate, and this conclusion is consistent with our observations that vibrational absorption bands generally show rotational fine structure only when the sample is a gas.

On the other hand, vibrational energy is less readily exchanged. The importance of the type of vibration that is excited is not yet clear, but it appears that something like 10^4 collisions might be required, on the average, before one, that brings about the transfer of vibrational energy. In such a "transfer" the excess vibrational energy probably appears as additional rotational and translational energy of both the colliding molecules. A vibrationally excited molecule in the liquid state may, therefore, have a lifetime of the order of $10^4 \quad 10^{-13} = 10^{-9}$ sec. This time is, it should be noted long compared with the period of about 10^{-13} sec for a typical vibration. A molecule, even in a liquid, will therefore complete many vibrational cycles before it is deactivated.

Finally, let us consider the way in which a molecule whose electronic arrangement and energy have been affected by the absorption of visible or ultraviolet light to dissipate the excess energy and return to its normal, or ground, electronic state. This process is relatively difficult; and to investigate it further, one needs to consider a number of different situations.

The simplest situation is that illustrated for an excited state and the ground electronic state in the following figure. The allowed vibrational energies for each electronic arrangement are shown. In addition, the potential energy vs internuclear-distance curves that can be deduced from each set of vibrational levels and, therefore, that correspond to each electronic arrangement, are shown. The absorption of radiation that produces the higher energy electronic configuration can be represented, by the vertical arrow. We must generally ask, therefore, how the molecule in a high-energy vibrational state and a high energy electronic arrangement loses all this excess energy.

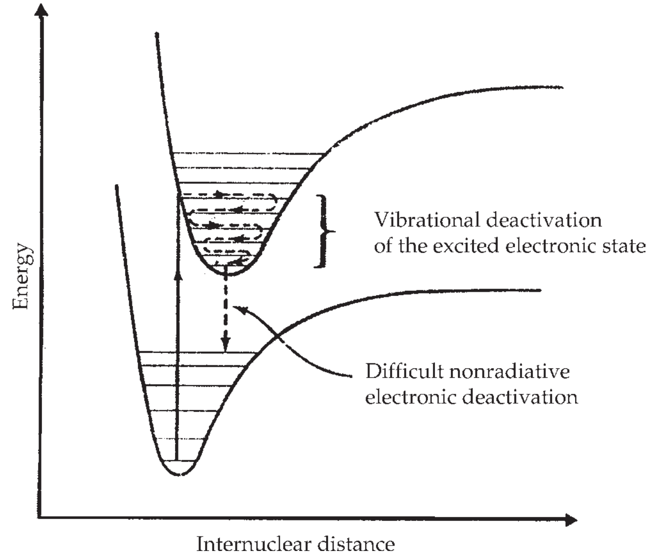


Fig. *The absorption and non-radiative deactivation for electronic states corresponding to the potential-energy curves shown. The dashed arrow is intended to suggest that collisions generally remove the excess vibrational energy one step at a time.*

The excess vibrational energy can be lost, as mentioned above, by repeated collisions with neighbouring molecules, and in liquid state, in the course of about 10^{-9} sec, the process schematically indicated by the dashed line will be complete. Further dissipation of energy would require, for the situation represented in the figure given above the removal of a large amount of energy in a single collision and the simultaneous rearrangement of the electronic structure of the molecule so that the ground state electronic configuration would be reached. It must be expected that it will be very unlikely for such a complicated process to accompany a single molecular collision.

It appears that such electronic deactivation by a collision process is very improbable. The dissipation of energy from the lowest vibrational level of an excited electronic state usually occurs as a result of emission of energy as radiation.

For most molecules, however, the representation of figure given above must be recognised as a simplification that is not valid. In the energy region not too far above that of the ground electronic state there will normally be a number of electronic arrangements. These arrangements will have potential energy curves that will cross one another, and the situation shown in the following figure must be expected to be more representative of the typical state of affairs.

With such a diagram it is possible, as suggested by the dashed line, for all the excess energy to be lost by small, vibrational sized steps. It appears that the deactivation path that is followed takes the originally excited state to a level where the potential energy of the first excited state crosses that of another state.

