UNIT 18 CHEMICAL KINETICS

Structure

18.1 INTRODUCTION

Chemical kinetics is the study of rates and mechanisms of chemical reactions. The rate of a reaction depends on many factors such as the concentration of the reactants, temperature, catalyst, etc. Some of these factors shall be examined in this unit. We shall study thermal reactions in this unit. In thermal reactions, the reactants gain the energy required for the reaction through molecular collisions. In Unit 19, we shall study reactions induced by light.

We shall start the unit explaining the dependence of rate of reaction on the concentrations of the reactants. In this process, we shall be defining the terms such as rate equation, rate law and order of a reaction. We shall then derive first order, second order and zeroth order equations. These equations will be used for calculating the rate constants of the reactions. We shall then explain the methods of determining the order of reaction.

We shall discuss the mechanism of simple reactions. We shall illustrate the significance of rate-determining step in explaining the rate law. We shall study the effect of temperature on reaction rates. We shall state the theories of reaction rates. Finally, the methods of studying fast reactions will be dealt with.

Objectives

After studying this unit, you should be able to:

- define rate law, rate constant and order of reaction,
- differentiate between order of reaction and stoichiometry,
- state the experimental methods for studying the reaction rates,
- derive integrated rate laws for first order, second order and zeroth order reactions and use them for calculating rate constants,
- state the methods for determining the order of reaction,
- define elementary reaction and molecularity,

- propose mechanism for simple reactions using the experimental rate law,
- discuss the theory of unimolecular reactions,
- explain Arrhenius equation, collision theory and activated complex theory, and
- describe the methods of studying fast reactions.

18.2 SOME FUNDAMENTAL CONCEPTS

Throughout this unit, the phrase 'rate of reaction' means instantaneous reaction rate.

In this section, we shall define some terms such as rate of reaction, rate law, rate constant, order of a reaction and stoichiometry.

Rate of Reaction

We shall shortly study the method of arriving at the reaction rates from the values of concentrations of a component at different time intervals.

The symbol ' Δ ' is to be read as delta. It denotes change in a property.

The rate of reaction or the velocity of reaction at a specified time is defined as the decrease in the concentration of a reactant or the increase in the concentration of a product per unit time. The rate of reaction at a specified time is also known as instantaneous rate of reaction; it can be generally defined as the rate of change of concentration of a specified species at a particular instant. While specifying the reaction rate, we must mention the component with respect to which it is stated. Let us consider a simple reaction,

$$A \rightarrow B$$

As per the reaction stoichiometry, one molecule of B is formed for every molecule of A consumed. The reaction rate can be specified in the following ways:

- We can measure the concentration of the reactant A at various time intervals. From these values, we can specify the decrease in concentration of A with respect to time at any particular instant. The reaction rate thus obtained is the rate of consumption of A.

$$\text{Rate of consumption of A} = \frac{\text{Decrease in the concentration of A}}{\text{Change in time}}$$

$$= \frac{-\Delta[A]}{\Delta t}$$

- $\Delta[A]$ means change in the concentration of A and $-\Delta[A]$ means the decrease in the concentration of A. While writing a rate expression with respect to a reactant, there is a preceding negative sign (since it is customary to express the rate of a reaction as a positive quantity).

- We can measure the concentration of the product B at various time intervals. From these values, we can arrive at the rate of formation of B at any particular instant.

$$\text{Rate of formation of B} = \frac{\text{Increase in the concentration of B}}{\text{Change in time}}$$

$$= \frac{\Delta[B]}{\Delta t}$$

The rates of consumption of reactants and the rates of formation of products are related through their stoichiometric coefficients. For example, consider the decomposition of NO_2.

$$2\,NO_2(g) \rightarrow 2\,NO(g) + O_2(g)$$

We can write the relationship between the rates of consumption of NO_2 and the rates of formation of NO and O_2 as follows:

$$\left.\begin{aligned} \frac{1}{2}\,(\text{Rate of consumption of } NO_2) &= \frac{1}{2}\,(\text{Rate of formation of NO}) \\ &= \text{Rate of formation of } O_2 \end{aligned}\right] \quad \ldots (18.1)$$

Using the convention as expressed by Eq. 18.2, we can write as shown below:

$$\text{Reaction rate} = \frac{1}{2}\left(\frac{-d[NO_2]}{dt}\right) = \frac{1}{2}\left(\frac{d[NO]}{dt}\right) = \left(\frac{d[O_2]}{dt}\right)$$

Convention For Expressing Reaction Rates

In order to obtain a single value for the reaction rate, it is necessary to divide the rate of consumption of a reactant or the rate of formation of a product by the stoichiometric coefficient of the respective species. To illustrate this, let us consider the reaction:

$$aA + bB \longrightarrow cC + dD$$

In this reaction, A and B are reactants, and C and D are products; a, b, c and d are the stoichiometric coefficients. The reaction rate is related to the rates of consumption of the reactants and the rates of formation of the products as follows:

Reaction rate

$$= \frac{1}{a}\left(\frac{-d[A]}{dt}\right) = \frac{1}{b}\left(\frac{-d[B]}{dt}\right)$$

$$= \frac{1}{c}\left(\frac{d[C]}{dt}\right) = \frac{1}{d}\left(\frac{d[D]}{dt}\right) \quad \ldots (18.2)$$

Using this general equation, you examine Eq. 18.1

The number preceding the formula of a substance in the balanced equation is its stoichiometric coefficient.

You can understand the above relationship if you bear in mind that if two molecules of NO_2 are consumed, two molecules of NO and one molecule of O_2 are formed. In other words, the reaction rate is equal to :

- half the rate of consumption of NO_2
- half the rate of formation of NO, and
- the rate of formation of O_2

Calculation of Reaction Rate

You may be curious to know as to how the reaction rates are calculated. Take for instance the following reaction:

$$2\,NO_2\,(g) \rightarrow 2\,NO\,(g) + O_2\,(g)$$

In Figs. 18.1 a, b and c, you can see concentration (c) against time (t) plots for NO_2, NO and O_2 as per the values given in Table 18.1. In these figures, the graphical method of calculation of the reaction rates for the consumption of NO_2 and for the formation of NO and O_2 are illustrated. The reaction rate at any particular instant is obtained by calculating the slope of a line tangent to the curve at that point.

From the slope of the tangent line drawn (corresponding to a particular time) to the concentration (c) against time (t) curve for a component, we can obtain the rate of the reaction.

Rate of reaction

$$= \frac{-(\text{Slope of tangent to the } c \text{ against } t \text{ curve for the reactant})}{\text{Stoichiometric coefficient of the reactant}}$$

$$= \frac{\text{Slope of tangent to the } c \text{ against } t \text{ curve for the product}}{\text{Stoichiometric coefficient of the product}}$$

Table 18.1: Concentrations of NO_2, NO and O_2 at Different Time Intervals at 673 K.

Time/s	$[NO_2]$/M	[NO]/M	$[O_2]$/M
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033

The concentrations of components are given in molarity (M) unit.

1 M = 1 mol dm^{-3}

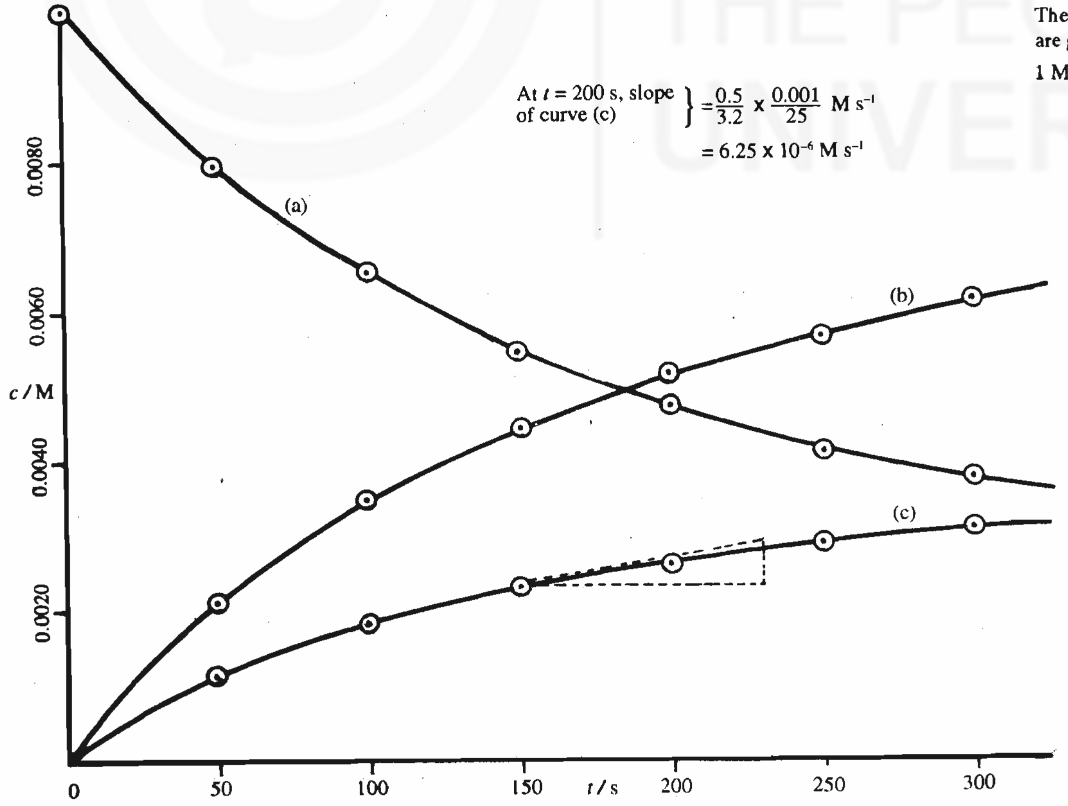

Fig: 18.1: a) Concentration against time plot for NO_2; note the falling nature of the curve which is characteristic of concentration against time plot for a reactant.

Rate of consumption of NO_2 at $t = 200$ s $= -$ Slope of the tangent line at $t = 200$ s

$= -(-1.31 \times 10^{-5})$ M s^{-1}

$= 1.31 \times 10^{-5}$ M s^{-1}

Reaction rate $= \frac{1}{2}$ (Rate of consumption of NO_2) $= \frac{1}{2} \times 1.31 \times 10^{-5}$ M s^{-1}

$= 6.55 \times 10^{-6}$ M s^{-1}

b) concentration against time plot for NO; note the rising nature of the curve which is characteristic of concentration against time plot for a product.

Rate of formation of NO at $t = 200$ s = Slope of the tangent line at $t = 200$ s

$= 1.30 \times 10^{-5}$ M s^{-1}

Reaction rate $= \frac{1}{2}$ (Rate of formation of NO)

$= 1/2 \times 1.30 \times 10^{-5}$ M s^{-1}

$= 6.50 \times 10^{-6}$ M s^{-1}

c) concentration against time plot for O_2; note again the rising curve.Compared to the curve for NO, the curve for O_2 rises slowly.

Rate of formation of O_2 at $t = 200$ s = Slope of the tangent line at $t = 200$ s

$= 6.25 \times 10^{-6}$ M s^{-1}

Reaction rate $=$ Rate of formation of O_2

$= 6.25 \times 10^{-6}$ M s^{-1}

For the curves (a) and (b), the tangents are not indicated.

From the slope values at $t = 200$ s , you can see that the following relationship is nearly correct.

Reaction rate $= \frac{1}{2}$ (Rate of consumption of NO_2) $= \frac{1}{2}$ (Rate of formation of NO)

$=$ Rate of formation of O_2

In our discussion, we are mainly interested in the concentration against time plots for the reactants. In other words, we want to study the reactions under conditions where the rate of the forward reaction is significant but the reverse reaction rate is low. This is made possible, if we study the reaction upto a point where the product amounts are not high. For example, in the decomposition of NO_2, there could be a decrease in the concentration of NO_2 upto a particular time. Afterwards, enough nitric oxide and oxygen are formed and the reverse reaction also could take place leading to the formation of NO_2. In order to simplify the situation, it is better to study the reaction rates before significant amounts of products are formed. In general, the rates of reactions are complex functions of the concentrations of the reactants and the products at a given temperature. However, there are some reactions in which the rates are proportional to the simple powers of the concentrations of the reactants. We shall be mostly concerned with this class of reactions.

Decomposition of N_2O_5

The decomposition of N_2O_5 in the gas phase was studied at 323 K.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

The instantaneous rates of this reaction calculated from $[N_2O_5]$ against time plot (similar to Fig. 18.1) are given in Table 18.2.

Table 18.2 : Rates for the Decomposition of N_2O_5 at 323 K

$[N_2O_5]$/M (i)	Rate/M s^{-1} (ii)	$\frac{\text{Rate}}{[N_2O_5]}$. s (iii)
0.300	2.73×10^{-4}	9.1×10^{-4}
0.150	1.37×10^{-4}	9.1×10^{-4}
0.100	9.10×10^{-5}	9.1×10^{-4}

From columns (i) and (ii), you can see that the rate for the decomposition of N_2O_5 decreases with the decrease in the concentration of N_2O_5. Further, column (iii) gives the ratio of the rate to the concentration of N_2O_5. In all the three cases, it is a constant. This shows that the rate is directly proportional to the concentration of N_2O_5

$$\text{i.e.,}\quad \frac{\text{Rate}}{[N_2O_5]} = k \qquad \text{... (18.3)}$$

$$\text{Hence, rate} = k\,[\,N_2O_5\,] \qquad \text{...(18.4)}$$

where k is proportionality constant.

Decomposition of Hydrogen Iodide

The decomposition of hydrogen iodide was followed at a constant temperature:

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

The instantaneous rates of this reaction were calculated using the [HI] against time plot like that of Fig.18.1. These values are given in Table 18.3.

Table 18.3: Rates for the Decomposition of HI

[HI]/M (i)	Rate/M s^{-1} (ii)	$\frac{\text{Rate}}{[HI]} \cdot s$ (iii)	$\frac{\text{Rate}}{[HI]^2} \cdot M\,s$ (iv)
3.00×10^{-2}	3.60×10^{-5}	1.2×10^{-3}	4.00×10^{-2}
2.00×10^{-2}	1.60×10^{-5}	8.0×10^{-4}	4.00×10^{-2}
1.50×10^{-2}	9.01×10^{-6}	6.0×10^{-4}	4.00×10^{-2}

From Table 18.3, you can see that the rate of decomposition of HI decreases with decrease in the concentration of HI, as in the case of the decomposition of N_2O_5. Further, it is evident from column (iii) that rate/[HI] is not a constant. But, as per column (iv), rate/[HI $]^2$ is a constant.

From Table 18.3, it is evident that

$$\text{Rate} / [\,HI\,]^2 = k \qquad \text{. . . (18.5)}$$

$$\text{Hence, rate} = k\,[\,HI\,]^2 \qquad \text{. . . (18.6)}$$

where k is a proportionality constant.

For many chemical reactions, the relationship between the reaction rate and the concentration can be expressed in a simple way as in Eq.18.4 or 18.6. We shall first consider these simple cases. Later we shall discuss those reactions for which the rate – concentration relationship is more complex.

Rate Law and Rate Constant

The relationship expressed as in Eq.18.4 or Eq.18.6 is called the **rate law**. **A rate law is an equation expressing the relationship between the instantaneous reaction rate and the concentrations of the reactants in a reaction.**

The rate law for a simple reaction with one reactant may be of the following type:

$$\text{Reaction rate} = k\,[\,\text{Reactant}\,]^n \qquad \text{. . . (18.7)}$$

where k is called the rate constant or rate coefficient or the specific rate of the reaction. Thus by definition, the rate constant is independent of concentration, but it may depend on other factors. In this equation, n refers to the order of the reaction. The **order** with respect to a component is the power to which the concentration of that component is raised in the rate law. Comparing Eq.18.7 with Eqs.18.4 and 18.6, we conclude that

From Eq. 18.7, it can be seen that if [reactant] = 1, then k = rate. For this reason, k is called the specific rate.

i) n =1 in Eq.18.4; i.e., decomposition of N_2O_5 is a **first order** reaction. The significance of this statement is that the reaction rate is proportional to the first power of concentration of N_2O_5.

$$\text{i.e., Rate} = k\,[\,N_2O_5\,]^1 \qquad \text{. . . (18.8)}$$

where k is the first order rate constant.

ii) $n = 2$ for the decomposition of HI; i.e., the decomposition of HI is a **second order reaction**. Again this means that the decomposition rate of HI is proportional to the second power or square of the concentration of HI.

$$\text{i.e., Rate} = k[\text{HI}]^2 \qquad \dots (18.9)$$

where k is the second order rate constant.

Order of Reaction and Stoichiometry

The rate laws as well as the order of the reaction must be determined experimentally; these cannot be predicted from the stoichiometry of the reaction. The stoichiometry of reaction gives the relationship between the amounts of the reactants and the amounts of the products. The stoichiometry of a reaction must be differentiated from the order of a reaction. Let us consider the following examples.

Example 1

The gas-phase decomposition of N_2O_5 yields NO_2 and O_2 at a particular temperature.

$$2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$$

The experimentally observed rate law for the reaction rate $= k[N_2O_5]$

Comment on the order and the stoichiometry of the reaction.

Solution

It can be seen that the stoichiometric coefficient of N_2O_5 is 2 whereas the order of reaction is 1.

Example 2

The balanced equation for the decomposition of nitrous oxide is given below:

$$2\,N_2O(g) \rightarrow 2\,N_2(g) + O_2(g)$$

The rate law is,

$$\text{rate} = k[N_2O]$$

Comment on the order of the reaction and the stoichiometry.

Solution

Again the stoichiometric coefficient of N_2O is 2 whereas the order of reaction is 1.

In the above two examples, the order of reaction and the stoichiometry are not identical. But there are cases where the order and stoichiometric coefficient are identical. One of the examples can be seen in the following reaction:

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

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

In the decomposition of HI, the order of reaction is two. The stoichiometric coefficient of HI is also 2.

From the above examples, you can see that the stoichiometric coefficient and the order of the reaction need not be the same always. You must bear in mind the following points while arriving at a rate law:

i) In the case of simple reactions, the concentrations of the reactants appear in rate law; but the concentrations of the products do not appear in the rate law. It is so since the rate measurements are done under the conditions where the reverse reaction rate is negligibly low.

ii) The order of the reaction must be determined experimentally; the experimental methods will be discussed in the next section.

iii) The order of a reaction need not be identical with the stoichiometric coefficient of the reactant.

So far we considered the reactions involving only one reactant. In case of reactions involving many reactants, the rate of a reaction may depend on the concentrations of more than one reactant. In such cases, we can calculate the order of the reaction with respect to the individual reactant and also the **overall order**. The overall order is the sum of the powers to which the individual concentrations are raised in the rate law.

In general, for a reaction,

$$A + B + C \rightarrow \text{products}$$

if the rate law is experimentally found to be,

$$\text{rate} = k[A]^m [B]^n [C]^p \qquad \ldots (18.10)$$

then, the overall order of the reaction $= m + n + p$.

For example in the following reaction,

$$BrO_3^-(aq) + 5\,Br^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O(l)$$

$$\text{Rate} = k[BrO_3^-][Br^-][H^+]^2 \qquad \ldots (18.11)$$

The overall rate of the reaction is four, being first order in BrO_3^-, first order in Br^- and second order in H^+

The rate laws discussed so far are called **differential rate laws**. Such rate laws describe the dependence of reaction rate on concentration. From these differential rate laws, we can obtain the **integrated rate laws** through integration. The integrated rate laws help us in relating the concentration of a substance to time. In other words, using the integrated rate laws, we can calculate the concentration of a substance at any specified time. In Secs.18.4 and 18.5, we shall discuss the derivation of the integrated forms of rate laws. In the next section, we shall discuss some experimental methods of studying the reaction rates.

For the $BrO_3^- - Br^- - H^+$ reaction let us compare the order of reaction and the stoichiometric coefficient for each reactant.