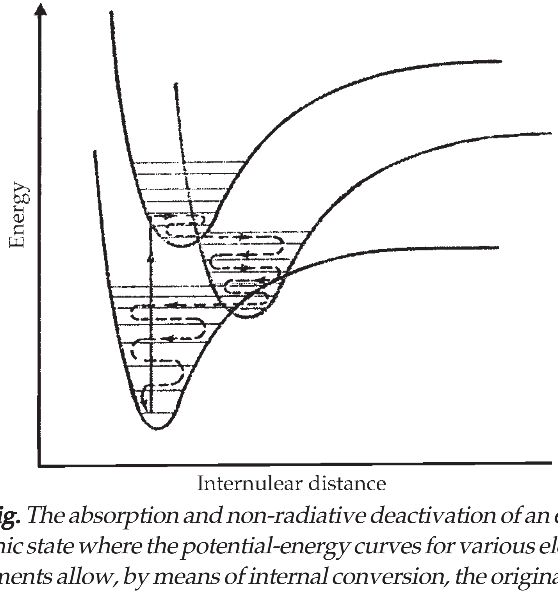


Fig. *The absorption and non-radiative deactivation of an excited electronic state where the potential-energy curves for various electronic arrangements allow, by means of internal conversion, the original ground state to be reached after a series of vibrational-energy steps.*

At this crossing point both electronic arrangements have, at a particular molecular geometry, the same potential energy. At such a point it may be relatively easy for the electronic arrangement to change from the corresponding to one set of allowed energy levels and the corresponding potential curve to that corresponding to the other set of levels and the other potential curve.

This process, known as *internal conversion,* appears to be much more probable than is the change in electronic arrangement that must be accompanied by a large energy transfer. It is by the processes of vibrational deactivation and internal conversion that a molecule raised to an excited state such as that of figure (given above) can return to its initial ground electronic and vibrational state by non-radiative processes.

It should be mentioned, in connection with a situation that will be very important when radiative processes are considered, that even when potential-energy curves or two different electronic arrangements cross, it is not necessarily an easy matter for the electronic arrangement to change over from the arrangement that corresponds to one of the potentia-energy curves to the arrangement that corresponds to the other curve.

This difficulty is most noticeable when the two electronic arrangements are such that the number of unpaired electrons is different in the two arrangements. Most often, one deals with situations in which one arrangement has no unpaired electrons and the other arrangement has one pair of electrons broken up so that there are two unpaired electrons. The former arrangement constitutes what is called a *singlet state,* while the latter is known as *triplet state.* It appears that internal conversion between singlet and triplet states can occur but it is not a rapid and easy process as conversion between electronic arrangements with equal numbers of unpaired electrons. The mechanism by which the direction of the spin of one electron relative to another is changed is apparently not very effective. Nevertheless, crossing over from one potential curve to another, with different net spin, can occur and non-radiative processes can, even in this case, return the molecule to its initial state.

The transfer of energy in a collision is as would be expected, more probable the harder the two molecules collide with each other, *i.e.,* the more they interact during the collision. This interaction can be greatly impeded by two effects. The first consists of cooling the sample down to liquid-nitrogen or liquid-helium temperatures and thereby decreasing the kinetic energy of the molecules and the effectiveness of collisions. In the second place the number of collisions can be decreased by dissolving the molecules under study in a solvent which, when cooled, sets to a rigid glassy material. (If the solvent crystallises, it will generally form pure crystals and leave the material in solution to form separate crystals). Often used for the formation of a glass is a mixture of ether, isopentene, and ethanol, although many suitable materials that set to glasses rather than form crystals are known. When materials are embedded in such glasses and cooled to low temperatures, the non-radiative processes for the elimination of the excess energy absorbed by a molecule are very ineffective and then the radiative processes becomes important.

Excited Molecules and Energy Dissipation

Light absorption leads to the excitation of molecules from the ground to excited states. But what is the fate of this energy? The half-lives of the excited states vary down from 10^{-9} to 10^{-4}s.

The reverse process corresponding to the emission of radiation of the same frequency is one of the simplest modes of losing energy, as is observed in emission spectra. Another process is known as predissociation. A third fate of the absorbed energy may lead to direct photodecomposition. It occurs when the vibrational states in the excited state are Continuous and is signalled with a continuous absorption in the spectrum.

Absorbed light may be degraded into thermal motion or it may be remitted. Such emission from an excited molecule is called fluorescence or phosphorescence. These two types of emission may be extinguished by the mechanism that generates them.

The mechanism of fluorescence is illustrated in the following figure. The incident light excites the molecule from the ground state, O. By the Frank-Condon principle this excitation should be vertically upwards along OD, producing a compressed excited molecules, which vibrates with a period of 10^{-13}s as shown by the upper curve. Vibrational excitation is thus coupled to electronic excitation. As molecules in the liquid state have a collision frequency of – 10^{12} times/s, solvent molecules collide with the excited molecules and rob them of their excess vibrational energy so that they reach at point E. Here two things may occur. One, the solvent may carry away the electronic energy and deactivate the molecule.

This is possible if the energy levels of the solvent and excited molecules match each other, for then there may be a resonant transfer of radiation to the solvent, which then fritters away its excitation into thermal motion. An alternative mode of decay is fluorescent decay along line EF, remitting light of whose mean frequency is proportional to the length EF and fells back into a lower electronic state. This emitted light is what is called fluorescence. Such a picture of the process enables one to visualise the following points.

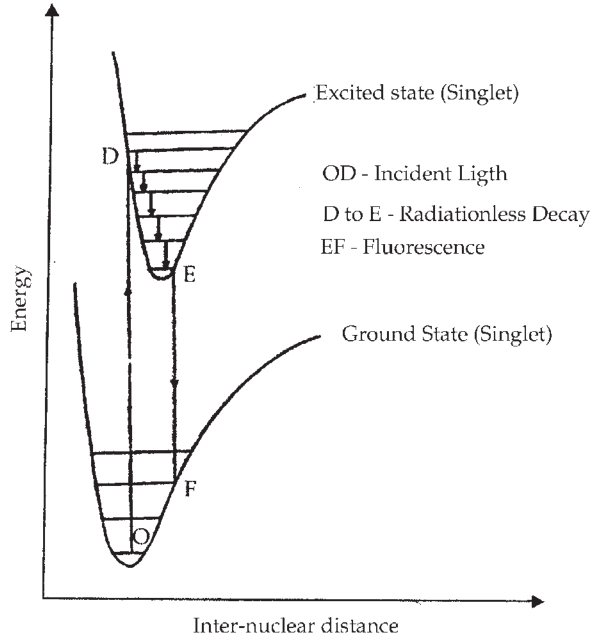


Fig. *The process leading to fluorescence and shift of latter to longer wavelength.*

1. Fluorescent light is always of smaller frequency than the incident light because EF is always less than OD.

2. The fluorescence spectrum shows a vibrational structure giving the vibrational frequency of the molecule in the ground state. This is in contrast to the electronic state. This follows that the fluorescent spectrum and electronic spectrum should appear as mirror images of each other, but this description should be taken literally.
3. The fluorescence spectrum is independent of the wavelength of absorbed light (within limits), since the fluorescence transition is from E downward, whatever higher level such as D was reached on light absorption.
4. The time for an electron to stay in excited state prior to the ground state is about 10^{-6} and 10^{-10} s.
5. Spin states of the involved state should not change, *i.e.,* all involved states are either singlets or triplets.

The conditions for fluorescence are much more favourable is aromatic and particularly in condensed hydrocarbons. These compounds absorb at relatively long wavelengths and have very rigid structure, making internal conversion quite difficult. Some of the experimental material has been assembled in table:

Table: *Florescence shown by some Substituted Hydrocarbon in Hexane Solution*

Compound	***Wavelength region of Fluorescence in nm***	***Compound***	***Wavelength region of Fluorescence in nm***
Benzene	270-310	Naphthalene	300-360
Toluene	270-310	Anthracene	370-460
o,m,p-Xylene	270-320	Phenanthrene	280-470
Styrene	290-365	Fluorene	300-370
Chlorobenzene	275-345	Biphenyl	290-360
Hexamethybenze	280-330	Triphenylmethane	280-340
Benzoic acid	310-390	o-Hydroxy benzoic acid	375-480
Aniline	310-405	Dimethylaniline	325-405

Substitution in aromatic hydrocarbon naturally shifts the wavelength of fluorescence in agreement with the effect of the same substitution on the absorption spectrum. Alkyl substitution has little effect. Chlorine and bromine weaken the florescence and iodine completely inhibits it. The simplest aromatic heterocyclics, pyridine, pyrrole, furan and thiophene do not show fluorescence.