	BrO_3^-	Br^-	H^+
Order	1	1	2
Stoichiometric coefficient	1	5	6

It may be noticed that the stoichiometric coefficients and the respective orders of reaction are not identical throughout.

SAQ 1

At 323 K, the rate of reaction for the decomposition of N_2O_5 at a particular instant is 2.74×10^{-4} M s^{-1}. Calculate the rate of formation of O_2. The reaction is represented below:

$$2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$$

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SAQ 2

In the decomposition of hydrogen iodide, what is the relationship between the rate of decomposition of HI and the rate of formation of H_2 ?

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18.3 EXPERIMENTAL METHODS OF RATE STUDIES

Many physical and chemical methods are available for studying the reaction rates. Some of them are listed below:

i) **Volume or Pressure Measurement**

When one or more of the components are gases, the reaction rate can be followed by measuring the volume or pressure change. The partial pressures of the species are to be calculated using the reaction stoichiometry.

ii) **Titrimetry**

Using acid-base or oxidation-reduction titrations, the reaction course can be followed if atleast one of the components in the reaction is an acid or a base or an oxidising agent or a reducing agent.

iii) **Conductometry or Potentiometry**

If one or more of the ions are present or produced in the reaction, suitable methods can be designed based on conductivity or potentiometric measurements.

Spectrophotometers have arrangements for generation of nearly monochromatic radiation in visible and ultraviolet regions and also for the measurement of radiation transmitted by the absorbing substance.

iv) **Spectrophotometry**

When a component of the reaction has a strong absorption band at a particular wavelength region, spectrophotometers could be used for measuring the reaction rate. Photoelectric colorimeters are cheaper instruments and are mainly useful for reaction rate studies in visible region.

Nowadays many sophisticated instruments such as nuclear magnetic resonance spectrometer, mass spectrometer etc, are used in reaction kinetics. We shall not discuss these aspects.

v) **Polarimetry**

When atleast one of the components of a reaction is optically active, the reaction rate can be studied from the measurements of optical rotation.

Depending on the reaction under study, the concentration of a reactant or a product is followed at various time intervals using any of the methods mentioned above. These values are then used for calculating the rate constant. Examples are worked out in the next section to illustrate the rate constant calculation. Before studying these examples, we shall discuss the method of arriving at the integrated forms of rate laws.

SAQ 3

State the name of a suitable experimental method that can be followed to monitor the reaction rate in each of the following cases:

i) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

Hint : Bromine absorbs strongly in the visible region , while hydrogen and hydrogen bromide do not .

ii) $CH_3COOC_2H_5(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + C_2H_5OH(aq)$

iii) $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$ (at constant volume conditions)

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18.4 FIRST ORDER AND SECOND ORDER REACTIONS

In this section, we shall derive integrated rate laws for first and second order reactions.

Integrated Rate Law for First Order Reactions

Let us consider the following reaction, which is experimentally found to be first order.

$$A \rightarrow \text{Products} \qquad \ldots (18.12)$$

Applying Eq. 18.7 , we can write

$$\text{rate} = \frac{-d[A]}{dt} = k[A]^1 \qquad \ldots (18.13)$$

where k is the first order rate constant and $n = 1$. This means that the rate of consumption of A at any given time is directly proportional to the first power of the concentration of A at that time.

In order to obtain the integrated rate for first order reaction, we have to know the concentrations of A at the start of the reaction and at a time t as mentioned below:

At time = 0 (i.e. , at the start), the concentration of A = $[A]_0$

At time = t, the concentration of A = $[A]_t$

Using these limits of concentration and time, we can integrate Eq.18.13 after rearranging it as follows:

$$\int_{[A]_0}^{[A]_t} -\frac{d[A]}{[A]} = \int_o^t k\,dt \qquad \ldots (18.14)$$

$$\text{i.e.,} -\Big\{\ln [A]\Big\}_{[A]_0}^{[A]_t} = k\,[\,t\,]_0^t \qquad \ldots (18.15)$$

$$-\Big\{\ln [A]_t - \ln [A]_0\Big\} = k\,(\,t - 0\,) \qquad \ldots (18.16)$$

$$\ln [A]_0 - \ln [A]_t = kt \qquad \ldots (18.17)$$

$$\text{Hence, } \ln \frac{[A]_0}{[A]_t} = kt \qquad \ldots (18.18)$$

In order to understand the transformation of Eq. 18.14 into Eq. 18.16, refer to Sec. 6.6 of Unit 6 of this course.

Eq. 18.18 can be written in the exponential form as follows:

$$[A]_t = [A]_0\, e^{-kt} \qquad \ldots (18.19)$$

The transformation of Eq. 18.18 into Eq. 18.19 could be explained as follows :

$$\ln \frac{[A]_0}{[A]_t} = k\,t \qquad \ldots (18.18)$$

$$-\ln \frac{[A]_t}{[A]_0} = k\,t$$

$$\ln \frac{[A]_t}{[A]_0} = -k\,t$$

Taking antilogarithms,

$$\frac{[A]_t}{[A]_0} = e^{-kt}$$

$$[A]_t = [A]_0\, e^{-kt} \qquad \ldots (18.19)$$

Corresponding to Eq. 18.19, we can draw the concentration vs. time plot for a first order reaction. This curve is of the type shown in Fig.18.2. Such a curve is called an exponential decay curve. In an exponential decay curve, there is a steep decrease in concentration initially. It is followed by a slow decrease in concentration subsequently. Note that the decay curve goes parallel to x - axis after longer time intervals indicating that the reaction will take infinite time for completion.

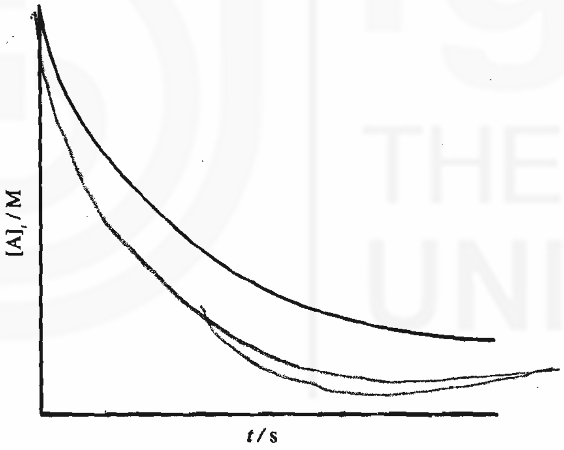

Fig. 18.2 : Exponential decay of A.

Radioactive decay is a good example of first order reaction. A detailed discussion on radioactive decay has been given in Unit 9 of "Atoms and Molecules" course.

Let us come back to Eq. 18.18. It is more convenient to work with **logarithms** to the base 10 (known as common logarithms). Hence we can rewrite Eq.18.18 as follows:

$$2.303 \;\log \frac{[A]_0}{[A]_t} = kt$$

or

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t} \qquad \ldots (18.20)$$

Remember the following formula :
$\ln x = 2.303 \;\log x$

Eq.18.20 is useful in calculating the concentration of the reactant at a time t (i.e., $[A]_t$ provided, its initial concentration (i.e., $[A]_0$), k and t are known. Also, k can be calculated, if $[A]_0$, $[A]_t$ and t are known. Using the graphical method, we can test whether a reaction follows first order or not.

Graphical Method of Calculating First Order Rate Constant

In order to facilitate graphical representation, Eq.18.20 is modified as follows:

$$\log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = \frac{kt}{2.303} \qquad \ldots(18.21)$$

Hence $$\log [\mathrm{A}]_0 - \log [\mathrm{A}]_t = \frac{kt}{2.303} \qquad \ldots(18.22)$$

i.e., $$-\log [\mathrm{A}]_t = \frac{kt}{2.303} - \log [A]_0 \qquad \ldots(18.23)$$

$$\log [\mathrm{A}]_t = \frac{-k}{2.303} t + \log [A]_0 \qquad \ldots(18.24)$$

By comparing Eq. 18.24 with the equation for a straight line,

$$y = mx + c,$$

we can infer that by plotting log $[\mathrm{A}]_t$ against time, a straight line must be obtained for a first order reaction. Such plots are shown in Figs. 18.3-18.5. The rate constant can be calculated from the slope as follows :

$$k = -2.303 \times \text{slope} \qquad \ldots(18.25)$$

From Eq. 18.21, we can derive Eq.18.27 by substituting the concentrations of A at time intervals t_1 and t_2 as follows :

At time $= t_1$,

concentration of A $= [\mathrm{A}]_1$.

At time $= t_2$,

concentration of A $= [\mathrm{A}]_2$

$$\log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_1} = \frac{k t_1}{2.303}$$

$$\log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_2} = \frac{k t_2}{2.303}$$

Hence,

$$\log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_2} - \log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_1} = \frac{k}{2.303}(t_2 - t_1) \qquad \ldots(18.26)$$

i.e., $$\log \frac{[A]_1}{[A]_2} = \frac{k}{2.303}(t_2 - t_1) \qquad \ldots(18.27)$$

Knowing the concentration of a reactant undergoing first order reaction at a particular time, it is possible to calculate its concentration at another time interval using Eq.18.27.

$$\log \frac{[\mathrm{A}]_1}{[\mathrm{A}]_2} = \frac{k}{2.303}(t_2 - t_1) \qquad \ldots(18.27)$$

The following hints may be useful while calculating the rate constants using the integrated rate law:

i) If the concentrations of the reactant are given at various time intervals, the concentration at $t = 0$ is equal to $[\mathrm{A}]_0$ and the concentration at any given time is $[\mathrm{A}]_t$; log $[\mathrm{A}]_t$ against t plot is made as described earlier. This principle is followed in Example 3.

ii) Instead of giving the concentrations of a reactant at various time intervals, parameters such as partial pressures, absorbances, volumes, titre values etc. which are proportional to the concentration of the reactant may be given. In these cases, the measurements made at zero time and at any given time t may be used instead of $[\mathrm{A}]_0$ and $[\mathrm{A}]_t$. For example, we can substitute the partial pressure of the reactant instead of its concentration in Eq.18.21 and obtain Eq. 18.28.

$$\log \frac{(p_{\mathrm{A}})_0}{(p_{\mathrm{A}})_t} = \frac{kt}{2.303} \qquad \ldots(18.28)$$

where $(p_{\mathrm{A}})_0$ and $(p_{\mathrm{A}})_t$ are the partial pressures of the reactant at the start and, after a time, t. In Example 4, we use this method.

iii) Sometimes the rate measurements are made in terms of the concentrations of the product formed. If the stoichiometry of the reaction is such that one molecule of the product is formed when one molecule of the reactant is consumed, then the concentration of the product at $t = \infty$ must be equal to initial concentration of the reactant. Let us assume that the concentration of the product at any given time is x. Then x also represents the decrease in the concentration of the reactant after a time, t. Thus, $[\mathrm{A}]_0$ = concentration of the product at $t = \infty$ and $[\mathrm{A}]_t = [\mathrm{A}]_0 - x$. Using these relationships, Eq.18.21 could be written as,

$$\log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_0 - x} = \frac{kt}{2.303} \qquad \ldots(18.29)$$

Calculation of this type is illustrated in Example 5.

Let us work out some examples to illustrate the calculation of k by graphical method.

Example 3

On heating cyclopropane to 770 K, it is converted into propene. In one experiment, the following data were obtained:

t/ s	0	300	600	900
[Cyclopropane]/M	1.50×10^{-3}	1.24×10^{-3}	1.00×10^{-3}	8.3×10^{-4}

Using graphical method, test whether the above data satisfy first order rate equation. Calculate the rate constant.

Solution

Using the data, log [cyclopropane]/M values are calculated and tabulated alongwith t values.

log [cyclopropane]/M	− 2.82	− 2.91	− 3.00	− 3.08
t/s	0	300	600	900

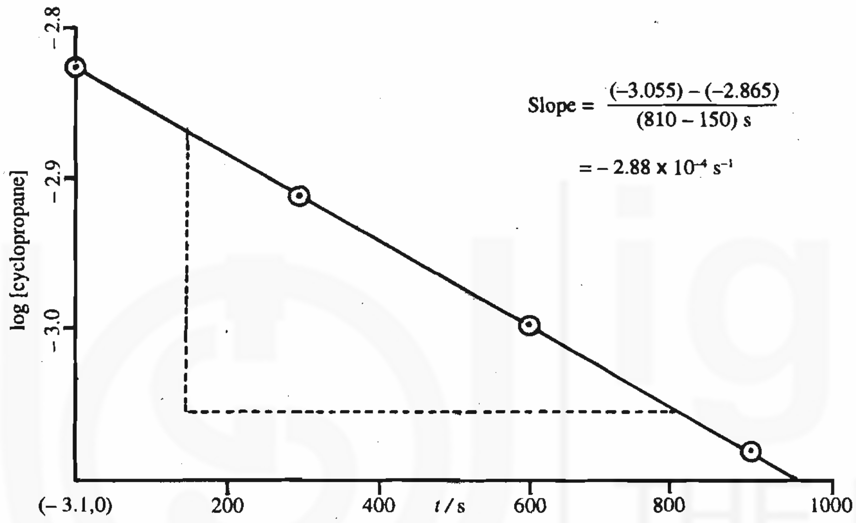

Fig. 18.3: log [cyclopropane] against t plot.

log [cyclopropane] vs. t plot is shown in Fig.18.3.

The graph is a straight line, confirming that the reaction is first order.

$$k = -2.303 \times \text{slope} = -2.303 \times (-2.88 \times 10^{-4})\ s^{-1}$$
$$= 6.63 \times 10^{-4}\ s^{-1}$$

Example 4

Azomethane ($CH_3 - N = N - CH_3$) decomposes at 600 K as per the equation:

$$CH_3 - N = N - CH_3\,(g) \rightarrow C_2H_6\,(g) + N_2\,(g)$$

The reaction rate was followed by measuring the partial pressure of azomethane (p_A) at different time intervals and the data are given below:

p_A / Pa	10.9	7.6	5.3	3.7	2.6
t / s	0	1000	2000	3000	4000

Using the data, test whether the reaction follows first order kinetics and calculate the rate constant.

Solution

Using Eq.2.41 of Unit 2 of this course, the concentration of azomethane (c_A) can be related to its partial pressure (p_A) as follows:

$$p_A = c_A RT \text{ or } p_A \propto c_A$$

So we can use partial pressure of azomethane in Eq.18.21 instead of concentration as shown in Eq.18.28. Rearranging Eq.18.28, we get,

$$\log\,(p_A)_t = \log\,(p_A)_0 - \frac{kt}{2.303}$$

where $(p_A)_0$ and $(p_A)_t$ are the partial pressures of azomethane at the start, and after a time, t. We tabulate the data accordingly:

$\log\,(p_A)_t$/Pa	1.04	0.88	0.72	0.57	0.41
t / s	0	1000	2000	3000	4000

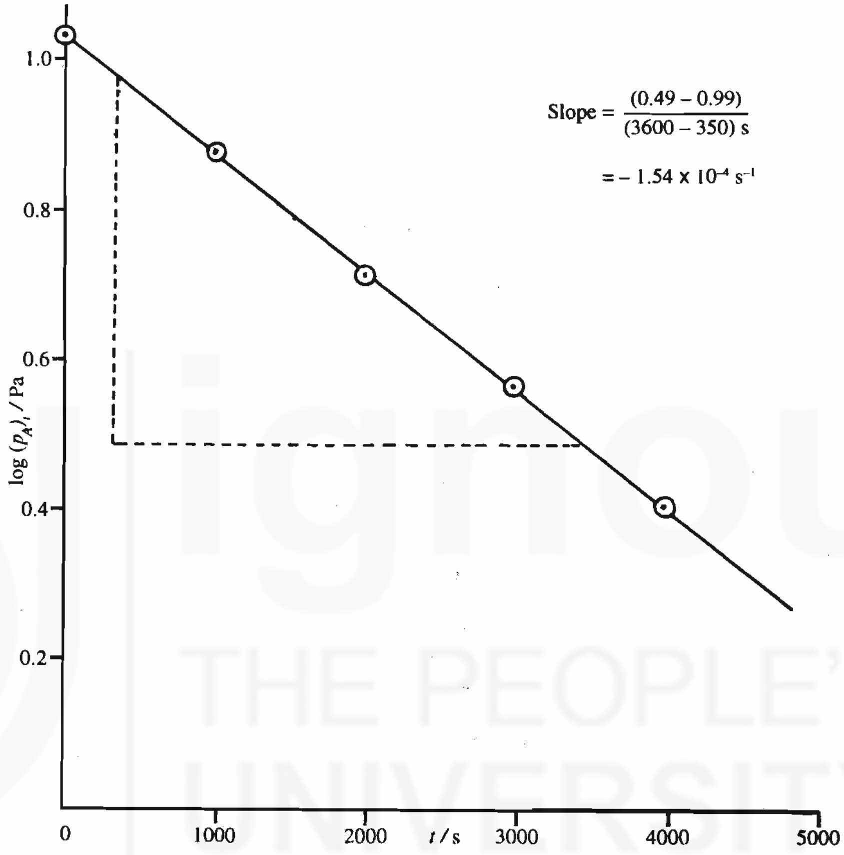

Fig.18.4 : log $(p_A)_t$ against t plot for the decomposition of azomethane.

$\log\,(p_A)_t$ is plotted against t as shown in Fig.18.4.

From Fig.18.4, we see that the graph is a straight line. Hence, the decomposition of azomethane is a first order reaction.

$$\text{Slope} = -1.54 \times 10^{-4}\,\text{s}^{-1}$$

$$k = -2.303 \times \text{slope} = -2.303 \times (-1.54 \times 10^{-4}\,\text{s}^{-1})$$

$$= 3.55 \times 10^{-4}\,\text{s}^{-1}$$

Example 5

The hydrolysis rate of benzene diazonium chloride ($C_6H_5N = NCl$) in its aqueous solution was followed by measuring the volume of nitrogen evolved at different time intervals. The reaction was found to be first order. Using the data given below, calculate the first order rate constant.

Time / s	0	1500	3000	4500	∞
$\frac{\text{Volume of N}_2}{\text{cm}^3}$	0	6.4	12.1	17.6	**81**

Solution

In this example, the rate measurement is done in terms of the product. The volume (V_t) of nitrogen produced at any given time, t, is proportional to the concentration of benzene diazonium chloride reacted (x). The volume at $t = \infty$ (i.e. ,V_∞) indicates the volume of nitrogen produced by the complete hydrolysis of benzene diazonium chloride and, it is proportional to the initial concentration of benzene diazonium chloride.

So, $$[A]_0 \propto V_\infty$$

$$x \propto V_t$$

and $$[A]_0 - x \propto V_\infty - V_t$$

Hence $$\frac{[A]_0}{[A]_0 - x} = \frac{V_\infty}{V_\infty - V_t}$$

Using this relationship in Eq.18.29,

$$\log \frac{V_\infty}{V_\infty - V_t} = \frac{kt}{2.303}$$

i.e., $$\log (V_\infty - V_t) = \log V_\infty - \frac{kt}{2.303}$$

Using the data given above, ($V_\infty - V_t$) and log ($V_\infty - V_t$) values are tabulated for different t values.

Time / s	0	1500	3000	4500
$(V_\infty - V_t)/\text{cm}^3$	81	74.6	68.9	63.4
$\log (V_\infty - V_t)/\text{cm}^3$	1.908	1.873	1.838	1.802

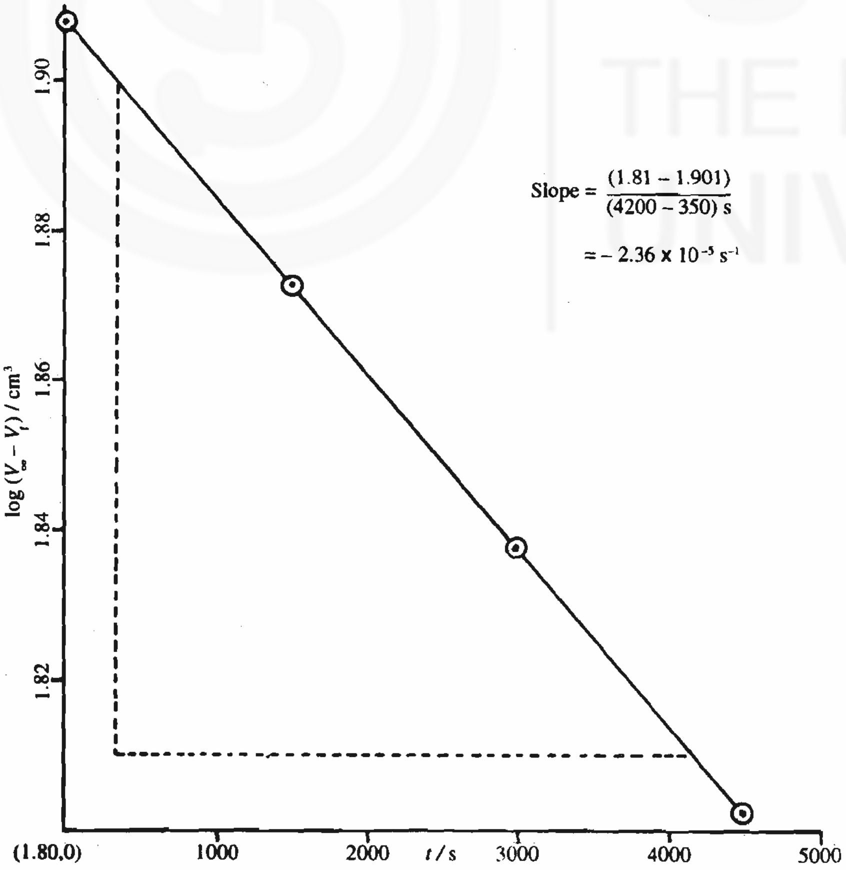

Fig.18.5: log ($V_\infty - V_t$) against t plot for the hydrolysis of benzene diazonium chloride.

$\log(V_\infty - V_t)$ is plotted against t as shown in Fig.18.5.

From Fig. 18.5,

$$\text{slope} = -2.36 \times 10^{-5}\ \text{s}^{-1}$$

$$k = -2.303 \times \text{slope}$$

$$= -2.303 \times (-2.36 \times 10^{-5}\ \text{s}^{-1})$$

$$= 5.44 \times 10^{-5}\ \text{s}^{-1}$$

Half-Life of First Order Reactions

The time taken for the concentration of a reactant to fall to half its initial value is called the half-life of a reaction. It is denoted by the symbol, $t_{1/2}$. We can derive an expression useful in calculating the half-life of a substance undergoing first order reaction using Eq.18.21.

$$\log \frac{[\text{A}]_0}{[\text{A}]_t} = \frac{kt}{2.303} \qquad \ldots(18.21)$$

We must bear in mind that when

$$t = t_{1/2},\ [\text{A}]_t = [\text{A}]_0/2$$

Using these relationships in Eq. 18.21, we get,

$$\log \frac{[\text{A}]_0}{[\text{A}]_0/2} = \frac{kt_{1/2}}{2.303}$$

i.e.,

$$\log 2 = \frac{kt_{1/2}}{2.303}$$

or

$$t_{1/2} = \frac{2.303 \log 2}{k} = \frac{0.693}{k} \qquad \ldots(18.30)$$

In a first order reaction, the amount of the reactant remaining after n half-life periods is given by the formula :

$$\begin{Bmatrix}\text{Concentration}\\ \text{of the reactant}\\ \text{remaining after}\\ n\ \text{half-lives}\end{Bmatrix} = \left(\frac{1}{2}\right)^n \times \begin{Bmatrix}\text{Initial}\\ \text{concentration}\\ \text{of the}\\ \text{reactant}\end{Bmatrix} \qquad \ldots(18.31)$$

From Eq.18.30, we understand that $t_{1/2}$ does not depend on initial concentration of the substance in the case of a first order reaction. This means that for a given first order reaction, half-life period is the same, whatever be the initial concentration. This leads to an interesting result that the time taken for the changes in the concentrations of the reactant such as,

$$[\text{A}]_0 \rightarrow [\text{A}]_0/2$$

or

$$[\text{A}]_0/2 \rightarrow [\text{A}]_0/4$$

or

$$[\text{A}]_0/4 \rightarrow [\text{A}]_0/8$$

is the same. The half-life periods required to bring about decrease in concentration of a reactant upto 12.5% of its initial concentration can be represented as in Fig.18.6.

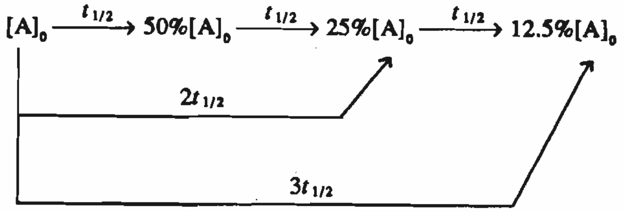

Fig.18.6: Change in % [A]$_0$ over the first three half-life periods of a first order reaction; $t_{1/2}$ is the half-life period for the conversion, [A]$_0$ → 50% [A]$_0$.

Example 6

The first-order rate constant for the decomposition of N_2O_5 at 340 K is $5.20 \times 10^{-3}\ s^{-1}$. Calculate the time required for the concentration of N_2O_5 to fall to (a) one-half and (b) one-fourth of its initial value.

Solution

a) Using Eq. 18.30, $t_{1/2} = \frac{0.693}{k}$

$$= \frac{0.693}{5.20 \times 10^{-3}\ s^{-1}}$$

$$= 133\ s$$

Hence, time taken for the concentration of N_2O_5 to decrease by 50% is 133 s.

b) The time required for the decrease in the concentration of N_2O_5 to 25% of its initial value is twice the half-life period, i.e., 266 s.

Having studied the equations useful in calculating the first order rate constant and the half-life period of the reactant, let us derive similar equations for second order reactions.

Integrated Rate Laws for Second Order Reactions

There are two types of second order reactions.

i) A single reactant could give rise to products through a second order reaction.

$$A \rightarrow \text{Products} \qquad \ldots(18.32)$$

The rate equation is

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^2 \qquad \ldots(18.33)$$

where k is the second order rate constant.

Two examples of this type are given below:

$$2\,NO_2(g) \rightarrow 2\,NO(g) + O_2(g)$$

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

ii) Two different reactant molecules could react to give products through a second order reaction.

$$A + B \rightarrow \text{Products} \qquad \ldots(18.34)$$

The rate equation is,

$$\text{reaction rate} = k[A]\,[B] \qquad \ldots(18.35)$$

Examples of this type are given below. Note that the stoichiometric ratio of the reactants is 1:1.

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

$$CH_3Br\,(aq) + OH^-(aq) \rightarrow CH_3OH\,(aq) + Br^-(aq)$$

$$CH_3COOC_2H_5\,(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + C_2H_5OH\,(aq)$$

Again the study of these reactions could be simplified if the initial concentrations of both the reactants ($[A]_0$ and $[B]_0$) are the same. i.e.,

i.e. $\quad [A]_0 = [B]_0$ and so $[A] = [B]$

where $[A]$ and $[B]$ are concentrations of the reactants at any given time, t.

Then, Eq.18.35 takes the same form as Eq.18.33.

$$\text{Rate} = \frac{-d[\mathrm{A}]}{dt} = k[\mathrm{A}][\mathrm{B}] = k[\mathrm{A}][\mathrm{A}]$$

$$= k[\mathrm{A}]^2 \qquad \ldots(18.33)$$

Thus, we could see that the rate equation takes the same form for a second order reaction, if the reaction is

i) second order in a single reactant or

ii) first order in each of the two reactants such that the concentrations of the two are same throughout the reaction.

We use Eq.18.33 as the rate law for both these two types. We derive the integrated rate law for these two under case (i).

Case (i): Integrated Rate Law for a Reaction that Follows Differential Rate Law as per Eq.18.33

We start with the differential rate law,

$$-\frac{d[A]}{dt} = k[\mathrm{A}]^2 \qquad \ldots(18.33)$$

The integrated form of this equation can be obtained using the following limiting conditions:

At time = 0 (i.e., at the start), the concentration of A = $[\mathrm{A}]_0$. At time = t, the concentration of A = $[\mathrm{A}]_t$.

Applying these limits on the rearranged form of Eq.18.33, we get,

$$-\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = \int_0^t k dt \qquad \ldots(18.36)$$

i.e.,

$$-\left[-\frac{1}{[\mathrm{A}]}\right]_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} = k(t-0) \qquad \ldots(18.37)$$

$$-\left[\frac{-1}{[\mathrm{A}]_t} + \frac{1}{[\mathrm{A}]_0}\right] = kt \qquad \ldots(18.38)$$

$$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = kt \qquad \ldots(18.39)$$

or

$$\frac{1}{[\mathrm{A}]_t} = \frac{1}{[\mathrm{A}]_0} + kt \qquad \ldots(18.40)$$

The second order rate constant can be calculated by plotting $1/[\mathrm{A}]_t$ against t. A straight line curve must be obtained, if the reaction is second order in the reactant. The slope of the straight line gives the second order rate constant.

$$k = \text{Slope} \qquad \ldots(18.41)$$

We shall later illustrate this method in Example 8.

Each successive half-life is double the preceding half-life in a second order reaction. In a first order reaction, all successive half-life periods are same.

Half-Life of a Second Order Reaction

For reactions following second order rate as per Eq.18.33, an equation could be derived which is useful in calculating the half-life period.

At the half-life period ($t = t_{½}$), $[\mathrm{A}]_t = [\mathrm{A}_0]/2$. Using this in Eq.18.40,

$$\frac{1}{[\mathrm{A}]_0/2} = \frac{1}{[\mathrm{A}]_0} + kt_{½}$$

i.e.,

$$\frac{2}{[\mathrm{A}]_0} = \frac{1}{[\mathrm{A}]_0} + kt_{½}$$

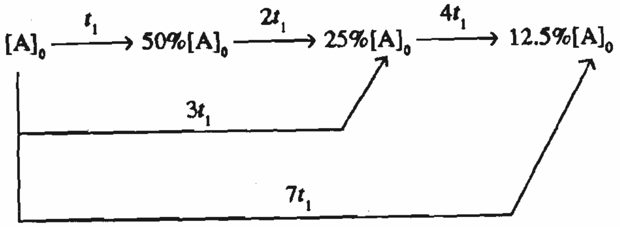

Fig.18.7: Change in % [A]₀ over three successive half-lives in a second order reaction; t_1 refers to half-life for the change in concentration from $[A]_0$ to $50\%[A]_0$

$$t_{½} = \frac{1}{k[A]_0} \qquad \ldots (18.42)$$

From Eq.18.42, we understand that $t_{½}$ is inversely proportional to initial concentration for a second order reaction. As initial concentration of the reactant decreases, $t_{½}$ increases. If for the decrease in concentration of A to 50% of its initial value, time required is 100 s, then for the change from 50% A to 25% A, it will require 200 s.

Three successive half-lives for a second order reaction can be represented by Fig.18.7.

Example 7

At 700 K, the second order rate constant for the reaction,

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

is $1.83 \times 10^{-3}\ M^{-1}\ s^{-1}$. Calculate the time taken for 1.00×10^{-2} M HI to fall to (a) one-half and (b) one-eighth of its initial concentration.

Solution

a) Using Eq. 18.42, $t_{½} = \frac{1}{k[A]_0} = \frac{1}{1.83 \times 10^{-3} \times 1.00 \times 10^{-2}}$ s

$$= 5.46 \times 10^{4}\ s.$$

Time needed for the decrease in concentration of HI to one-eighth of its initial value is seven times the value calculated above as shown in Fig.18.7; i.e., time needed is 3.82×10^{5} s.

Now we derive the integrated rate law for a reaction that is second order overall and is first order in each of the two reactants having different initial concentrations.

Case (ii): Integrated Rate Law for a Reaction that Follows Rate Law as per Eq.18.35

Let us start the reaction between A and B with different initial concentrations, $[A]_0$ and $[B]_0$. Let these two react to give products as per the rate law given in Eq.18.35.

$$A + B \rightarrow \text{Products} \qquad \ldots (18.34)$$

$$\text{Reaction rate} = k[A][B] \qquad \ldots (18.35)$$

For simplicity we have taken the reaction in which the stoichiometric coefficients of the reactants are same. But similar methods can be followed for reactions with different stoichiometric coefficients.

As per the reaction stoichiometry, A and B react in the ratio 1:1. After t seconds, let the concentrations of A and B be $[A]_0 - x$ and $[B]_0 - x$.

Hence, the reaction rate $= \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = k[A][B]$

i.e. $$\frac{-d\{[A]_0 - x\}}{dt} = k\{[A]_0 - x\}\{[B]_0 - x\}$$

i.e., $$\frac{-d[A]_0}{dt} + \frac{dx}{dt} = k\{[A]_0 - x\}\{[B]_0 - x\}$$

So
$$\frac{dx}{dt} = k\{[A]_0 - x\}\{[B]_0 - x\} \qquad ...(18.43)$$

$$\frac{d[A]_0}{dt} = 0 \text{ since } [A]_0 \text{ is a constant.}$$

In order to get the integrated form, we have to transform Eq.18.43 as shown below:

$$\frac{dx}{\{[A]_0 - x\}\{[B]_0 - x\}} = k dt \qquad ...(18.44)$$

Let us write the expression, $\frac{1}{\{[A]_0 - x\}\{[B]_0 - x\}}$ as follows:

$$\frac{1}{\{[A]_0 - x\}\{[B]_0 - x\}} = \frac{p}{\{[A]_0 - x\}} + \frac{q}{\{[B]_0 - x\}} \qquad ...(18.45)$$

i.e.,
$$\frac{1}{\{[A]_0 - x\}\{[B]_0 - x\}} = \frac{p\{[B]_0 - x\} + q\{[A]_0 - x\}}{\{[A]_0 - x\}\{[B]_0 - x\}}$$

In other words, $p\{[B]_0 - x\} + q\{[A]_0 - x\} = 1$ ...(18.46)

Put $x = [A]_0$, then $p\{[B]_0 - [A]_0\} = 1$

or
$$p = \frac{1}{[B]_0 - [A]_0} \qquad ...(18.47)$$

Hence,
$$p = -\frac{1}{[A]_0 - [B]_0} \qquad ...(18.48)$$

Put $x = [B]_0$ in Eq.18.46.

Hence $q\{[A]_0 - [B]_0\} = 1$

or
$$q = \frac{1}{[A]_0 - [B]_0} \qquad ...(18.49)$$

From Eqs. 18.45, 18.48 and 18.49,

$$\frac{1}{\{[A]_0 - x\}\{[B]_0 - x\}} = -\frac{1}{\{[A]_0 - [B]_0\}\{[A]_0 - x\}} + \frac{1}{\{[A]_0 - [B]_0\}\{[B]_0 - x\}} \qquad ...(18.50)$$

We have adopted the **partial fraction procedure** in the above steps.

Using Eq.18.50 in Eq.18.44,

$$-\frac{dx}{\{[A]_0 - [B]_0\}\{[A]_0 - x\}} + \frac{dx}{\{[A]_0 - [B]_0\}\{[B]_0 - x\}} = k dt \qquad ...(18.51)$$

You can see that the two terms in the L.H.S. of Eq.18.51 contain either $\{[A]_0 - x\}$ or $\{[B_0] - x\}$ in the denominator. The splitting of the expression in L.H.S of Eq.18.44 through partial fraction method facilitates usage of Formula 2 of Sec.6.6 of Unit 6 for integration.

At time = 0, $x = 0$ ("x" denotes the change in concentration of A or B due to reaction)

At time = t, $x = x_t$

$$\int_0^{x_t} \frac{dx}{\{[A]_0 - [B]_0\}\{[B]_0 - x\}} - \int_0^{x_t} \frac{dx}{\{[A]_0 - [B]_0\}\{[A]_0 - x\}} = k\int_0^t dt \qquad ...(18.52)$$

$$\frac{1}{[A]_0 - [B]_0}\Big[-\ln([B]_0 - x)\Big]_0^{x_t} - \frac{1}{[A]_0 - [B]_0}\Big[-\ln([A]_0 - x)\Big]_0^{x_t} = kt \qquad ...(18.53)$$

$$\frac{-1}{[A]_0 - [B]_0}\{\ln([B]_0 - x_t) - \ln[B]_0\} + \frac{1}{[A]_0 - [B]_0}\{\ln([A]_0 - x_t) - \ln[A]_0\}$$

$$= kt$$

$$\frac{1}{[A]_0-[B]_0}\ \ln\ \frac{([A]_0-x_t)\,[B]_0}{([B]_0-x_t)\ [A]_0} = k\,t \qquad \ldots(18.54)$$

$$\log\ \frac{([A]_0-x_t)\,[B]_0}{([B]_0-x_t)\ [A]_0} = \frac{k\{[A]_0-[B]_0\}}{2.303}\ t \qquad \ldots(18.55)$$

$$\log\ \frac{[A]_0-x_t}{[B]_0-x_t} = \log\ \frac{[A]_0}{[B]_0} + \frac{k([A]_0-[B]_0)}{2.303}\ t \qquad \ldots(18.56)$$

By plotting $\log \frac{[A]_0-x_t}{[B]_0-x_t}$ against t, a straight line is obtained. The slope of the straight line is equal to $\frac{k([A]_0-[B]_0)}{2.303}$.

$$k = \frac{2.303 \times \text{slope}}{([A]_0-[B]_0)} \qquad \ldots(18.57)$$

Let us discuss the saponification of ester as an example for the calculation of second order rate constant. The hydrolysis of ester by an alkali is called saponification. For example, the saponification of methyl acetate can be represented by the following equation:

The name saponification is derived from the fact that soaps are produced by the hydrolysis of esters of long-chain fatty acids using alkalies.

$$CH_3COOCH_3 + OH^- \rightarrow CH_3COO^- + CH_3OH$$

The saponification rate is studied as follows. A reaction mixture is prepared with known concentrations of alkali and ester. At regular intervals, certain volume of the solution is withdrawn and titrated against standard HCl. From the titre values, the concentrations of the unreacted alkali and the unreacted ester could be determined at various time intervals.

The rate constant can be determined using,

i) Eqs.18.40 and 18.41, if the initial concentrations of ester and alkali are same;

ii) Eqs.18.56 and 18.57, if their initial concentrations are different.

Now study the following example.

Example 8

The saponification of methyl acetate using sodium hydroxide was studied at 298 K. The initial concentrations of the alkali and ester in the reaction mixture were both 1.00×10^{-2} M. The reaction rate was followed by titration of a definite volume of the reaction mixture with standard HCl. The concentrations of unreacted alkali, $[A]_t$, at various time intervals are given below:

Time / s	240	550	720	1000	1550
$10^3\,[A]_t/M$	6.85	4.81	4.17	3.38	2.49

$1/[A]_t$ is calculated in each case as shown in the following example:

$10^3[A]_t/M = 6.85$;

$[A]_t/M = 6.85 \times 10^{-3}$

$$\frac{1}{[A]_t}M = \frac{1}{6.85 \times 10^{-3}} = \frac{1000}{6.85} = 146$$

Calculate the second order rate constant.