A similar situation results if emission occurs from one of the excited electronic state reached by internal conversion. The process then would be as that shown in the following figure. Even in this case the emission process that connects the two states has same number of unpaired electrons — two singlet states or two states with half-lives in the range 10^{-9}-10^{-4}S.

Another type of fluorescence invariably accompanying irradiation of some compounds but not due to the excited molecules occurs when the compound undergoes a photochemical reaction or decomposition. Many carbonyl compounds, photochemically dissociate to form acryl radicals, which in turn, dimerise. The dimeric biacyls themselves fluorescence in the visible, and give the appearance that the original carbonyl compound show fluorescence. The fluorescence intensity increases with time suggesting that fluorescing species is formed during irradiation.

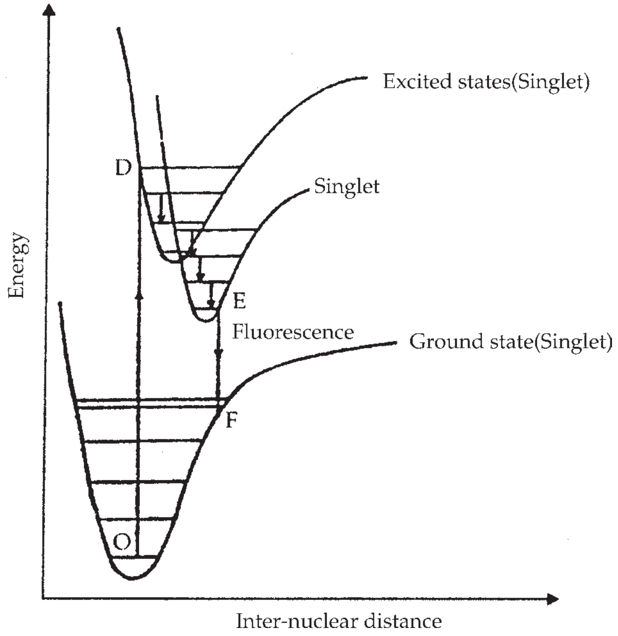


Fig. *Fluorescence following the internal conversion.*

In general, compounds absorbing only in the far UV or middle UV, decay fluorescence because predissociation deactivates excited states. Consequently, it is no surprising that aliphatic and simple non-conjugated olefins, hydrocarbons and their substitute derivatives do not show fluorescence.

Role of Phosphorescence

The electronic excitation is accompanied by a vibrational excitation and this vibrational energy is transferred to the surrounding molecules by the type of process described in fluorescence. If the vibrational deactivation is not too fast, another process may intervene. Let there be a triplet state of the excited molecules. This is illustrated as curve T_1.

There is probability of a molecule switching from the singlet state to the triplet as it loses energy and is named to result from inter-system crossing. At the bottom of energy curve, T_1 it finds itself trapped; it cannot radiate its electronic energy and drop to the ground state, which involves singlet-triplet-singlet transitions. It cannot go back to the crossing point, because the collisions with the lattice cannot supply that much energy.

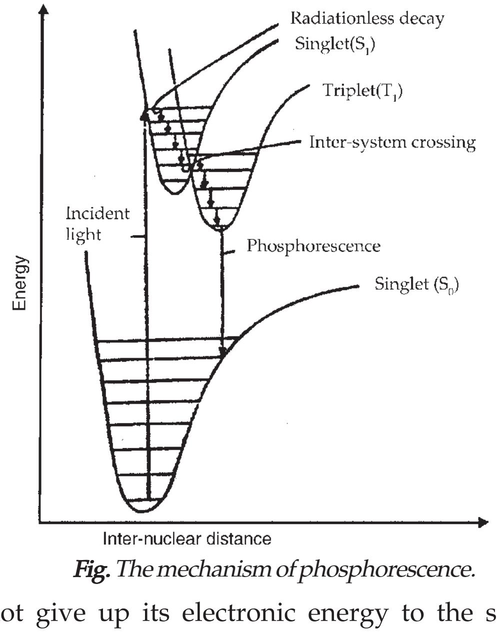


Fig. *The mechanism of phosphorescence.*

It cannot give up its electronic energy to the surrounding molecules by a radiation less transition because the vibrational deactivation involves smaller energy and is thus weak. If the foregoing description were true, the molecule would be stuck in this triplet state. In actual practice, the molecule does come down to the ground state.