Solution

Since the initial concentrations of the alkali and the ester are same, we can use Eqs.18.40 and 18.41 for solving this problem. We tabulate $\frac{1}{[A]_t}$ values against various time intervals as follows:

$\frac{1}{[A]_t}$ M	146	208	240	296	402
t / s	240	550	720	1000	1550

Note the unit for the slope of the curve in Fig. 18.8.

$$\text{Unit of slope} = \frac{\text{Unit of } 1/[A]_t}{\text{Unit of } t} = M^{-1}\ s^{-1}$$

As suggested by Eq.18.40, $1/[A]_t$ against t plot is a straight line (Fig.18.8) showing that the saponification of methyl acetate follows second order kinetics.

$$\text{Using Eq.18.41, } k = \text{Slope}$$

$$= 0.194 \text{ M}^{-1}\text{ s}^{-1}.$$

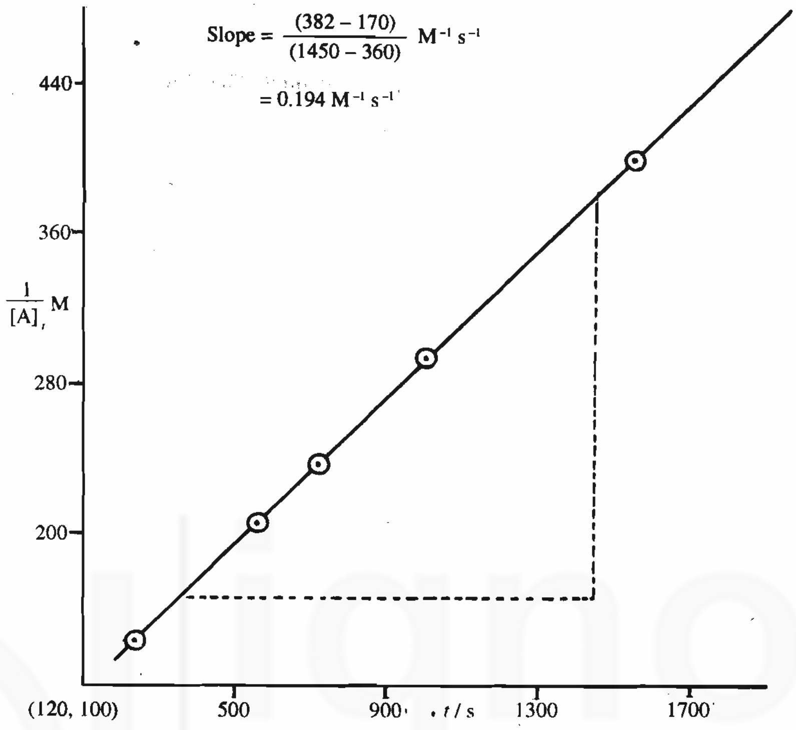

Fig. 18.8: $1/[A]_t$ against t plot for the saponification of methyl acetate.

Having some experience with the differential and the integrated forms of rate laws for first order and second order reactions, we shall discuss zeroth order reactions in the next section. Also, we shall give some examples of third order reactions.

SAQ 4

State the units of the rate constants for zeroth order, first order and second order reactions. The rate of reaction is measured in M s^{-1} units.

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SAQ 5

The decomposition of HI is a second order reaction. At 700 K, the rate constant for the reaction is 1.83×10^{-3} M^{-1} s^{-1}. If the initial concentration of HI is 1.00×10^{-2} M, calculate its concentration after 1.68×10^{5} s.

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18.5 ZEROTH ORDER AND THIRD ORDER REACTIONS

Let us study zeroth order reactions.

Zeroth order reaction is generally a heterogeneous reaction.

Zeroth Order Reactions

The rate law for a zeroth order reaction is of the following form,

$$-\frac{d[A]}{dt} = k[A]^0 = k \qquad \ldots(18.58)$$

since $[A]^0 = 1$

In a zeroth order reaction, the reaction rate is independent of the concentrations of the reactant.

Some examples of zeroth order reactions are given below:

i) Decomposition of ammonia on a hot platinum surface.

$$2\,NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$$

ii) Decomposition of nitrous oxide on a hot platinum surface.

$$2\,N_2O(g) \xrightarrow{Pt} 2N_2(g) + O_2(g)$$

iii) Decomposition of hydrogen iodide on finely divided gold at 320 K.

$$2\,HI(g) \xrightarrow{Au} H_2(g) + I_2(g)$$

Let us derive the integrated rate law for a zeroth order reaction.

Integrated Rate Law for Zeroth Order Reaction

Let us consider the zeroth order reaction:

$$A \rightarrow \text{Products}$$

Let the concentration of A at the start be $[A]_0$ and its concentration at the time t be $[A]_t$. The integrated form of Eq.18.58 can be derived as follows:

$$\int_{[A]_0}^{[A]_t} -d[A] = \int_0^t k\,dt \qquad \ldots(18.59)$$

$$-\Big\{[A]\Big\}_{[A]_0}^{[A]_t} = k(t-0)$$

$$-[A]_t + [A]_0 = kt$$

i.e., $[A]_0 - [A]_t = kt$

or $$[A]_t = [A]_0 - kt \qquad \ldots(18.60)$$

On plotting $[A]_t$ against t, a straight line is obtained for a zeroth order reaction. The slope is equal to $-k$.

$$k = -\text{Slope} \qquad \ldots(18.61)$$

Example 9

The decomposition of hydrogen iodide on gold at 323 K is zeroth order reaction and the rate constant is $1.20 \times 10^{-4}\ M\ s^{-1}$.

a) If the initial concentration of hydrogen iodide is 0.500 M, calculate its concentration after 3.00×10^3 s.

b) How long will it take for all of the hydrogen iodide to decompose?

Solution

(a) Using Eq.18.60, $[A]_t = [A]_0 - kt$

$$= (0.500 - (1.20 \times 10^{-4} \times 3.00 \times 10^3))\ M$$

$$= 0.140\ M$$

(b) If hydrogen iodide completely decomposes, then $[\,\mathrm{A}\,]_t = 0$

or
$$t = \frac{[\,\mathrm{A}\,]_0}{k} = \frac{0.500 \text{ M}}{1.20 \times 10^{-4} \text{ M s}^{-1}}$$
$$= 4.17 \times 10^{3} \text{ s}$$

Hence, the reaction will be complete after 4.17×10^3s.

Half-Life of a Zeroth Order Reaction

As discussed for first and second order reactions,

$$[\,\mathrm{A}\,]_t = [\,\mathrm{A}\,]_0/2 \text{ when } t = t_{1/2}$$

Hence, Eq.18.60 becomes,

$$[\,\mathrm{A}\,]_0/2 = [\,\mathrm{A}\,]_0 - kt_{1/2}$$

or
$$kt_{1/2} = [\,\mathrm{A}\,]_0/2$$
$$t_{1/2} = \frac{[\,\mathrm{A}\,]_0}{2\,k} \qquad \ldots (18.62)$$

This means that the half-life of a zeroth order reaction is directly proportional to the initial concentration of the reactant.

Example 10

Calculate the half-life for the decomposition of hydrogen iodide on gold at 323 K. Use the data from Example 9.

Solution

Using the data from Example 9 in Eq.18.62,

$$t_{1/2} = \frac{[\,\mathrm{A}\,]_0}{2\,k} = \frac{0.500 \text{ M}}{2 \times 1.20 \times 10^{-4} \text{ M s}^{-1}} = 2.08 \times 10^{3} \text{ s}$$

From Examples 9 and 10, you can understand that the zeroth order reaction is complete in two half-lives as shown in Fig.18.9.

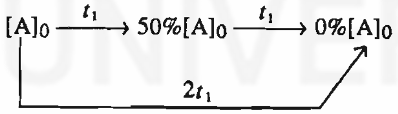

Fig.18.9: Completion of a zeroth order reaction; t_1 is the time taken for both the conversions, $[\,\mathrm{A}\,]_0 \rightarrow 50\%[\,\mathrm{A}\,]_0$ and $50\%[\,\mathrm{A}\,]_0 \rightarrow 0\%[\,\mathrm{A}\,]_0$.

Third Order Reactions

There are a few third order reactions. Two examples are given below:

$$2\,\mathrm{NO}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\,\mathrm{NO_2}\,(g)$$

$$2\,\mathrm{NO}\,(g) + \mathrm{Br_2}\,(g) \rightarrow 2\,\mathrm{NOBr}\,(g)$$

The methods of arriving at differential and integrated rate laws for third order reactions are similar to those of first and second order reactions. We are not going to discuss the same.

SAQ 6

Using the data in Example 9, calculate the time required for the decomposition of HI on gold at 323 K to proceed to 75%.

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18.6 PSEUDO FIRST ORDER REACTIONS

One of the ways of simplifying the study of reactions involving more than one reactant is to study under pseudo first order conditions. For example, consider the reaction:

$$CH_3Br\,(aq) + OH^-\,(aq) \rightarrow CH_3OH\,(aq) + Br^-\,(aq) \qquad \ldots (18.63)$$

$$\text{Reaction rate} = k\,[CH_3Br]\,[OH^-] \qquad \ldots (18.64)$$

If the concentrations of CH_3Br and OH^- are comparable, then the reaction is second order overall as indicated by Eq.18.64. Suppose that the concentration of OH^- is much larger (say, 10 times or more) than the concentration of CH_3Br. In such cases the concentration of OH^- does not change much during the reaction and can be considered constant. Hence, the reaction rate depends on the concentration of CH_3Br only .

$$\text{Reaction rate} = k'\,[CH_3Br]$$

where $k' = k\,[OH^-]$; k' is the pseudo first order rate constant. The reaction can be treated as first order for calculation purposes. Hence, the integrated rate law is similar to Eq.18.21. .

$$\log \frac{[CH_3Br]_0}{[CH_3Br]_t} = \frac{k't}{2.303}$$

In general, the reactions like the above which are effectively first order due to large excess of one of the reactants are called pseudo first order reactions.

Let us discuss the following two reactions which are studied under pseudo first order conditions.

i) **Acid Hydrolysis of Ester**

The hydrolysis of ethyl acetate in presence of a mineral acid (say, HCl) can be represented by the following equation:

$$CH_3COOC_2H_5 + H_2O + H_3O^+ \rightarrow CH_3COOH + C_2H_5OH + H_3O^+$$

The reaction rate depends on [ester], [water] and [H_3O^+]. Here H_3O^+ ion is a catalyst. Since the concentration of the catalyst does not change during the reaction, and water is present in large amount, the reaction becomes pseudo first order in ester.

$$\text{Rate} = k'\,[\text{ester}]$$

where k' includes concentrations of water and H_3O^+. If the reaction is carried out in a solvent other than water, the first order dependence on [water] also could be seen.

The pseudo first order rate constant is determined by titrating a definite volume of the reaction mixture containing ester and to HCl with standard alkali. Let V_0, V_t and V_∞ be the volumes of standard alkali at the start, after a time t and after the completion of the reaction.

Infinite reading (V_∞) is usually taken after heating the reaction mixture for a few minutes or after keeping the reaction mixture at the experimental temperature for a long time.

V_∞ = Volume of alkali equivalent to i) acetic acid liberated after the completion of the reaction and ii) HCl present.

V_t = Volume of alkali equivalent to i) acetic acid produced at the time t and ii) HCl present.

V_0 = Volume of alkali equivalent to HCl only.

Since the concentration of HCl is constant throughout the experiments,

$[A]_0$ (i.e, Initial concentration of ester) $\propto (V_\infty - V_0)$

and $[A]_t$ (i.e, Concentration of ester remaining unreacted at t) $\propto (V_\infty - V_t)$

We can calculate pseudo first order rate constant for the acid hydrolysis of ethyl acetate by using the following modified form of Eq.18.21.

$$\frac{k't}{2.303} = \log \frac{[A]_0}{[A]_t} = \log \frac{V_\infty - V_0}{V_\infty - V_t} \qquad \ldots (18.65)$$

where k' is the pseudo first order rate constant.

ii) Inversion of Sucrose

The hydrolysis of sucrose to form glucose and fructose in presence of mineral acid is similar to the acid hydrolysis of ester as far as the reaction kinetics is concerned.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O + H_3O^+ \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} + H_3O^+$$

Sucrose turns the plane-polarised light to the right, (i.e., it is dextro rotatory). Glucose also turns the plane-polarised light to the right, while fructose turns it to the left (i.e., it is laevo rotatory). On completion of the reaction, the reaction mixture is laevo rotatory, since the angle of rotation is more for fructose than for glucose. To start with, the reaction mixture is dextrorotatory due to sucrose. Thus, the completion of reaction (infinite reading) is marked by the change in the sign of rotation. Due to this reason, the reaction is called inversion of sucrose.

If r_0, r_t and r_∞ are the angles of rotation at the beginning, after time t and after completion of the reaction, then the pseudo first order rate constant (k') for the inversion of sucrose is given by,

$$k' = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty} \qquad \ldots (18.66)$$

Eq. 18.66 is a modified form of Eq. 18.21, where $[\,A\,]_0$ is proportional to $(r_0 - r_\infty)$ and $[\,A\,]_t$ and is proportional to $(r_t - r_\infty)$.

SAQ 7

Give the details of the graphical method of obtaining the pseudo first order rate constant for

i) acid hydrolysis of ethyl acetate

ii) inversion of sucrose.

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18.7 DETERMINING THE ORDER OF REACTION

In order to write the rate law, we must know the order of reaction with respect to each reactant. In this section, we discuss some methods for determining the order of reaction.

1) **Method of Initial Rates**

The instantaneous rate of reaction extrapolated to the instant when the reagents were just mixed is called the initial rate of the reaction. Let us consider the reaction,

$$A + B \rightarrow \text{Products}$$

Let the rate of reaction be represented as,

$$v = k[\,A\,]^m[\,B\,]^n$$

where the reaction is m^{th} order in A and n^{th} oder in B. The rate constant for the reaction is k. We have to obtain the initial rates from atleast two experiments in which the initial concentrations of A (a_1 and a_2) are different while the initial concentration of B (b_1) is constant.

Extrapolation is the process of extending a curve upto a desired x or y coordinate to obtain the corresponding y or x value.

$$\text{Rate in Experiment I} = v_1 = k\,a_1^m\,b_1^n$$

$$\text{Rate in Experiment II} = v_2 = k\,a_2^m\,b_1^n$$

From the ratio $\frac{v_1}{v_2}$, we can calculate m, since a_1 and a_2 are known.

Initial reaction rate, could be graphically arrived at by plotting the concentration of a reactant against time. The tangent to the concentration curve is drawn at the very start of the reaction and its slope is calculated. The negative of the slope value is the initial rate.

$$\frac{\text{Rate in Experiment I}}{\text{Rate in Experiment II}} = \frac{v_1}{v_2} = \frac{k\,a_1^m\,b_1^n}{k\,a_2^m\,b_1^n} = \left(\frac{a_1}{a_2}\right)^m \qquad \ldots (18.67)$$

Taking logarithms we can write,

$$\log \frac{v_1}{v_2} = m \log \frac{a_1}{a_2} \qquad \ldots (18.68)$$

Similarly, the rate is measured for one more experiment in which the initial concentration of A is a_2 and the initial concentration of B is b_2.

So, rate in Experiment III = $v_3 = k\, a_2^m\, b_2^n$

$$\frac{\text{Rate in Experiment II}}{\text{Rate in Experiment III}} = \frac{v_2}{v_3} = \frac{k\, a_2^m\, b_1^n}{k\, a_2^m\, b_2^n} = \left(\frac{b_1}{b_2}\right)^n \qquad \ldots (18.69)$$

$$\text{i.e., } \log \frac{v_2}{v_3} = n \log \frac{b_1}{b_2} \qquad \ldots (18.70)$$

Since v_2, v_3, b_1 and b_2 are known, n can be calculated. The overall reaction order = $m + n$. You can understand this method from the following example.

Example 11

For the reaction, $Cl_2(g) + 2\,NO(g) \rightarrow 2\,NOCl(g)$, the initial concentrations, $[Cl_2]_0$ and $[NO]_0$ are given along with initial rates.

$$\text{Rate} = \frac{-d[Cl_2]}{dt}$$

$[Cl_2]_0$/M	$[NO]_0$/M	Initial rate / M s^{-1}
0.10	0.10	3.0×10^{-3}
0.20	0.10	6.0×10^{-3}
0.20	0.20	2.4×10^{-2}

Calculate (i) order of the reaction with respect to each of the reactants and the overall order; (ii) what is the rate law? (iii) calculate the rate constant.

Solution

i) We can write the rate law as $k\,[Cl_2]^m\,[NO]^n$.

Similar to Eqs. 18.68 and 18.70, we can write the logarithmic ratios and, calculate m and n as follows:

$$v_1 = k\,(0.10)^m\,(0.10)^n = 3.0 \times 10^{-3}\ \text{M s}^{-1}$$

$$v_2 = k\,(0.20)^m\,(0.10)^n = 6.0 \times 10^{-3}\ \text{M s}^{-1}$$

$$v_3 = k\,(0.20)^m\,(0.20)^n = 2.4 \times 10^{-2}\ \text{M s}^{-1}$$

$$\text{Using Eq. 18.68,} \quad m = \frac{\log \dfrac{3.0 \times 10^{-3}}{6.0 \times 10^{-3}}}{\log \dfrac{0.10}{0.20}} = \frac{\log \dfrac{6.0}{3.0}}{\log \dfrac{0.20}{0.10}} = 1$$

$$\text{Using Eq. 18.70,} \quad n = \frac{\log \dfrac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}}}{\log \dfrac{0.10}{0.20}} = \frac{\log \dfrac{24}{6.0}}{\log \dfrac{0.20}{0.10}} = 2$$

Hence, the reaction is second order in NO and first order in Cl_2. The overall order is 2 + 1 = 3.

ii) The rate law is given below:

$$\text{Rate} = k\,[Cl_2]\,[NO]^2$$

iii) The rate constant can be calculated using any one of the three rates given above.

$$v_1 = 3.0 \times 10^{-3}\ \mathrm{M\ s^{-1}} = k\,(0.10\ \mathrm{M})\,(0.10\ \mathrm{M})^2$$

$$k = \frac{3.0 \times 10^{-3}}{(0.10)^3}\ \mathrm{M^{-2}\,s^{-1}} = 3.0\ \mathrm{M^{-2}\,s^{-1}}$$

Care must be taken in applying the method of initial rates. For complex reactions like the formation of HBr (discussed in the next section) the product also affects the rate. The method of initial rates is applicable to simple reactions only.

Clock Reactions

In the case of some reactions, the time taken for the colour change of the reaction mixture can be used for measuring the initial rate. Such self-indicating reactions are known as clock reactions. For example, the kinetics of the reaction,

Only those reactions in which the reaction mixture undergoes a colour change can be used as clock reactions. The colour change may be due to a reactant or a product or an added indicator.

$$2\,KI + K_2S_2O_8 \rightarrow 2\,K_2SO_4 + I_2$$

Potassium
perdisulphate

can be monitored as a clock reaction. A reaction mixture is prepared using potassium perdisulphate and potassium iodide in a higher concentration and sodium thiosulphate in much lower concentration. A drop of starch is also present in the reaction mixture. The reaction mixture is colourless in the beginning and it turns blue after some time.

$1/\Delta t$ is a measure of the initial rate.

The time, Δt, between the mixing of the reactants and the appearance of blue colour is noted. The blue colour develops due to the liberation of free iodine, after sodium thiosulphate (present in less concentration) is consumed completely as per the reaction:

$$2\,Na_2S_2O_3 + I_2 \rightarrow 2\,NaI + Na_2S_4O_6$$

Sodium
tetrathionate

The order of the reaction with respect to KI (m) and the order of the reaction with respect to $K_2S_2O_8$ (n) can be calculated by using the following formula:

$$\log(1/\Delta t) = m \log[\mathrm{KI}] + n \log[K_2S_2O_8] + \text{constant}$$

A plot of $\log(1/\Delta t)$ against log [KI] is made using Δt values obtained by varying [KI] and keeping $[K_2S_2O_8]$ constant. The slope of the straight line gives m. Similarly n is obtained from the slope of the straight line got by plotting $\log(1/\Delta t)$ against $\log[K_2S_2O_8]$. For the second plot, Δt is obtained by varying $[K_2S_2O_8]$ and keeping [KI] constant. Experimentally it has been found that $m = 1$ and $n = 1$.

$$\text{Hence, } \frac{-\mathrm{d}[K_2S_2O_8]}{\mathrm{d}t} = k\,[\mathrm{KI}]\,[K_2S_2O_8]$$

For clock reactions, two more examples are given below:

1) Acid catalysed iodination of acetone

2) Saponification of ester (using phenolphthalein indicator).

Some methods of studying fast reactions will be discussed in Sec. 18.12.