The fallacy is that the singlet-triplet transitions are not strictly forbidden. If it were so, the molecule would have been unable to cross from the singlet state. S_1 to the triplet state T_1. The fact that it did cross implies that there is enough spin-orbit coupling present to break down the singlet triplet selection rule and so this becomes weakly allowed. However, as it is only weakly allowed, the transition $T_1 \rightarrow S_0$ is slow and may persist even after the illumination has ceased. Thus phosphorescence occurs under the following conditions.

1. There is a suitable triplet state in the vicinity of the excited singlet state.
2. There is sufficient spin-orbit coupling to induce inter-system crossing.
3. There is sufficient time for the molecule to cross from one curve to the other. This means that the vibrational deactivation must be slow so that the molecule is quenched and taken below the point where the curves intersect before inter-system crossing interaction has time to operate.
4. The wavelength of the emitted light is longer than the fluorescent emission.
5. Since singlet-triplet transition is not allowed, consequently, the transition is slow. This makes phosphorescence emission long after the irradiating light is switched off. This does not happen in fluorescence.

The involvement of the triplet state an unequivocally be studied by applying electron-spin resonance to the phosphorescent state. From this, the time of deactivation can also be obtain.

Phosphorescence is most easily attained in a solid state rather than in the liquid state. In solid-state dissipation of energy by virtue of collision is minimised and time to the excited state increased. This result in increase in probability of inter system crossing and consequently to phosphorescent. Solid like rigidity and phosphorescence can also be attained by absorption of molecule on a surface or by using a Micelle to stabilise the molecules.

Importance of Jablonski Diagram

Once a molecule is excited into an electronically excited state by absorption of photon, it can undergo a number of primary processes. Photochemical processes are those in which the excited species dissociates, isomerise, rearranges or react with another molecules.

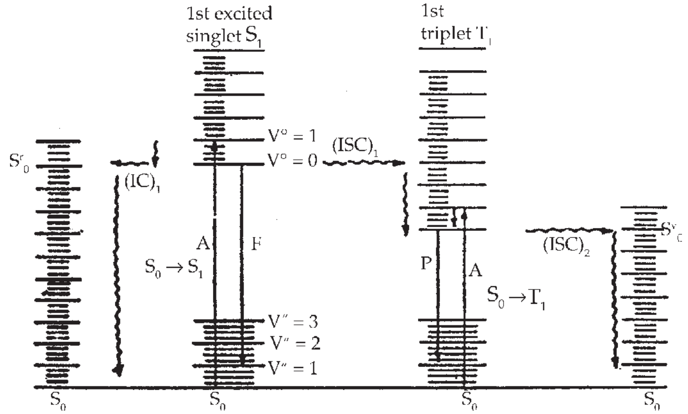


***Fig.** Jablonski diagram illustrating photophysical radiative and non-radiative transitions. S_o = ground singlet state, S_1 = 1st excited singlet state. T_1 = 1st triplet state. A = absorption of light, F = florescence, P = phosphoresces,* IC *= internal conversion. ISC = intersystem crossing. Radiative transitions are shown by solid lines, non-radiative by wavy lines. Photochemical processes are not indicated.*

Photophysical processes include radiative transition in which excited molecule emits light in the form fluorescence or phosphorescence and returns to the ground state, intra-molecular non-radiative transitions, in which some of the energy of the absorbed photon ultimately gets converted to heat.

These photophysical processes are often displayed in the form of the Jablonski type energy level diagram shown in the figure given above. Common singlet states are labelled as S_o, S_1, and S_3 and triplets are labelled as T_1, T_2, T_3, and so on in order of increasing energy. Vibrational states are shown as being approximately equally spaced horizontal lines. Radiative transitions for example florescence (F) and phosphorescence (P) are shown as solid lines and non-radiative transitions as wavy lines. Vertical distances between the vibrational levels of the singlet ground state S_o and the two electronically excited states, the first excited singlet S_1, and its triplet T_1 corresponding to their energy gaps.