2) Trial and Error Method

We can determine the order of reaction

i) by substitution of experimental data into Eqs. 18.21, 18.40 and 18.60, or

ii) by graphical method using plots such as log [A] against t, 1/[A] against t and [A] against t. The order of the reaction is one, two or zero depending on

  i) which of the equations gives rise to a constant value for k or

  ii) which of the plots gives a straight line.

3) Half-Life Method

The half-lives are determined using different initial concentrations of the reactant. If the half-life is independent of initial concentration, the reaction is first order. If the half-life is inversely proportional to the first power of initial concentration, the reaction is second order. If the half-life is directly proportional to the first power of initial concentration, the reaction is zeroth order.

In general, half-life period (t) is proportional to $[\mathrm{A}]_0^{1-n}$ where $[\mathrm{A}]_0$ is the initial concentration of the reactant and n is the order of the reaction.

If the half-life periods are t_1 and t_2 corresponding to the initial concentrations $[\mathrm{A}]_1$ and $[\mathrm{A}]_2$ of a reactant, then

$$\frac{t_2}{t_1} = \left(\frac{[\mathrm{A}]_2}{[\mathrm{A}]_1}\right)^{1-n} = \left(\frac{[\mathrm{A}]_1}{[\mathrm{A}]_2}\right)^{n-1}$$

$$n-1 = \frac{\log t_2/t_1}{\log [\mathrm{A}]_1/[\mathrm{A}]_2}$$

or

$$n = 1 + \frac{\log t_2/t_1}{\log [\mathrm{A}]_1/[\mathrm{A}]_2} \qquad \text{...(18.71)}$$

Example 12

For the decomposition of acetaldehyde in gas-phase at 791 K, the half-life periods are 328 s and 572 s corresponding to the initial concentrations 9.72×10^{-3} M and 4.56×10^{-3} M. What is the order of the reaction?

Solution

Using Eq. 18.71,

$$n = 1 + \frac{\log 572/328}{\log 9.72 \times 10^{-3}/4.56 \times 10^{-3}} = 1 + \frac{0.2415}{0.3287} = 1.735$$

The order of the reaction is 1.735. Note that the order of the reaction is fractional.

4. Isolation Method

In the case of reactions having more than one reactant, the rate law can be simplified if the concentrations of all reactants except one are taken in excess. The reaction rate then depends on the reactant present in lesser quantity. The order of the reaction is determined by one of the methods given above. It is equal to the order in the reactant present in lesser quantity. This procedure is repeated in turn with each of the reactants being in lesser amount while others are in excess. This procedure is called van't Hoff's isolation method.

For example, consider the reaction,

$$\mathrm{A} + \mathrm{B} \rightarrow \text{Products}$$

for which the rate law is,

$$\text{rate} = k[\mathrm{A}]^m[\mathrm{B}]^n \qquad \text{...(18.72)}$$

In the first set of experiments B is in excess as compared to A, such that the rate depends on A only.

Hence, the rate $= k_1[\mathrm{A}]^m$ ...(18.73)

where $k_1 = k\,(\text{Initial concentration of B})^n$ ...(18.74)

Since B is in excess as compared to A, the concentration of B almost remains a constant throughout the experiment. From the rate measurements, m can be found out using graphical method.

In the second set of experiments, [A] is much large as compared to [B]. The rate measurements are made and using the rate law stated below, n is calculated.

$$\text{rate} = k_2[\mathrm{B}]^n \qquad \text{...(18.75)}$$

Where $k_2 = k\,(\text{Initial concentration of A})^m$ ...(18.76)

The overall order of the reaction is $m + n$.

SAQ 8

For the alkaline hydrolysis of ethyl nitrobenzoate, the half-life periods and the initial concentrations are given below:

$[A]_0/10^{-2}$ M	5.00	4.00
$t_{½}$/s	240	300

Calculate the order of reaction.

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18.8 SOME REACTION MECHANISMS

Many chemical reactions take place through a series of steps. Each step is known as an **elementary reaction.** A **reaction mechanism** is a series of elementary reactions proposed for explaining the rate law for the overall reaction. The elementary reactions are written as chemical equations. Such chemical equations give a possible explanation for the reaction path.

For an elementary reaction, the molecularity is the same as the order of reaction.

The rate law for each elementary reaction can be written using **molecularity**. The molecularity is the number of reactant molecules or atoms in an elementary reaction. If there is only one reactant molecule (or atom) in an elementary reaction, the reaction is said to be unimolecular. An elementary reaction in which two molecules (or atoms) react is called a bimolecular reaction. Most reaction mechanisms consider mainly unimolecular and bimolecular reactions. The chance of termolecular reactions (where three species are to combine) occurring is much less, because the probability of three species colliding simultaneously is quite low. An example each for unimolecular and bimolecular reactions is given below:

Unimolecular Reaction

$$O_3\,(g) \rightarrow O_2\,(g) + O\,(g) \qquad ...(18.77)$$

A unimolecular reaction has a first order rate law, hence, the rate of decomposition of O_3 could be represented as follows:

$$\text{Rate} = k\,[O_3] \qquad ...(18.78)$$

Bimolecular Reaction

$$O_3\,(g) + O\,(g) \rightarrow 2O_2\,(g) \qquad ...(18.79)$$

A bimolecular reaction has an overall second order rate law, being first order in each reactant. Hence, for the elementary reaction given in Eq.18.79, rate can be expressed as follows:

$$\text{Rate} = k\,[O]\,[O_3] \qquad ...(18.80)$$

Some of the guidelines followed in suggesting a reaction mechanism are given below:

1) The elementary reactions when added must be equal to the overall balanced chemical equation for the reaction.

   For example, the overall reaction in the decomposition of O_3 in the upper atmosphere is,

   $$2O_3\,(g) \rightarrow 3O_2(g) \qquad ...(18.81)$$

   This reaction could be taken as the result of the following two elementary reactions:

   Step (i) : $O_3\,(g) \rightarrow O_2\,(g) + O\,(g)$ ...(18.77)

   Step (ii) : $O_3\,(g) + O\,(g) \rightarrow 2O_2\,(g)$ ...(18.79)

   Overall reaction: $2O_3\,(g) \rightarrow 3O_2\,(g)$ (same as in Eq. 18.81)

2) While writing such a mechanism, one possible support is proving the presence of **intermediates**. For example, in the mechanism suggested above, atomic oxygen is an intermediate. Such intermediates can be detected by physical or chemical methods. They are generally reactive species. Further an intermediate is produced and ultimately used up.

3) The mechanism must agree with the overall rate law determined experimentally. In other words, the rate laws for the elementary reactions must be combined in such a

way that the overall rate law is explained. In order to accomplish this, we must be able to decide the **rate determining step** . Out of the elementary reactions suggested, the slowest one is called the rate determining step. The overall reaction rate cannot be faster than the slowest step in a mechanism. The rate determining step decides the rate of the overall reaction.

For example, in the mechanism suggested for the decomposition of ozone, step ii (i.e., Eq.18.79) is possibly the rate determining step. We shall explain this shortly.

4) The possibilities of both forward and reverse reactions occurring fast must also be considered. That is, the possibility of a dynamic equilibrium must also be examined. This is one of the ways to

- find a suitable relationship for expressing the concentration of an intermediate and
- eliminate the term denoting the concentration of the intermediate from the rate expression for the overall reaction.

5) Kinetic information can only support a proposed mechanism; it should not be taken as a proof since a mechanism cannot be proved absolutely.

Only a few guidelines are given here for proposing a reaction mechanism. However, these are sufficient for studying the reaction mechanisms of simple reactions.

The studies on organic and inorganic reaction mechanisms have led to the growth of separate branches of chemistry. You are advised to take up the course on Organic Reaction Mechanisms; if you desire to study theories of organic reactions.

Now, we shall discuss the reaction mechanisms involving

- a fast equilibrium followed by a slow step,
- a slow step followed by a fast step, and
- a chain reaction.

We shall also state the following types with an example in each case without discussing the reaction mechanisms.

- Consecutive reactions,
- Opposing reactions, and
- Parallel reactions

Example 13

For the decomposition of O_3,

$$2O_3\,(g) \rightarrow 3O_2\,(g) \qquad \text{...(18.81)}$$

the overall rate law is given below:

$$\text{Overall rate} = k\frac{[O_3]^2}{[O_2]} \qquad \text{...(18.82)}$$

Suggest a possible mechanism to explain the observed rate law.

Solution

You can see that the overall rate contains the term for the concentration of oxygen which is a product. This indicates that the mechanism consists of more than one step. A possible mechanism is suggested through Eqs.18.83 and 18.79.

$$\text{Step i): } O_3\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2\,(g) + O\,(g) \qquad \text{(fast)} \qquad \text{...(18.83)}$$

$$\text{Step ii): } O_3\,(g) + O\,(g) \xrightarrow{k_2} 2O_2\,(g) \qquad \text{(slow)} \qquad \text{...(18.79)}$$

Note that the addition of Eq.18.79 and the forward reaction of Eq.18.83 gives the overall balanced equation as per Eq.18.81. In the mechanism suggested above, k_1 and k_{-1} are the rate constants for the forward and the reverse reactions as per Eq.18.83; k_2 is the rate constant for the reaction as per Eq.18.79.

As per the mechanism suggested above,

$$\text{Overall rate} = k_2 [\mathrm{O_3}][\mathrm{O}] \qquad ...(18.80)$$

Now we shall eliminate [O] in Eq. 18.80. For this purpose, we shall assume the following:

$$\text{Rate of formation of O} = \text{Rate of Consumption of O} \qquad ...(18.84)$$

i.e.,

$$k_1 [\mathrm{O_3}] = k_{-1} [\mathrm{O_2}][\mathrm{O}] + k_2 [\mathrm{O_3}][\mathrm{O}] \qquad ...(18.85)$$

This assumption is valid because [O] is extremely small at any given time. Its variation with time (d [O]/d*t*) is still small and it may be taken to be zero. This type of assumption is called steady-state approximation and we shall discuss it in Sec. 18.9.

The above equation is written on the basis of the proposed mechanism which implies that oxygen atom is formed in the forward reaction of step (i) and is consumed in the reverse reaction of step (i) and, in step (ii). The forward and reverse reactions as per step (i) are much faster than the reaction as per step (ii). In other words, $k_2 [\mathrm{O_3}][\mathrm{O}]$ is negligibly smaller than $k_{-1} [\mathrm{O}][\mathrm{O}]$.

Hence, Eq.18.85 becomes,

$$k_1 [\mathrm{O_3}] = k_{-1} [\mathrm{O_2}][\mathrm{O}] \qquad ...(18.86)$$

or

$$[\mathrm{O}] = \frac{k_1 [\mathrm{O_3}]}{k_{-1} [\mathrm{O_2}]} \qquad ...(18.87)$$

Using Eq.18.87 in Eq.18.80,

$$\text{Overall rate} = k_2 [\mathrm{O_3}][\mathrm{O}]$$

$$= \frac{k_1 k_2}{k_{-1}} \frac{[\mathrm{O_3}][\mathrm{O_3}]}{[\mathrm{O_2}]} \qquad ...(18.88)$$

$$\text{i.e., overall rate} = k \frac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]} \qquad ...(18.89)$$

where k is the composite rate constant since it combines the rate constants, k_1, k_2 and k_{-1} as per the equation,

$$k = \frac{k_1 k_2}{k_{-1}} \qquad ...(18.90)$$

You can see that Eq.18.89 is the same as Eq.18.82.

Example 14

The rate expression for the reaction,

$$\mathrm{NO_2}\,(g) + \mathrm{CO}\,(g) \rightarrow \mathrm{NO}\,(g) + \mathrm{CO_2}\,(g) \qquad ...(18.91)$$

is given below:

$$\text{Overall rate} = k [\mathrm{NO_2}]^2 \qquad ...(18.92)$$

Spectroscopically $\mathrm{NO_3}$ radical has been detected. Suggest a mechanism in keeping with these facts.

Solution

While suggesting the mechanism, the following facts must be borne in mind:

i) The stoichiometry for the overall reaction must be as per Eq.18.91.

ii) As per Eq.18.92, the rate does not depend on [CO] but depends on $[\mathrm{NO_2}]^2$. This means that the reaction consists of more than one step and CO does not take part in the rate determining step.

iii) NO_3 is a probable intermediate in the reaction. Keeping in view the above features, the following mechanism is proposed:

Step i): $NO_2\,(g) + NO_2\,(g) \rightarrow NO_3\,(g) + NO\,(g)$ (slow) ...(18.93)

Step ii) : $NO_3\,(g) + CO\,(g) \rightarrow NO_2\,(g) + CO_2\,(g)$ (fast) ...(18.94)

Overall reaction: $NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$

The stoichiometry is as per Eq.18.91. Since [CO] does not appear in the rate expression, step (i) is assumed to be slower than step (ii). It is also assumed that the intermediate, NO_3, is consumed at a faster rate than it is formed. In other words,

i.e., Overall rate = Rate of formation of NO_3

$$\left.\begin{array}{l}\text{But rate of formation of}\\ NO_3\text{ (as per Eq. 18.93)}\end{array}\right] = k\,[\,NO_2\,]^2$$

Hence, the overall rate $= k\,[NO_2]^2$

which is same as Eq.18.92.

Example 15

The rate law for the reaction between hydrogen and bromine is quite complex as given by Eq.18.96.

$$H_2\,(g) + Br_2\,(g) \rightarrow 2HBr\,(g) \qquad ...(18.95)$$

$$\frac{d\,[\,HBr\,]}{dt} = \frac{k\,[\,H_2\,]\,[\,Br_2\,]^{1/2}}{1 + \dfrac{k'\,[\,HBr\,]}{[\,Br_2\,]}} \qquad ...(18.96)$$

Suggest a mechanism which could explain the above rate law.

Solution

To explain the rate law, a reaction sequence is proposed as follows:

$Br_2 \xrightarrow{k_1} 2Br$ Chain initiation ...(18.97)

$Br + H_2 \xrightarrow{k_2} HBr + H$ ...(18.98)

$H + Br_2 \xrightarrow{k_3} HBr + Br$ Chain propagation ...(18.99)

$H + HBr \xrightarrow{k_4} H_2 + Br$ ...(18.100)

$2Br \xrightarrow{k_5} Br_2$ Chain termination ...(18.101)

The rate of reaction can be represented by Eq.18.102, noting that HBr is formed as per Eqs.18.98 and 18.99 and consumed as per Eq.18.100.

$$\frac{d\,[\,HBr\,]}{dt} = k_2\,[\,Br\,]\,[\,H_2\,] + k_3\,[\,H\,]\,[\,Br_2\,] - k_4\,[\,H\,]\,[\,HBr\,] \qquad ...(18.102)$$

The negative sign preceding $k_4\,[\,H\,]\,[\,HBr\,]$ in Eq.18.102 is due to the consumption of HBr as per Eq.18.100. The reaction sequence given above is an example of a chain reaction. In a chain reaction, an intermediate reacts to produce another intermediate. For example, Br, a radical intermediate produced as per Eq.18.97 reacts with H_2 to produce another radical intermediate, H. Again H reacts with Br_2 as per Eq.18.99 to give Br and so on. Reaction represented by Eq.18.97 is the **chain initiation** reaction, since it is the start of the chain reaction. Reactions such as Eqs.18.98-18.100 are known as **chain propagation** reactions. Although Eq.18.100 represents a propagation reaction in producing Br, it also results in the consumption of HBr. For the latter reason, Eq.18.100 represents an **inhibiting reaction.** Eq.18.101 is a **chain terminating reaction** since the intermediates combine to give a molecule.

Often an intermediate in a chain reaction is a free radical. A free radical is an atom or a fragment of a molecule and has an unpaired electron.

To simplify Eq.18.102, we must express [H] and [Br] in terms of [Br_2], [H_2] and [HBr]. Such a step is required since the concentrations of the intermediates are not easy to measure whereas the concentrations of the reactants and products could be measured. Such a simplification is possible assuming that the net rates of formations of intermediates are equal to zero.

i.e.,
$$\frac{d[\,Br\,]}{dt} = 0 \qquad ...(18.103)$$

and
$$\frac{d[\,H\,]}{dt} = 0 \qquad ...(18.104)$$

As per the elementary reactions given above, Br is formed as per Eqs.18.97, 18.99 and 18.100; Br is consumed as per Eqs.18.98 and 18.101. Also two bromine atoms are formed as per Eq.18.97 for every bromine molecule dissociated and two bromine atoms are consumed as per Eq.18.101 for every bromine molecule formed. Using these ideas and Eq.18.103, we can write,

$$\frac{d[\,Br\,]}{dt} = 0 = 2k_1[\,Br_2\,] - k_2[\,Br\,][\,H_2\,] + k_3[\,H\,][\,Br_2\,] + k_4[\,H\,][\,HBr\,] - 2k_5[\,Br\,]^2 \qquad ...(18.105)$$

Similarly, H is formed as per Eq.18.98 and consumed as per Eqs.18.99 and 18.100. Using these ideas and Eq.18.104, we can write,

$$\frac{d[\,H\,]}{dt} = 0 = k_2[\,Br\,][\,H_2\,] - k_3[\,H\,][\,Br_2\,] - k_4[\,H\,][\,HBr\,] \qquad ...(18.106)$$

By adding Eqs.18.105 and 18.106, we get,

$$2k_1[\,Br_2\,] = 2k_5[\,Br\,]^2$$

or
$$[\,Br\,] = \left(\frac{k_1}{k_5}\right)^{1/2}[\,Br_2\,]^{1/2} \qquad ...(18.107)$$

From Eq.18.106, we can write,

$$[\,H\,] = \frac{k_2[\,H_2\,][\,Br\,]}{k_3[\,Br_2\,] + k_4[\,HBr\,]} \qquad ...(18.108)$$

Using Eqs.18.107 and 18.108, we get,

$$[\,H\,] = \frac{k_2\left(\frac{k_1}{k_5}\right)^{1/2}[\,H_2\,][\,Br_2\,]^{1/2}}{k_3[\,Br_2\,] + k_4[\,HBr\,]} \qquad ...(18.109)$$

Rearranging Eq.18.102, we get,

$$\frac{d[\,HBr\,]}{dt} = k_2[\,H_2\,][\,Br\,] + [\,H\,](\,k_3[\,Br_2\,] - k_4[\,HBr\,]\,) \qquad ..(18.110)$$

Using Eqs.18.107, 18.109 and 18.110, we get,

$$\frac{d[\,HBr\,]}{dt} = k_2\left(\frac{k_1}{k_5}\right)^{1/2}[\,Br_2\,]^{1/2}[\,H_2\,] + \frac{(\,k_3[\,Br_2\,] - k_4[HBr])\,(\,k_2\,(\,k_1/k_5\,)^{1/2}[H_2[Br_2]^{1/2}}{k_3[\,Br_2\,] + k_4[\,HBr\,]}$$

$$= \frac{2k_2k_3\,(\,k_1/k_5\,)^{1/2}[\,Br_2\,]^{3/2}[\,H_2\,]}{k_3[\,Br_2\,] + k_4[\,HBr\,]} \qquad ...(18.111)$$

Dividing the numerator and denominator of R.H.S. by k_3 [Br_2],

$$\frac{d[\,HBr\,]}{dt} = \frac{2k_2\,(k_1/k_5\,)^{1/2}[\,H_2\,][\,Br_2\,]^{1/2}}{1 + \frac{k_4[\,HBr\,]}{k_3[\,Br_2\,]}} \qquad ...(18.112)$$

By comparison you can see that Eqs.18.96 and 18.112 are same, where

$$k = 2k_2\left(\frac{k_1}{k_5}\right)^{1/2} \quad \text{and} \quad k' = \frac{k_4}{k_3}$$

The presence of the term [HBr]/[Br_2] in the denominator of Eq.18.96 or Eq.18.112, has the following significance:

- HBr formed inhibits the rate of the reaction,
- At high [Br_2], the inhibition is less.

Both these predictions have been verified experimentally.