The excited molecule can undergo the following process in addition to direct photoionisation:

(a) If the excited state is completely repulsive, *i.e.,* there are no attractive forces strong enough to lead to a potential energy minimum, then dissociation into two or more molecular fragments, free radicals ions will occur within approximately one vibration ($10^{-12} - 10^{-13}$).

(b) Even if the excited electronic state is 'bound', *i.e.,* it possesses a potential energy minimum, the absorbed photon may be of sufficient energy to raise the vibrational energy to a dissociative limit. This type of direct photodissociation may also be extremely rapid for diatomic molecules. An example of photodissociation is a spin allowed dissociation of O_3 at $\lambda < 320$ nm.

$$O_3\,(B_2) + h\nu\ (\lambda < 320\text{ nm}) \rightarrow O(^1D) + O_2\,(^1\Delta_g)$$

Term symbols of the electronic states are indicated in brackets. Both O_2 and O are in their electronic excited states. With more complex species, may make its dissociative lifetime very large and either of the competitive process de-excitation or chemical reaction may take place.

(c) Fluorescence (F) is defined as emission of light due to a transition between states of like multiplicity, *i.e.,* $S_1 \rightarrow S_0 + h\nu$. The molecule may return to the stable ground state by radiative emission of light from the lowest vibrational level. This is an allowed transition and hence the life time of upper state with respect to fluorescence is usually short, typically.

(d) $10^{-6} - 10^{-9}s$. However, this emission will be of lower energy than the excitation energy for molecule because of the non-radiative dissipation of vibrational energy in the excited state (F). For example, the fluorescence life of OH in the electronically excited $^2\Sigma^+$ state is 0.7 μs.

(e) Phosphorescence (P) is defined as emission light due to a transition between states of different spin multiplicities. Because this is not an allowed transition for an ideal unperturbed molecule, phosphorescence lifetimes tend to be relatively long $10^{-3} = 10^{-2}$s.

(f) Intersystem crossing (ISC) is the infra-molecular crossing from one state to another of different multiplicity without emission of radiation. In the figure above, (ISC), shows the transfer from first excited singlet state, S_1 to the first excited triplet state. Since the process is horizontal, the total energy remains initially produced in upper vibrational level of T_1 from which it is deactivated as shown by the vertical wavy line. Since this is a non-radiative process, it is not limited by the $\Delta S = 0$. The resulting new excitation can no longer undergo a rapid radiative decay to ground state because it is forbidden. Similarly, $(ISC)_2$ shows the inter systems crossing from T_1 to upper vibrational states of the ground state, S_o from which vibrational deactivation to $V'' = 0$ then occurs.

(g) Internal conversion (IC) process is the intramolecular crossing of an excited molecule from one state to another of the same multiplicity without the emission of radiation. The horizontal wavy line (IC) represent the internal conversion of $S_1 \rightarrow S_o$ this is generally followed by vibrational deactivation to $V'' = 0$ but no chemical change. Such process is quite rare but found in aromatic molecules and cyanine dyes.

(h) The excited (donor D) molecular may be deactivated by radiation less energy transfer to another (acceptor A) molecule. Because of the forbidden character of triplet state in phosphorescence, triplet state is long lived than the excited singlet state. It can, therefore, readily undergo collision energy transfer at normal encounter of distance by (the spin allowed reaction).

D(Triplet) + A(Singlet) → D(Singlet) +A(Triplet)

Provided the transfer is exothermic ($\Delta E_{acceptor} < \Delta E_{donor}$) or at least less than approximately 10 kJ endothermic. Triplet states are quenched in most fluid solutions by this type of energy transfer to dissolved oxygen and solvent impurities, even in the absence of added quenchers.

Role of Chemiluminescence

In photochemical reactions chemical change result from absorption of light. The converse of this process is emission of light by a system at ordinary temperature as a result of a chemical reaction. Such emission of cold light is called chemiluminescences. It is a well-known phenomenon.