In the H_2–Br_2 reaction, inhibition takes place due to the product formed. Sometimes, impurities are deliberately added to some materials to inhibit undesirable reactions. For example, food products generally get spoiled due to chain reactions involving oxidation. To preserve the food products, it is customary to use the preservatives which inhibit oxidation by removing chain-propagating radicals. Such "antioxidants" are also added to plastics and rubber to prevent their degradation.

Free-Radical Reactions

In H_2–Br_2 reaction, H and Br atoms have unpaired electrons and these are monoatomic free-radicals. In 1929, Paneth and Hofeditz reported the formation of polyatomic free radicals (CH_3 radicals) by the thermal decomposition of lead tetramethyl. It was found that lead was deposited as a mirror, in the hot portion of a tube through which hydrogen gas carrying lead tetramethyl vapour was passed.

$$Pb\,(CH_3)_4 \longrightarrow Pb + 4CH_3 \qquad ...(18.113)$$

After the discovery of this reaction, many free radical reactions were studied and chain mechanisms were proposed to explain their reaction rates. An example is the thermal decomposition of ethane for which the mechanism proposed is given below:

$$C_2H_6 \xrightarrow{k_1} 2CH_3$$

$$CH_3 + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5$$

$$C_2H_5 \xrightarrow{k_3} C_2H_4 + H$$

$$H + C_2H_6 \xrightarrow{k_4} H_2 + C_2H_5$$

$$H + C_2H_5 \xrightarrow{k_5} C_2H_6$$

The free-radicals such as CH_3 and C_2H_5 are detected by direct experimental methods or from the products they give. Experimentally obtained rate law is given by the equation,

$$\text{rate} = k\,[C_2H_6] \qquad ...(18.114)$$

where k is the overall rate constant; k is the complex combination of the rate constants of the individual elementary reactions.

The radical intermediates can be removed by using substances like NO. Since NO molecule has an unpaired electron, it combines with a radical intermediate which also has an unpaired electron. This could result in chain termination. Here NO molecule is called the radical scavenger and it is said to quench the chain reaction. To prove the chain mechanism, such radical scavengers are used.

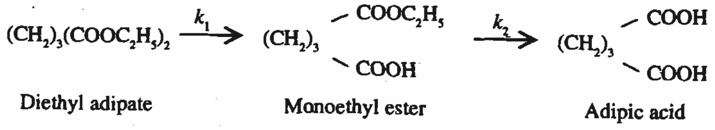
Just as we can terminate a chain reaction using radical scavengers, we can start a chain reaction using free radical sensitizers such as $Pb(CH_3)_4$ or Hg $(CH_3)_2$. To increase the decomposition rate of an organic compound, Pb $(CH_3)_4$ or Hg $(CH_3)_2$ is added. These substances decompose, and introduce CH_3 radicals into the system. This starts the decomposition of the organic compounds through a chain reaction. Pb $(CH_3)_4$ and Hg $(CH_3)_2$ are said to sensitize the decomposition of organic compounds.

Consecutive Reactions

We have postulated the existence of intermediates. In many cases, the intermediate in one step is the reactant in the next step. Such reactions are called consecutive reactions. The rates of consecutive reactions could be stated in terms of the concentrations of the reactant taken initially and the products formed in each stage.

Example

Acid hydrolysis of diethyl adipate.

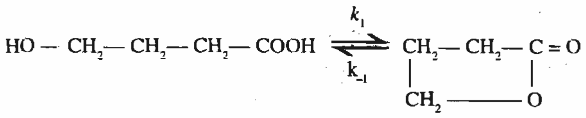


Opposing Reactions

In opposing reactions, rates of forward and reverse reactions are both appreciable. While proposing a mechanism both the reaction rates must be considered.

Example

Formation of butyrolactone from γ-hydroxybutyric acid.

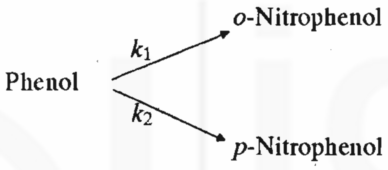


Parallel Reactions

If a reactant can undergo more than one reaction, the resulting reactions are called parallel reactions. The rates of a set of parallel reactions can be measured in terms of the concentrations of the products formed in each case.

Example

Nitration of phenol yielding *o*-nitrophenol and *p*-nitrophenol,



In the next section we shall explain the theory of unimolecular reaction rates.

SAQ 9

For the following elementary reactions, write the rate laws:

i) $O_3\,(g) + NO\,(g) \rightarrow O_2\,(g) + NO_2\,(g)$

ii) $CH_3NC\,(g) \rightarrow CH_3CN\,(g)$

iii) $Cl_2\,(g) \rightarrow 2Cl\,(g)$

....

....

....

SAQ 10

For the reaction,

$$2NO\,(g) + O_2\,(g) \rightarrow 2NO_2\,(g)$$

the rate law is given below:

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

Is the following mechanism consistent with the rate law?

Step i) $NO + O_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} NO_3$ Both rates fast and equal

Step ii) $NO_3 + NO \xrightarrow{k_3} 2NO_2$ Slow

Hint: Consider NO_3 as an intermediate.

....

....

....

18.9 THEORY OF UNIMOLECULAR REACTIONS

A unimolecular reaction is an elementary reaction in which only one molecule or a radical reacts. The unimolecular reaction follows first order kinetics. A number of gas phase reactions follow first order kinetics. These reactions are assumed to proceed through unimolecular rate-determining step. But how does the reactant molecule attain the activation energy? The activation energy is the minimum energy needed for the reactant molecules to react and yield products. If the molecules obtain their activation energy through collisions, it is difficult to explain first order kinetics. A collision process needs atleast two molecules and hence, second order kinetics could be expected but not first order kinetics. In 1922, Lindemann and Hinshelwood proposed a mechanism which could explain the unimolecular reactions in which molecules attain their activation energy through collisions.

Let two molecules of the reactant gas (X) collide yielding an activated molecule (X^*) and a normal molecule (X). Such a collision is called an activating collision.

$$X + X \xrightarrow{k_a} X^* + X \qquad ...(18.115)$$

$$\text{Rate of activation of } X = k_a [X][X] \qquad ...(18.116)$$

The activated molecule, X^*, can undergo either of the following reactions:

i) X^* can undergo collision with another molecule X and lose its excess energy. Such a collision is called a deactivating collision.

$$X^* + X \xrightarrow{k'_a} X + X \qquad ...(18.117)$$

$$\text{Rate of deactivation of } X^* = k'_a [X^*][X] \qquad ...(18.118)$$

ii) Alternatively, X^* can decay to yield the product, Y.

$$X^* \xrightarrow{k_b} Y \qquad ...(18.119)$$

$$\text{Rate of decay of } X^* = \text{Rate of product formation} = \frac{d[Y]}{dt} = k_b [X^*] \qquad ...(18.120)$$

Note that decay of X^* is a unimolecular reaction.

If the decay of X^* yielding products is the rate-determining step, then the overall rate of the reaction is given by the following expression.

$$\text{Rate} = k_b [X^*] \qquad ...(18.121)$$

In order to express the concentration of X^*, an active species, in terms of concentrations of reactants (or products) in the ground state, **steady-state approximation** is used. According to this procedure, it is assumed that a steady-state is reached after a reaction starts such that the concentration of the activated species is more or less a constant and does not change with time.

According to steady-state approximation, the concentrations of all reactive intermediates are constant and small during the major part of the reaction.

i.e., $$\frac{d[X^*]}{dt} = 0 \qquad ...(18.122)$$

This means that the activated species, X^*, is consumed as soon as it is formed. Since X^* is formed as per Eq.18.115 and is consumed as per Eqs.18.117 and 18.119,

$$\frac{d[X^*]}{dt} = 0 = k_a [X]^2 - k'_a [X][X^*] - k_b [X^*] \qquad ...(18.123)$$

i.e., $$[X^*](k'_a [X] + k_b) = k_a [X]^2$$

or $$[X^*] = \frac{k_a [X]^2}{(k'_a [X] + k_b)} \qquad ...(18.124)$$

Using Eqs.18.121 and 18.124,

$$\text{rate} = \frac{k_a k_b [X]^2}{(k_a' [X] + k_b)} \qquad \text{...(18.125)}$$

From Eq. 2.41 of this course, $p = cRT$ or $p \propto c$. Hence, when the pressure of a gas is high, its concentration is high. When the concentration is high, there will be large number of collisions.

At High Pressures

At high pressures, the number of collisions is large and the probability of deactivating collisions occurring is high. That is, the rate of deactivation is larger than the rate of product formation (through decay); the unimolecular decay of X^* is the rate-determining step at high pressures; i.e.,

$$k_a' [X^*][X] >> k_b [X^*]$$

or

$$k_a' [X] >> k_b \qquad \text{...(18.126)}$$

In other words, $k_a' [X] + k_b \simeq k_a' [X]$ ...(18.127)

Using this in Eq. 18.125, we get

$$\text{rate} = \frac{k_a k_b [X]^2}{k_a' [X]} = \frac{k_a k_b}{k_a'} [X] \qquad \text{...(18.128)}$$

In other words, the rate is first order at high pressures.

At Low Pressures

Eqs. such as 18.127 or 18.130 are instances of **limiting conditions**. Using such approximation procedure, it is possible to simplify a complicated equation as Eq. 18.125.

At low pressures, the number of collisions decreases. This means that the activated molecule yields the product as soon it is formed and there is not much time left for deactivating collision to occur. In other words, the bimolecular formation of X^* is the rate-determining step. Further, the rate of deactivating collisions is much small as compared to the rate of product formation.

$$k_b [X^*] >> k_a' [X^*][X]$$

or

$$k_b >> k_a' [X] \qquad \text{...(18.129)}$$

or

$$k_a' [X] + k_b \simeq k_b \qquad \text{...(18.130)}$$

Using this in Eq. 18.125,

$$\text{rate} = \frac{k_a k_b [X]^2}{k_b} = k_a [X]^2 \qquad \text{...(18.131)}$$

Hence the reaction follows second order kinetics at low pressures.

The variation of the order of reaction with pressure as predicted by Lindemann - Hinshelwood theory could be observed in reactions such as the decomposition of N_2O_5. Using this theory, we could explain the unimolecular decomposition of N_2O_5 at high pressures.

18.10 THEORIES OF REACTION RATES

The rates of many reactions increase with the rise in temperature. Arrhenius proposed the following empirical relationship between the rate constant, k, and temperature, T.

$$\ln k = \ln A - E_a/RT \qquad \text{...(18.132)}$$

As the reaction rate varies with temperature, temperature also must be specified while stating the values of rate constants.

or

$$\log k = \log A - E_a/2.303RT \qquad \text{...(18.133)}$$

where A is called the Arrhenius factor or frequency factor or pre-exponential factor and E_a is the activation energy. Activation energy is the minimum excess energy that the reactant molecules must have in order to react. If $\log k$ is plotted against $\frac{1}{T}$, a straight line (Fig. 18.10) is obtained for many reactions. In such cases, the slope of the line is $-E_a/2.303R$ and the intercept at $\frac{1}{T} = 0$ gives $\log A$.

Eqs. 18.132 is also written in the exponential form as follows:

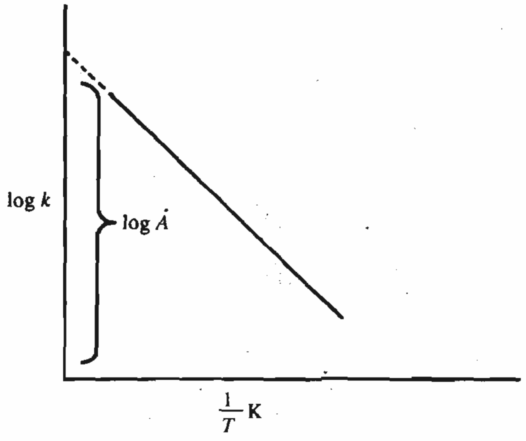


Fig. 18.10: Plot of log k against $\frac{1}{T}$

$$k = A\,e^{-E_a/RT} \qquad \text{...(18.134)}$$

A possible reason for the deviation from Arrhenius equation in some reactions is that A and E_a may vary with temperature. The temperature dependence of Arrhenius factor will be discussed in collision theory. In the present discussion, we consider that A and E_a are constants for a reaction. If the activation energy is high for a reaction, it means that the temperature dependence of the reaction rate is also high. In such cases, even a small change of temperature results in a large change in the rate constant.

Although activation energy of a reaction can be calculated from log k vs $1/T$ plot, another way of obtaining it is to calculate rate constants (k_1 and k_2) at two temperatures (T_1 and T_2). Assuming E_a and A to be constant and using Eq. 18.133, we get

$$\log k_1 = \log A - E_a/2.303RT_1 \qquad \text{...(18.135)}$$

and

$$\log k_2 = \log A - E_a/2.303RT_2 \qquad \text{...(18.136)}$$

The unit of A depends on the unit of k. For first order reactions, A has s^{-1} unit which is the same as the unit for frequency. This could be a reason for its name, frequency factor. A is also called the pre-exponential factor since it precedes the exponential term in Eq. 18.134.

Substracting the terms in Eq. 18.136 from those in Eq. 18.135,

$$\log \frac{k_2}{k_1} = \frac{-E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$= \frac{-E_a}{2.303R}\;\frac{(T_1 - T_2)}{T_1 T_2}$$

i.e.,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\;\frac{(T_2 - T_1)}{T_1 T_2} \qquad \text{...(18.137)}$$

Let us work out an example.

Example 16

The rate constants for the decomposition of SO_2Cl_2 are $1.01 \times 10^{-6}\ s^{-1}$ at 552 K and $3.85 \times 10^{-5}\ s^{-1}$ at 600 K. Calculate the activation energy and the frequency factor for the reaction, assuming them to be independent of temperature.

Solution

From Eq. 18.137,

$$E_a = 2.303\,\frac{RT_1T_2}{(T_2 - T_1)}\,\log\frac{k_2}{k_1}$$

$$E_a = \left(\frac{2.303 \times 8.314 \times 552 \times 600}{48}\,\log\frac{3.85 \times 10^{-5}}{1.01 \times 10^{-6}}\right) \text{J mol}^{-1}$$

$$E_a = 2.09 \times 10^{5}\ \text{J mol}^{-1}$$

Substituting for $T = 600$ K, $E_a = 2.09 \times 10^{5}\ \text{J mol}^{-1}$ and $k = 3.85 \times 10^{-5}\ s^{-1}$ in Eq. 18.133

we get,
$$\log A = \log k + E_a/2.303RT$$
$$= -4.4145 + \frac{2.09 \times 10^5}{2.303 \times 8.314 \times 600}$$
$$\log A = -4.4145 + 18.1924 = 13.7779$$
$$A = \text{Antilog of } 13.7779$$
$$A = 6.00 \times 10^{13}\ \mathrm{s}^{-1}$$

We can understand the significance of the terms, E_a, A and $e^{-E_a/RT}$ during the discussion on collision theory of reaction rates.

Collision Theory

Collision theory is applicable to bimolecular reactions in gas phase. With some modifications, this can be applied to unimolecular (see Sec. 18.9) and termolecular reactions also. We explain collision theory using a gas-phase bimolecular elementary reaction of the following type:

$$X + Y \rightarrow \text{Products} \qquad \text{...(18.138)}$$

As per collision theory, the rate of a bimolecular reaction depends on

- the total collision frequency and
- Boltzmann factor.

Although the steric factor is also to be considered while calculating the reaction rate, it will be treated under the refinement of collision theory.

Total Collision Frequency

Total collision frequency (Z_{XY}) is the number of collisions between the molecules of X and the molecules of Y in unit time in unit volume. Only X–Y collisions are counted but not X–X or Y–Y collisions, since only X–Y collisions are responsible for the reaction indicated in Eq. 18.138.

In Sec. 2.11 of Unit 2 of this course, we derived Eq. 2.52 for calculating the total collision frequency among the molecules of a single gas. The total collision frequency (Z) in general, can be derived using the following relationship:

$$Z = \begin{cases} \pi \times (\text{collision diameter})^2 \\ \times\ (\text{average relative speed of gas molecules}) \\ \times\ (\text{number density}) \\ \times\ (\text{number density}) \\ \times\ (\text{correction factor}) \end{cases} \qquad \text{...(18.139)}$$

For calculating the total collision frequency (Z_{XY})among the molecules of X and Y, as per Eq. 18.139, we use the following relationships:

1) **Collision diameter** $= \sigma_{XY} = 1/2\,(\sigma_X + \sigma_Y)$ ...(18.140)

   where σ_X and σ_Y are the diameters of the molecules, X and Y, respectively. The collision diameter σ_{XY} is the distance of closest approach between a molecule of X and a molecule of Y.

ii) Average relative speed of the molecules of X and Y $= \left(\dfrac{8\,k_b\,T}{\pi\mu}\right)^{1/2}$ ...(18.141)

   where k_b is the Boltzmann constant (subscript b is added to k to differentiate it from the rate constant), T is temperature and μ is reduced mass.

   Note that $\dfrac{1}{\mu} = \dfrac{1}{m_X} + \dfrac{1}{m_Y}$ ...(18.142)

To understand the significance of Eq. 18.139, see Appendix I.

As per Eq. 2.47 of Sec. 2.9 of Unit 2,

$$\text{average speed of a gas molecule } (\bar{u}) = \left(\frac{8RT}{\pi M_m}\right)^{1/2}$$

$$\text{i.e., Average speed of a gas molecule } (\bar{u}) = \left(\frac{8k_bT}{\pi m}\right)^{1/2} \qquad \text{... (18.144)}$$

Since $R = N_A k_b$, $M_m = N_A\, m$

Where M_m is the molar mass and m is the mass of one molecule of gas and N_A is Avogadro constant.

While calculating the relative motion of particles, it is customary to use reduced mass in the place of mass of one molecule of the gas.

$$\left.\begin{matrix}\text{Hence average relative} \\ \text{speed of the molecules} \\ \text{of X and Y}\end{matrix}\right] = \left(\frac{8k_bT}{\pi\mu}\right)^{1/2}$$

which is same as Eq. 18.141.

$$\mu = \frac{M_X M_Y}{M_X + M_Y} \cdot \frac{1}{N_A} \qquad \text{...(18.145)}$$

where M_X , M_Y and N_A are the molar mass of X, molar mass of Y and Avogadro constant.

Eq. 18.145 comes from Eq. 18.143 since,

$$\text{mass of one molecule of a substance} = \frac{\text{Molar mass}}{\text{Avogadro constant}}$$

or
$$\mu = \frac{m_X\, m_Y}{m_X + m_Y} \qquad \text{...(18.143)}$$

where m_X and m_Y are the masses of one molecule of X and Y, respectively.

iii) Let us now calculate the factor, (number density) × (number density). Since we have two types of molecules, X and Y, we have to consider number densities of both X and Y. Using Eq. 18.148,

(number density of X) × (number density of Y)

$$= N_A\,[X]\,.\,N_A\,[Y] = N_A^2\,[X]\,[Y] \qquad \text{...(18.149)}$$

Number density of a gas has been defined in Subsec. 2.8.2 of Unit 2.

Number density

$$= \frac{\text{Number of molecules of the gas}}{\text{Volume of the gas}}$$

$$= \frac{\text{Pressure of the gas}}{\text{Boltzmann constant} \times \text{temperature}}$$

$$= \frac{p}{k_bT} \qquad \text{...(18.146)}$$

Also note that from Eq. 2.41,. concentration of a gas

$$= \frac{\text{Number of moles of the gas}}{\text{Volume of the gas}}$$

$$= \frac{p}{RT}$$

i.e., Concentration of a gas

$$= \frac{p}{N_A\, k_bT} = \frac{\text{Number density}}{N_A} \qquad \text{...(18.147)}$$

where N_A is Avogadro constant.

i.e., Number density of a gas = N_A × (concentration of the gas) ...(18.148)

In the case of collision between the molecules of X and Y (i.e., between molecules of different gases), there is no necessity for the correction factor. It is because we calculate the collisions between each molecule of X and each molecule of Y. Each collision is counted only once. So omitting the correction factor and using Eqs. 18.139, 18.140, 18.141 and 18.149, we get,

$$Z_{XY} = \pi\,\sigma_{XY}^2 \left(\frac{8k_bT}{\pi\mu}\right)^{1/2} N_A^2\,[X]\,[Y] \qquad \text{...(18.150)}$$

Thus we have obtained a relationship useful in calculating the total collision frequency for the collisions between each molecule of X and each molecule of Y. Next we study the significance of Boltzmann factor.