When yellow-phosphorus is oxidised in oxygen or air at low pressures and at temperatures between –10 and 40 C, the phosphorus is converted to P_2O_5 with the emission of a visible greenish-white luminescence. Similarly the oxidation of certain Grignard reagents, silicon compounds, 3-aminophthalic acid and hydrazine in alkaline solution is accompanied by light emission. In all these instances part or all of the energy change of the reaction, instead of appearing as heat, goes to activate electronically some molecule. The activated molecule emits the energy as radiation and reverts to a normal state.

The chemiluminescence, which is possibly best, understood is that emitted in the reaction of alkali metal vapours with halogens. When streams of alkali metal vapours and halogens at pressures of 10^{-2} to 10^{-3} nm Hg are mixed, alkali halides are formed with the emission of luminescence. The probable mechanism suggested is:

(i) $Na + Cl_2 \rightarrow NaCl + Cl$

(ii) $Na_2 + Cl_2 \rightarrow NaCl + Na$

(iii) $Na + Cl \rightarrow NaCl$

It is believed that in the *(ii)* step sufficient energy is acquired by the NaCl molecule to excite a Na atom on collision as

$$NaCl + Na \longrightarrow NaCl + Na^*$$

Na* atom on returning to ground state emits characteristics spectrum or exhibit chemiluminescence.

Grignard reagent produces greenish blue luminescence in its reaction with chloropicrin or on its oxidation by air. Only aryl magnesium halides in which Magnesium atom is attached to one unsaturated carbon atom exhibit chemiluminescence's in solution while in solid state, both alkyl and aryl magnesium halides show this phenomenon.

Importance of Photoelectric Cells

Solar energy conversion to electricity through semi-conductors is based on the production of additional charge carriers-electrons in n-type and holes in p-type semi-conductors by the incident solar radiation. Charge separation occurs and the energy conversion is done by either photovoltaic or photoelectrochemical (PEC) cells. The former is an all solid state device which has been developed to an advanced level with about 15-18 per cent efficiency. The cost of silicon-based photovoltaic devices has been brought down by innovations in silicon production technology. PEC cell is a combination of a semi-conductor with an electrolyte containing a redox system and is said to be a regenerative called liquid junction photocell. The PEC was introduced by Gerischer in 1960 and has been the subject of intensive research since then. Many semi-conductors have been studied in a variety of solvents.

The solar energy conversion efficiency is (a maximum of 10 per cent over short periods) is still poor. However, research on these cells has greatly enhanced our understanding of semi-conductor-electron interphases, the chemistry and physics of semi-conductors, charge transfer at modified surfaces, semi-conductors as electrocatalys and photoassisted electrolysis of water towards production of hydrogen. Another kind of solar energy conversion occurs in the so called photogalvanic (PG) cell in which the incident light brings about changes in redox states in solution, leading to the development of a galvanic cell. The efficiencies reported for such cells is less than 0.1 per cent.

It may be pointed out that metals are totally unsuitable for light energy conversion because their excited electronic states have extremely short lifetime and the energy is rapidly dissipated as heat. Only semi-conducting materials can store the energy obtained from incident light and allow the stored energy to be converted to other forms. The basic properties of these semi-conductors have to be clearly understood in order to gain further insight into the electrochemical kinetics of charge transfer at semi-conductor-solution interface.

While attempting any developments in solar energy conversion, the following points must be kept in mind.

1. Solar energy is diffuse.
2. The light flux is of relatively low power.
3. There are daily and seasonal fluctuations in solar energy incidences.
4. The energy conversion devices should preferably be storage devices, for use when light incidence is absent *(i.e.,* at night).

The following table gives an outline of some semi-conductor conversion devices:

***Table:** Features of some Semi-conductor Conversion Devices*

Device	*Material*	*Efficiency*	*Remarks*
Solid State p-n junction	Si, Ga, As n-Cds/p-CdS	12–22%	Single crystal, highcost, well established.
Schottky barrier M/Scor MO/SC	Au/nGa As	9–12%	—
Photogalvanic cells	$\mathrm{Pt}\left\vert\begin{array}{cc}\mathrm{Fe}^{2+} & \mathrm{Fe}^{3+}\\ \mathrm{TH}_3^{+} & \mathrm{TH}^{+}\end{array}\right\vert\mathrm{Pt}$	< 0.2%	All other PG system have very low efficiency.
PEC(liquid junction)	$\text{n-Cds}\left\vert\begin{array}{c}\mathrm{Fe\ (CN)}_6^{3-14-}\\ \mathrm{pH}=13\end{array}\right\vert\mathrm{Pt}$	5-6%	Higher efficiency reported by coating semiconductor with a sensitizer dyes.