Boltzmann Factor

You must realise that not all collisions between the molecules of X and Y would result in the product formation. Only those collisions, in which, the energy of the colliding molecules equals or exceeds some critical value E_a (known as activation energy as per Arrhenius equation), are effective in bringing about the reaction between X and Y. If $E_a >> RT$, then the Boltzmann factor, $e^{-E_a/RT}$, gives the fraction of the collisions in which the colliding molecules possess energy equal to or greater than the activation energy.

$$\text{Boltzmann factor} = e^{-E_a/RT} \qquad \text{...(18.151)}$$

Boltzmann factor is helpful in calculating the number of molecules possessing energy equal to or greater than a particular value. Boltzmann factor, in other words, is helpful in calculating the population of the energy levels.

Calculation of Reaction Rate

The product of the total collision frequency and the Boltzmann factor gives the **number of molecules of X or Y in unit volume reacting per unit time.** This follows from the definitions of the terms, total collision frequency and the Boltzmann factor. In order to obtain the reaction rate in terms of concentrations of X or Y (or the **number of moles of X or Y** in unit volume) consumed per unit time, we have to divide the product, $Z_{XY}\, e^{-E_a/RT}$ by Avogadro constant.

$$[X] = \frac{\text{Number of moles of X}}{\text{Volume}} = \frac{\text{Number of molecules of X}}{N_A \times \text{Volume}} = \frac{\text{Number density of X}}{N_A}$$

$$\text{Reaction rate} = \frac{-\,d[X]}{dt} = \frac{-d[Y]}{dt}$$

$$= \frac{Z_{XY}\, e^{-E_a/RT}}{N_A} \qquad \text{...(18.152)}$$

Using Eqs. 18.150 and 18.152,

$$\text{reaction rate} = \pi\,\sigma_{XY}^2 \left(\frac{8k_bT}{\pi\,\mu}\right)^{1/2} N_A^2\,[X]\,[Y]\,e^{-E_a/RT} \times \frac{1}{N_A}$$

$$= \pi\,\sigma_{XY}^2 \left(\frac{8k_bT}{\pi\,\mu}\right)^{1/2} N_A\,[X]\,[Y]\,e^{-E_a/RT} \qquad \text{...(18.153)}$$

By definition, the reaction rate for a bimolecular elementary reaction as per Eq. 18.138 is as follows:

$$\text{Reaction rate} = k\,[X]\,[Y] \qquad \text{...(18.154)}$$

Comparing Eqs. 18.153 and 18.154,

$$k = \pi \sigma_{XY}^2 \left(\frac{8k_b T}{\pi \mu} \right)^{1/2} N_A e^{-E_a/RT} \qquad ...(18.155)$$

Eq. 18.155 gives the theoretical value of the rate constant for a bimolecular reaction as per collision theory. $\pi \sigma_{XY}^2$ is called the mean collision cross-section.

Collision Theory and Arrhenius Theory–a Comparison

You compare Arrhenius Equation (Eq. 18.134) with Eq. 18.155. You can see that the frequency factor A is given by,

$$A = \pi \sigma_{XY}^2 \left(\frac{8k_b T}{\pi \mu} \right)^{1/2} N_A \qquad ...(18.156)$$

From Eq. 18.156, you can see that A is not independent of temperature as predicted by Arrhenius equation. However, over a short range of temperature, the variation in A is not significant. Arrhenius factor can be written as a product of A' and $T^{1/2}$ where A' is a temperature-independent constant and T is temperature.

$$A = A' T^{1/2}$$

where $$A' = \pi \sigma_{XY}^2 \left(\frac{8k_b}{\pi \mu} \right)^{1/2} N_A$$

The factor $T^{1/2}$ indicates the temparature dependence of A as given in Eq. 18.156.

Hence $\log A = \log A' T^{1/2} = \log A' + 1/2 \log T$

Using this in Eq. 18.133,

$$\log k = \log A' + 1/2 \log T - E_a/2.303RT$$

or $$\log k - 1/2 \log T = \log A' - E_a/2.303RT$$

A better method of arriving at the experimental values of E_a and A is to plot $\log k - 1/2 \log T$ against $1/T$.

The slope of the plot gives E_a value since

$$\text{slope} = -E_a/2.303\,R$$

The intercept gives $\log A'$ value. From A' values, A at any temperature can be found out since

$$A = A' T^{1/2}$$

The value of A so obtained is the experimental value.

It was found that in the case of reactions between simple molecules, the agreement between the experimental value of A and the value obtained as per collision theory (Eq. 18.156) is fairly good. In the case of reactions involving complex molecules, there is a discrepancy between the two values of A. To explain the discrepancy between the two values of A, a refinement was suggested for Eqs. 18.155 and 18.156 in terms of steric factor.

Steric Factor

Although the molecular collisions may have requisite energy, the reaction would take place only if the molecules have proper orientation. In other words, the reacting species must have proper spatial orientation for the reaction to occur. In the case of complex molecules, the probability of attaining proper orientation for the reaction is much less as compared to simple molecules. To stress the need for the proper spatial requirement, **steric factor or probability factor** (P) was also added to the right hand side of Eq.18.155.

Hence $$k = P \pi \sigma_{XY}^2 \left(\frac{8k_b T}{\pi \mu} \right)^{1/2} N_A e^{-E_a/RT} \qquad ...(18.157)$$

$$A = P\pi\sigma_{XY}^2\left(\frac{8k_bT}{\pi\mu}\right)^{1/2} N_A \qquad ...(18.158)$$

Also, $$P = \frac{A_{\text{Experimental}}}{A_{\text{Theoretical}}} \qquad ...(18.159)$$

The steric factor is smaller for reaction between complex molecules. We expect the steric factor to be less than unity. But many fast reactions are known for which the steric factor is much greater than unity. Collision theory cannot explain such cases. Let us now study the **Activated Complex Theory** which gives a better method of calculating reaction rates.

Activated Complex Theory

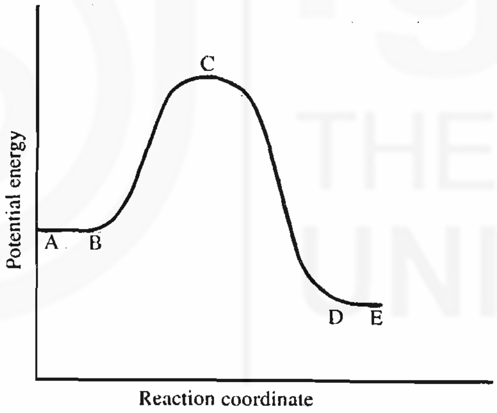
The activated complex theory or the absolute theory of reaction rates depicts the formation of activated complex ($A^\ddagger$) from the reactants (X and Y) as a preceding step for the formation of the product, P.

$$X + Y \rightarrow A^\ddagger$$

$$A^\ddagger \rightarrow P$$

The main features of the activated complex theory are given here.

The reactant molecules come into contact with each other. In this process, a few bonds get distorted, some bonds start forming with the exchange or release of atoms or groups. The composite molecule so formed from the reactants prior to the formation of the product is called the activated complex. The activated complex then decomposes to give the product. The reaction sequence could be represented as in Fig.18.11.



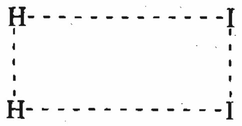
Activated complex is the configuration of the atoms which the reactant molecules have near the top of the energy barrier that separates the reactants from the products. Transition state is the highest point in the potential energy curve.

Fig.18.11: Graphical representation of the change in potential energy as a function of reaction coordinate.

The total potential energy of the system is depicted in the *y*-axis and the **reaction coordinate** in the *x*-axis. Reaction coordinate is the sequence of simultaneous changes in bond distances and bond angles. Such changes result during the formation of the products from the reactants.

Consider the reaction between a molecule of H_2 and a molecule of I_2. To start with, let us imagine that the two molecules are far part and the total potential energy of the system is the sum of the potential energies of H_2 and I_2. This part of the reaction course is represented by the horizontal portion AB of the curve in Fig. 18.11. As the two molecules approach each other to such an extent that the orbitals begin to overlap (point B in the curve), H–H and I–I bonds begin to stretch and H–I bond begins to form. The total potential energy starts increasing and this is represented by the rising portion of the curve BC. As the extent of H–H and I–I bond breakage and H–I bond formation increase, a point is reached when the potential energy is maximum (point C). The activated complex, represented below as a composite molecule, has the maximum potential energy.

The bond-breaking is an energy demanding process and the bond-making is an energy releasing process. The net energy requirement for the formation of the activated complex and its decomposition to products must be available through the translational or the vibrational energy of the reactants.



Activated Complex

The maxima point in the potential energy curve is called the transition state. Even a slight distortion of the bonds in the form of compression of H–I bond and stretching of H–H and I–I bonds enables the activated complex pass through the transition state. The path along CD represents the course of the events which result in the complete breakage of H–H and I–I bonds along with the formation of H–I bond. The horizontal portion DE represents the total potential energy of two H–I molecules. Although a fraction of the activated complex molecules could form the reactants (along the path CB) the formation of the products is almost a certainty, once the activated complex is at the transition state. The fraction of the activated complex converted into products is called the transmission coefficient and, in majority of cases, it is unity.

Energy Requirement for the Reaction

Now let us consider the energy criteria for the reaction. The energy requirement for the reactants to cross the energy barrier is to be met from translational or the vibrational energy of the molecules. At the transition state, the activated complex has some complicated vibration-like motion of all atoms. The activated complex has one particular mode of vibration along which it is unstable. If the activated complex vibrates with the frequency corresponding to this vibrational mode, the activated complex decomposes into products.

Rate Constant Calculation using Activated Complex Theory

Based on statistical thermodynamics, Eyring developed the activated complex theory. The basic postulate of the theory is that there exists an equilibrium between the activated complex and the reactants. Let us consider the **bimolecular gas phase reaction,**

$$X + Y \rightarrow A^{\ddagger} \qquad \text{...(18.160)}$$

where X and Y are the reactants, and $A^{\ddagger}$ is the activated complex. The activated complex then decomposes to give the product, P

$$A^{\ddagger} \rightarrow P \qquad \text{...(18.161)}$$

The rate of formation of the product depends on,

(i) the concentration of the activated complex and

ii) the frequency with which it is converted into the product. This is the frequency of one of the vibrational modes with respect to which the activated complex is unstable. Using detailed calculations, it is possible to derive an expression useful in calculating the rate constant (k) of the elementary reaction, X + Y → P (for which the steps are given in Eqs. 18.160 and 18.161). We shall only state the final expression without going through the derivation in full.

$$k = \frac{RT}{p^0}\cdot\frac{k_bT}{h}\cdot K_p = \frac{Rk_bT^2}{p^0h}\cdot K_p \qquad \text{...(18.162)}$$

where K_p = The equilibrium constant for the formation of the activated complex after adjusting for its vibration with respect to which it is unstable.

T = Temperature

k_b = Boltzmann constant

RT/p^0 is the correction term where p^0 is the standard pressure (1 bar)

h = Planck constant

R = Gas constant.

Using van't Hoff isotherm (Eq. 14.17 of Unit 14 of this course),

$$\Delta G^{\ddagger} = -RT \ln K_p \qquad \text{...(18.163)}$$

where $\Delta G^{\ddagger}$ is molar Gibbs energy of activation.

Hence, $$K_p = e^{-\Delta G^{\ddagger}/RT} \qquad \text{...(18.164)}$$

Using Eq. 18.164 in Eq. 18.162,

$$k = \frac{Rk_bT^2}{hp^0} e^{-\Delta G^{\ddagger}/RT} \qquad \text{...(18.165)}$$

Using Eq. 9.15 of Unit 9,

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad \text{...(18.166)}$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the molar enthalpy of activation and molar entropy of activation, respectively.

Using Eq. 18.166 in Eq. 18.165,

$$k = \frac{Rk_bT^2}{hp^0} e^{-(\Delta H^{\ddagger} - T\Delta S^{\ddagger})/RT}$$

$$k = \frac{Rk_bT^2}{hp^0} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \qquad \text{...(18.167)}$$

$$e = 1 + \frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \cdots$$

$\simeq 2.718$

Note that 1!, 2!, etc., are to be read as factorial 1, factorial 2, etc.

Also $1! = 1$;
$2! = 1 \times 2$;
$3! = 1 \times 2 \times 3$

Finally '....' in the above expression means that it is a continuous series.

Using differential form of Eq. 18.132, it is possible to find the following relationship for a bimolecular gas phase reaction (See Appendix II):

$$\Delta H^{\ddagger} = E_a - 2RT \qquad \text{...(18.168)}$$

Using Eqs. 18.167 and 18.168,

$$k = \frac{Rk_b T^2}{hp^0} e^{-(E_a - 2RT)/RT} e^{\Delta S^{\ddagger}/R}$$

$$k = \frac{Rk_b T^2}{hp^0} e^{-E_a/RT} e^2 e^{\Delta S^{\ddagger}/R} \qquad \text{...(18.169)}$$

Comparing Arrhenius equation (Eq. 18.134) with Eq. 18.169,

$$A = \frac{Rk_b T^2}{hp^0} e^2 e^{\Delta S^{\ddagger}/R} \qquad \text{...(18.170)}$$

Hence $$e^{\Delta S^{\ddagger}/R} = \frac{hp^0}{Rk_bT^2 e^2} \cdot A$$

i.e., $$e^{\Delta S^{\ddagger}/R} = 7.8119 \times 10^{-11} \frac{A}{T^2} \qquad \text{...(18.171)}$$

(substituting for the constants)

Taking natural logarithms,

$$\Delta S^{\ddagger}/R = \ln 7.8119 \times 10^{-11} \frac{A}{T^2}$$

$$\Delta S^{\ddagger} = 2.303R\,(\log 7.8119 \times 10^{-11} + \log A/T^2)$$

$$= (19.15 \log A/T^2 - 193.6)\ \text{J mol}^{-1}\,\text{K}^{-1} \qquad \text{...(18.172)}$$

Thus $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ can be calculated at any given temperature, if A and E_a are known from Arrhenius plot (Fig. 18.10).

While discussing collision theory or the activated complex theory, we consider only the gas-phase reactions. The study of rection rates in solutions is complicated due to the role of the solvent. In this course, we shall not discuss the reaction rates in solutions.

Comparison of Collision Theory and Activated Complex Theory

To account for the discrepancy between the experimentally obtained value of A and the value calculated as per collision theory, we had to introduce steric factor in Eq. 18.157. The activated complex theory has the factor, $e^{\Delta S^{\ddagger}/R}$, which takes care of the steric factor automatically.

It is observed that $\Delta S^{\ddagger}$ is negative for many reactions. Such a negative value indicates decrease in disorderliness. This is understandable since during collisions, the particles have to approach each other, thereby causing a decrease in randomness. The negative value of $\Delta S^{\ddagger}$ brings down the value of $e^{\Delta S^{\ddagger}/R}$ and hence of A as per Eq. 18.170. A large negative value for the entropy of activation is generally observed for reactions involving complex molecules. The demand for proper orientation is more in the case of a complex molecule and this causes larger reduction in randomness. Thus the entropy of activation, and hence, the frequency factor could be expected to be much less for reactions involving complex molecules.

SAQ 11

The second order rate constants of a reaction are given below at two temperatures:

T/K	298	308
$10^5 \times k/\mathrm{M^{-1}\,s^{-1}}$	8.8	28

Calculate the activation energy of the reaction.

....

....

....

SAQ 12

For the reaction,

$$2\mathrm{NOCl} \rightarrow 2\mathrm{NO} + \mathrm{Cl_2}$$

Arrhenius factor at 298 K is $9.4 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$. Calculate entropy of activation for this reaction at 298 K.

....

....

....

18.11 FAST REACTIONS

Many reactions are so fast that ordinary experimental methods mentioned in Sec. 18.3 are inadequate to make measurements of reaction rates or the rate constants. Such reactions are called fast reactions and the half-life periods of fast reactions are less than 10^{-2}s. Some of the special techniques used for measuring the rate constants of fast reactions are:

- flash photolysis,
- flow method, and
- relaxation method.

Of the above three, we shall discuss the first method in Unit 19 of this course. Now we consider the principles of the other two methods.

Flow Method

Two techniques are available under flow method. In continuous flow method (Fig. 18.12), the reacting solutions or gases are taken in separate containers (A and B) and are allowed to flow through the mixing chamber (C) into an observation tube (D). At various points along the observation tube, the composition of the mixture is determined by some physical methods.

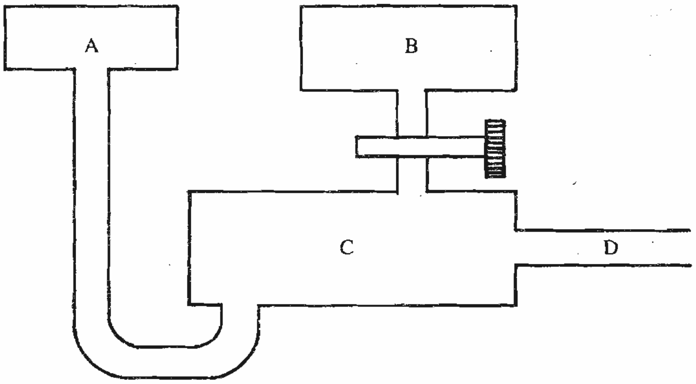


Fig. 18.12: Apparatus for continuous flow method

Using this method, reactions which get completed within 10^{-3}s can be studied. But this method requires a large volume of the reactants. In order to study the reaction rates using small volumes of samples, a refined method is used which is known as stopped-flow method. The reacting solutions are forced through jets into a mixing chamber where mixing occurs very rapidly (within 10^{-3}s). The solution passes at once into the reaction vessel from the mixing chamber. The flow is then stopped suddenly and measurements are made using suitable physical methods. This method is widely used for the study of enzyme kinetics.

Relaxation Method

For studying reactions, which are complete within 10^{-5} s or even less, one of the problems encountered is that the time of mixing the reactants should be much smaller than the time taken for the completion of the reaction. To avoid this problem, relaxation methods have been developed. In a relaxation method, we disturb a reaction at equilibrium using an external influence such as sudden variation of pressure or temperature (known as pressure jump or temperature jump). The system is said to be perturbed from its equilibrium position. The perturbed system then returns to a new equilibrium position. Relaxation refers to the passage of a perturbed system to the new equilibrium. The concentration of the perturbed system is recorded at various time intervals using suitable physical methods. From these measurements, it is possible to measure the rate constants.

18.12 SUMMARY

In this unit, we started with the definitions of the terms such as, rate of reaction, rate law, order of reaction and stoichiometry. We described experimenal methods for rate studies. We derived the integrated forms of rate expressions for first order, second order and zeroth order reactions. We defined and illustrated the pseudo first order reactions. We explained the methods of determination of order of reaction. We discussed the steps followed in arriving at the mechanisms of simple reactions. We described the theory of unimolecular reaction rates. Arrhenius equation, collision theory and the activated complex theory were discussed. Finally, we gave an outline of the methods of studying fast reactions.

18.13 TERMINAL QUESTIONS

1) In the formation of ammonia,

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

the rate of consumption of hydrogen at a particular instant is 4.78×10^{-4} M s^{-1}. What is the rate of formation of ammonia?

2) The rate constant for the decomposition of N_2O_5 at 340 K is 5.20×10^{-3} s^{-1}. This reaction follows first order kinetics. If the initial rate of decomposition of N_2O_5 is

2.60×10^{-4} M s^{-1}, calculate the initial concentration of N_2O_5.