It may be observed that in the conversion of solar energy to electricity directly, PEC devices have to compete with highly efficient photovoltaic devices. PEC cells, like other conventional batteries, involve electrochemical oxidation and reduction processes with necessary charge transfer made to occur at low electrodes (semi-conductor and metal)-solution interfaces, making the flow of electrons unidirectional. The redox specie may be generated *in situ* by the incidence of light (as in PG cells). Alternatively, the potential gradient necessary for charge transfer is produced by the incidence of light on the semi-conductor electrode. The PG cell is essentially a concentration cell where effect of the light energy is felt within solution. For the production of electricity from solar energy in the PEC cells semi-conductor electrodes are chosen that the effect of incident light energy is felt directly on the semi-conductor material. This makes available electrons for reduction or holes for oxidation of the species in solution. The semi-conductor electrode can be combined with a counter electrode made of a metal or another semi-conductor so that both oxidation and reduction process occur at the appropriate electrodes and electrons flow in the external circuit. Semi-conductor material must be stable in medium.

A typical PG cell is depicted as

$$\begin{array}{c}\mathrm{Pt}\\ \text{Illuminated}\end{array}\left\vert\begin{array}{cc}\mathrm{Fe}^{2+} & \mathrm{Fe}^{3+}\\ \mathrm{TH}_3^{+} & \mathrm{TH}^{+}\\ \multicolumn{2}{c}{\text{Acid}}\end{array}\right\vert\begin{array}{c}\mathrm{Pt}\\ \text{dark}\end{array}$$

The two half cells are separated by an opaque material so that one half can be illuminated and other half kept in dark. TH^+ stands for thionine—a thiazine dye which can be photochemically converted to TH_2^+. The major reactions which can occur in the cell leading to production of electric energy

$$\text{Thionine } (TH^+) \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}} \text{ semithionine } (TH_2^+)$$

The λ_{max} in water for TH^+ is 597 nm and those for TH_2^+ are 390 and 770 nm. The TH_2^+ can be reduced to leucothionine (TH_3^+) in the dark

$$2\ TH_2^+ \underset{\text{dark}}{\overset{\text{dark}}{\rightleftharpoons}} TH^+ + TH_3^+$$

and leucothionine can be oxidised by Fe^{3+} according to

$$TH_3^+ + Fe^{3+} \xrightarrow{dark} TH_2^+ + Fe^{2+} + H^+$$

Several other systems have been investigated in this context. An important condition that has to be satisfied while choosing system, is that the free energy of photochemical steady state under sun light illumination should be greater than that when it is dark. Methylene blue and Fe^{2+}, Co-EDTA complex and thionine, and excited tri-bipyridyl complex of Ru^{2+} and Fe^{2+} are a few systems that satisfy this condition. The equilibrium in dark with the bipyridyl system is

$$\text{Ru}(\text{byp})_3^{2+} + \text{Fe}^{3+} \rightleftharpoons \text{Ru}(\text{byp})_3^{3+} + \text{Fe}^{2+}$$

The E of the bipyridyl system is 1.2 V and that of the Fe^{2+}/Fe^{3+} system 0.7. The equilibrium is shifted to the left. When the system is illuminated the excitation reaction occurs as

$$\text{Ru}(\text{byp})_3^{2+} \xrightarrow{h\nu} {}^*\text{Ru}(\text{byp})_3^{3+} \xrightarrow{\text{Fe}^{2+}} \text{Ru}(\text{byp})_3^{2+} + \text{Fe}^{3+}$$

There is a change in the ratio of the concentration Fe^{2+}/Fe^{3+} and Ru^{2+}/Ru^{3+} with consequent alteration in the redox potentials and hence a small change in the emf of cell. If the oxidation of Ru^{2+} to Ru^{3+} and reduction of Fe^{3+} to Fe^{2+} are made to occur at two electrodes current will flow in the external circuit.