3) What is the time required for 87.5% decomposition of N_2O_5 at 340 K? Use data from the previous question.

4) What is the half-life period for the first order decomposition of azomethane at 600 K if $k = 3.55 \times 10^{-4}\ s^{-1}$?

5) The reaction ,

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

was studied at 298 K. The following results were obtained where

$$\text{rate} = -\frac{\Delta[S_2O_8^{2-}]}{\Delta t}$$

$[I^-]_0$ and $[S_2O_8^{2-}]_0$ denote the initial concentrations of the two species.

$10^2 \times [I^-]_0$/M	$10^2 \times [S_2O_8^{2-}]_0$/M	$10^6 \times$ Initial rate / M s^{-1}
8.0	4.0	12.50
4.0	4.0	6.25
4.0	2.0	3.12

Determine the rate law.

6) In the reaction

$$2NO_2Cl \longrightarrow 2NO_2 + Cl_2$$

the mechanism proposed below agrees with the experimentally observed rate law:

$$NO_2Cl \xrightarrow{k_1} NO_2 + Cl \qquad \text{(slow)}$$

$$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2 \qquad \text{(fast)}$$

What is the rate law?.

7) For the decomposition of N_2O at 773 K, $k = 1.00 \times 10^{-5}\ s^{-1}$ and $E_a = 250$ kJ mol^{-1}. Calculate A using Arrhenius equation.

8) For the reaction,

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

the steric factor is 1.7×10^{-6} and mean collision cross- section ($\pi\sigma^2$) is 0.46 nm^2 Calculate A at 628 K. Use Eq.18.158.

Given: i) $k_b = 1.381 \times 10^{-23}$ J K^{-1}

ii) The relative molecular masses of ethylene and hydrogen are 28.05 and 2.016, respectively.

iii) $N_A = 6.022 \times 10^{23}$ mol^{-1}

9) Explain the reason for the negative value of entropy of activation in the case of many reactions.

10) Explain two methods for the study of fast reactions.

11) The relaxation methods are suitable for measuring the rates of fast reactions. The experimental techniques (such as titrimetry mentioned in Sec. 18.3) are not useful for this purpose. Explain the reason.

18.14 ANSWERS

Self Assessment Questions

1) Using Eq. 18.2, $\frac{d[O_2]}{dt}$ = Rate

$$= 2.74 \times 10^{-4}\ \text{M s}^{-1}$$

2) $\frac{1}{2}\left(\frac{-d\,[HI]}{dt}\right) = \frac{d\,[H_2]}{dt}$

3) i) Spectrophotometry

ii) pH measurement, conductance or titration

iii) pressure measurement

4) Units of k :

zeroth order : M s^{-1}

first order : s^{-1}

second order : $\text{M}^{-1}\,\text{s}^{-1}$

5) Substituting in Eq.18.40,

$$\frac{1}{[A]_t} = \left(\frac{1}{[\,1.00 \times 10^{-2}\,]} + 1.83 \times 10^{-3} \times 1.68 \times 10^{5}\right)\text{M}^{-1}$$

$$[\,A\,]_t = 2.45 \times 10^{-3}\ \text{M}$$

6) Using Eq.18.60,

$$[A]_t = \frac{25}{100} \times 0.500\ \text{M} = 0.125\ \text{M}$$

$$t = \frac{(\,0.500 - 0.125\,)}{1.20 \times 10^{-4}}\ \text{s}$$

$$= 3.13 \times 10^{3}\ \text{s}$$

7) i) After obtaining V_0, V_t and V_∞ as explained in sec.18.6, log ($V_\infty - V_t$) is plotted against t.

$k' = -2.303 \times \text{slope}$

where k' is the pseudeo first order rate constant for the acid hydrolysis of ester.

ii) Using r_0, r_t and r_∞ values, log ($r_t - r_\infty$) is plotted against t.

$k' = -2.303 \times \text{slope}$

where k' is the pseudo first order rate constant for the inversion of sucrose.

8) Using Eq.18.71; $n = 1 + \frac{\log 300/240}{\log 5.00 \times 10^{-2}/4.00 \times 10^{-2}}$

$$n = 1 + \frac{0.0969}{0.0969} = 2$$

9) i) Rate = $k[O_3]\,[NO]$

ii) Rate = $k[CH_3NC]$

iii) Rate = $k\,[Cl_2]$

10) The rate law is given below as per the proposed mechanism:

$$\text{Rate} = k_3\,[NO_3]\,[NO] \qquad ...(1)$$

But $K = \frac{k_1}{k_2} = \frac{[NO_3]}{[NO]\,[O_2]}$

Hence, $[NO_3] = K[NO][O_2]$ ...(2)

Using (2) in (1),

$$\text{rate} = k_3 K [NO]^2 [O_2]$$

$$= k[NO]^2[O_2]$$

which is same as the rate law obtained experimentally.

11) Using Eq.18.137,

$$E_a = \frac{2.303\, RT_1 T_2}{(T_2 - T_1)} \log k_2/k_1$$

$$= \frac{2.303 \times 8.314 \times 298 \times 308}{10} \log \frac{28 \times 10^{-5}}{8.8 \times 10^{-5}}$$

$$= 88.3 \text{ kJ mol}^{-1}$$

12) According to Eq.18.172,

$$\Delta S^{\ddagger} = (19.15 \log A/T^2 - 193.6)\text{ J mol}^{-1}\text{ K}^{-1}$$

$$= \left(19.15 \log \frac{9.4 \times 10^9}{298^2} - 193.6\right)\text{J mol}^{-1}\text{ K}^{-1}$$

$$\Delta S^{\ddagger} = -97.4 \text{ J mol}^{-1}\text{ K}^{-1}$$

Terminal Questions

1) $$\frac{1}{3}\left(\frac{-d[H_2]}{dt}\right) = \frac{1}{2}\frac{d[NH_3]}{dt}$$

Hence, $$\frac{d[NH_3]}{dt} = \frac{2}{3}\left(\frac{-d[H_2]}{dt}\right) = \frac{2}{3} \times 4.78 \times 10^{-4}\text{ M s}^{-1}$$

$$= 3.19 \times 10^{-4}\text{ M s}^{-1}$$

2) $$\frac{-d[N_2O_5]}{dt} = k[N_2O_5]$$

Hence, $$[N_2O_5] = \frac{1}{k}\frac{-d[N_2O_5]}{dt} = \frac{2.60 \times 10^{-4}\text{ M s}^{-1}}{5.20 \times 10^{-3}\text{ s}^{-1}}$$

$$= 5.00 \times 10^{-2}\text{ M}$$

3) $[A]_t = 12.5\%\,[A]_0 = [A]_0/8$

Using Eq. 18.20, $$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0/8}$$

$$= \left(\frac{2.303}{5.20 \times 10^{-3}} \log 8\right)\text{s} = 400\text{ s}$$

4) Using Eq. 18.30, $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3.55 \times 10^{-4}}\text{ s} = 1950\text{ s}$$

5) Let us write the rate law as,

$$v = k[I^-]^m\,[S_2O_8^{2-}]^n$$

As in Example 11, $$m = \frac{\log 12.50 \times 10^{-6}/6.25 \times 10^{-6}}{\log 8.0 \times 10^{-2}/4.0 \times 10^{-2}} = 1$$

$$n = \frac{\log 6.25 \times 10^{-6}/3.12 \times 10^{-6}}{\log 4.0 \times 10^{-2}/2.0 \times 10^{-2}} = 1$$

The rate law is,

$$\text{rate} = k[I^-][S_2O_8^{2-}]$$

UNIT 19 PHOTOCHEMISTRY

Structure

19.1 INTRODUCTION

In Unit 9 of this course, we stated that free energy must decrease for a physical or a chemical process to be feasible. This is applicable to thermal reactions (also known as dark reactions). The conversion of carbon dioxide and water into starch is a reaction in which free energy increases. Under laboratory conditions, this reaction is not possible. But plants carry out starch synthesis using sunlight. Ozonisation of oxygen and decomposition of ammonia are also nonspontaneous reactions under laboratory conditions; but these could take place by using light of proper energy. Such possibilities of new reactions and new synthetic methods encouraged the scientists to probe into light-initiated reactions.

In photochemistry, we study the absorption and emission of light by matter. It consists of the study of various photophysical processes and photochemical reactions. Two important photophysical processes are fluorescence and phosphorescence. During fluorescence, light emission takes place in the presence of exciting radiation; but the light emission stops, once the exciting radiation is removed. In contrast to this, during phosphorescence, light emission takes place even after the removal of the exciting radiation.

In photochemical reactions, the substances acquire the necessary activation energy through light absorption. Again this is in contrast to the thermal reactions in which the reactants acquire their activation energy through collisions between molecules.

In this unit, we shall discuss the laws of photochemistry. We shall then describe some photochemical reactions and photophysical processes. We shall also explain some photosensitised reactions. Finally we shall discuss the applications of photochemical studies.

Objectives

After studying this unit, you should be able to

- explain the mathematical form of Beer-Lambert law,
- state Grotthuss-Draper law and Stark-Einstein law,
- calculate the quantum yield of a reaction using the given experimental data,
- explain the reason for the higher energy requirement for the photochemical dissociation of a molecule as compared to its thermal dissociation,

- derive rate expressions for simple photochemical reactions,
- explain some photophysical properties such as fluorescence and phosphorescence,
- list some photosensitised reactions,
- state the applications of photochemical studies, and
- define chemiluminescence..

19.2 LAWS OF PHOTOCHEMISTRY

Grotthuss-Draper law and Stark-Einstein law are the two laws concerning the interaction between matter and light. Before discussing these two laws, let us state the mathematical form of Beer-Lambert law discussed in Unit 8 of Atoms and Molecules course.

Beer-Lambert law is useful in calculating the concentration of a solution on the basis of its light absorption. This law relates the intensity of the transmitted monochromatic light to the concentration of the solution and the thickness of the cell in which the solution is kept.

Mathematical form of Beer-Lambert law is given below:

$$\log I_0/I = A = \varepsilon c l \qquad \ldots (19.1)$$

where I_0 = Intensity of the incident radiation

I = Intensity of the transmitted radiation

$A = \log I_0/I$ = Absorbance or optical density of the solution

c = Concentration of the solution expressed in mol m^{-3} units

l = thickness of the cell

ε = Molar extinction coefficient; expressed in m^2 mol^{-1}

The molar extinction coefficient of a substance can be determined using a colorimeter or a spectrophotometer as follows. The absorbances of a solution are measured at different known concentrations using a cell of known thickness (l). The plot of A against c gives a straight line (Fig. 19.1) and its slope is equal to ε l.

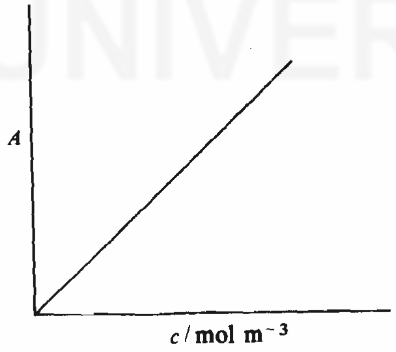


Fig. 19.1: A vs c plot.

$$\text{Hence, } \varepsilon = \frac{\text{slope}}{l}$$

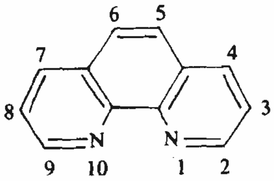
Since l is known, ε can be calculated. Using this ε value, the concentration of a solution can be determined by measuring its absorbance.

Colorimeters and spectrophotometers are commercially available for the measurement of absorbances. In colorimeters, colour filters are used to get the incident radiation in a particular wavelength range. Spectrophotometers have arrangements for obtaining nearly monochromatic incident radiation. Both colorimeters and spectrophotometers have devices for converting the light transmitted into suitable signal through detector devices (see Sec. 19.3). The signal generated from transmitted light is directly read as absorbance values.

Study the following example carefully. The calculation shown below is used in chemical actinometers (Example 3 in Sec. 19.3) for estimating the intensity of the light absorbed during a photochemical reaction. This example illustrates the use of Eq. 19.1 in calculating the concentration of a solution.

Example 1

A solution of the red complex formed by Fe^{2+} ion with 1,10-phenanthroline is taken in a cell of thickness 1.00 cm. If ε for the complex is $1.11 \times 10^3\ m^2\ mol^{-1}$ and the absorbance of the solution is 0.391, calculate the concentration of the complex in mol m^{-3} units.



1,10 – Phenanthroline (Phen)

Solution

$$A = 0.391;\ l = 1.00\ \text{cm} = 1.00 \times 10^{-2}\ \text{m};$$

$$\varepsilon = 1.11 \times 10^3\ \text{m}^2\ \text{mol}^{-1}$$

$$\text{Rearranging Eq. 19.1, } c = \frac{A}{\varepsilon l} = \frac{0.391}{1.11 \times 10^3 \times 1.00 \times 10^{-2}}\ \text{mol m}^{-3}$$

$$= 0.0352\ \text{mol m}^{-3}$$

We shall now state the two laws of photochemistry.

Grotthuss-Draper Law

According to this law, only the light that is absorbed by a molecule can produce a photochemical change in it. This means that it is not sufficient to pass light through a substance to bring about a chemical reaction; but the light must be absorbed by it. Stark-Einstein law of photochemical equivalence provides a quantum mechanical form to Grotthuss-Draper law.

Stark-Einstein Law of Photochemical Equivalence

Stark-Einstein law of photochemical equivalence can be stated as follows:

Each molecule taking part in a photochemical reaction absorbs one quantum of radiation which causes the reaction.

This law is applicable to the primary act of excitation of a molecule by light absorption. This law helps in calculating the quantum efficiency (Φ) which is a measure of the efficiency of the use of light in a photochemical reaction.

Stark-Einstein law is applicable only if the intensity of light is not very high.

The quantum efficiencies for the formation of a product and for the disappearance of the reactant are defined below:

$$\left\{\begin{array}{l}\text{The quantum efficiency}\\ \text{for the formation of a}\\ \text{product } (\phi_P)\end{array}\right\} = \left\{\begin{array}{c}\dfrac{\text{Number of molecules of product formed in 1 second}}{\text{Number of quanta absorbed in 1 second}}\end{array}\right\} \quad \ldots (19.2)$$

$$= \frac{dN_P/dt}{I_a}$$

In this equation, dN_P/dt denotes the rate of formation of the product. The units for $\frac{dN_P}{dt}$ are molecules per second. I_a refers to the number of photons absorbed per second. Similarly we can define the quantum efficiency for the disappearance of a reactant.

$$\left\{\begin{array}{l}\textbf{The quantum efficiency for}\\ \textbf{the disappearance of the}\\ \textbf{reactant } (\phi_R)\end{array}\right\} = \left\{\begin{array}{c}\dfrac{\text{Number of molecules of reactant consumed in 1 second}}{\text{Number of quanta absorbed in 1 second}}\end{array}\right\} \quad \ldots (19.3)$$

$$= \frac{-\,dN_R/dt}{I_a}$$

where $-\mathrm{d}N_R/\mathrm{d}t$ is the rate of consumption of the reactant. The minus sign in $-\mathrm{d}N_R/\mathrm{d}t$ is due to the decrease in concentration of the reactant with time.

As per Stark - Einstein law, each reacting molecule absorbs one quantum of light. Hence,

$$\left\{\begin{array}{l}\text{the energy absorbed by one}\\ \text{mole of a substance undergoing}\\ \text{photochemical reaction}\end{array}\right\} = N_A h\nu = \frac{N_A h c}{\lambda} \quad \ldots (19.4)$$

This unit of energy is also called einstein and, as apparent from Eq. 19.4, the value of einstein depends on ν or λ.

where $N_A = 6.022 \times 10^{23}\ \mathrm{mol}^{-1}$

$h = 6.626 \times 10^{-34}\ \mathrm{J\,s}$

$c = 3 \times 10^{8}\ \mathrm{m\,s}^{-1}$

λ = wavelength of the light in m unit

ν = frequency in s^{-1} unit

To calculate the quantum efficiency, use the following steps:

i) **Calculation of Energy Absorbed per Quantum**

$$\left\{\begin{array}{l}\text{Energy per quantum}\\ \text{of radiation absorbed}\end{array}\right\} = h\nu = \frac{hc}{\lambda}$$

Unit for energy per quantum

$=$ joule photon^{-1}

Unit for $I_a = \dfrac{\text{joule second}^{-1}}{\text{joule photon}^{-1}}$

$=$ photon second^{-1}

ii) **Calculation of I_a**

Usually intensity of light absorbed is given in J s^{-1} units. From this, I_a could be calculated using the following equation :

$$\left\{\begin{array}{l}\text{Intensity in terms of}\\ \text{number of photons}\\ \text{absorbed in 1 second } (I_a)\end{array}\right\} = \frac{\text{Intensity in J s}^{-1}\text{units}}{\text{Energy per quantum}}$$

iii) **Calculation of** $\dfrac{-\mathrm{d}N_R}{\mathrm{d}t}$ or $\dfrac{\mathrm{d}N_P}{\mathrm{d}t}$

First we have to obtain the number of moles of reactant consumed or of product formed **in 1 second** by dividing the respective amount by the time in second unit.

In order to calculate the rate of formation or rate of disappearance in molecule per second units, we have to use the following equations:

$$\frac{-\mathrm{d}N_R}{\mathrm{d}t} = \left\{\begin{array}{l}\text{Number of moles of reactant}\\ \text{decomposed in 1 second}\end{array}\right\} \times N_A \quad \ldots (19.5)$$

Also,

$$\frac{\mathrm{d}N_P}{\mathrm{d}t} = \left\{\begin{array}{l}\text{Number of moles of product}\\ \text{formed in 1 second}\end{array}\right\} \times N_A \quad \ldots (19.6)$$

iv) **Calculation of Quantum Efficiency**

Using Eq. 19.2 or 19.3, ϕ_P or ϕ_R can be calculated.

Let us illustrate the calculation of quantum efficiency for a reaction.

Example 2

In photochemical decomposition of acetone using 313 nm light, 7.57×10^{-6} mol of carbon monoxide is formed in 20 minutes. If the light absorbed corresponds to $2.41 \times 10^{-3}\ \mathrm{J\,s}^{-1}$, calculate the quantum efficiency for the formation of carbon monoxide.

i) $$\left\{\begin{array}{l}\text{Energy absorbed}\\ \text{per quantum}\end{array}\right\} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{313 \times 10^{-9}}\ \text{joule photon}^{-1}$$

$$= 6.35 \times 10^{-19}\ \text{joule photon}^{-1}$$

ii) $$I_a = \frac{\text{Intensity in joule second}^{-1}}{6.35 \times 10^{-19}\ \text{joule photon}^{-1}}$$

$$= \frac{2.14 \times 10^{-3}\ \text{joule second}^{-1}}{6.35 \times 10^{-19}\ \text{joule photon}^{-1}}$$

i. e., $I_a = 3.80 \times 10^{15}$ photons second^{-1}

iii) Amount of carbon monoxide formed in 1 second $= \frac{7.57 \times 10^{-6}\ \text{mol}}{20 \times 60\ \text{s}}$

$$= 6.31 \times 10^{-9}\ \text{mol s}^{-1}$$

$$\frac{dN_{CO}}{dt} = 6.31 \times 10^{-9} \times 6.022 \times 10^{23}\ \text{molecule second}^{-1}$$

$$= 3.80 \times 10^{15}\ \text{molecule second}^{-1}$$

iv) Using Eq. 19.2, ϕ_{CO} = Quantum efficiency for the formation of carbon monoxide

$$= \frac{\frac{dN_{CO}}{dt}}{I_a} \approx 1$$

In the next section, we shall discuss the experimental method of determining the quantum efficiency of a reaction. Before studying this, work out the following SAQ.

SAQ 1

A radiation of 250 nm incident on HI results in the decomposition 1.85×10^{-2} mol within a particular time interval. Light energy absorbed during this time interval is 4.18 k J. Calculate the quantum efficiency for the decomposition of HI.

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19.3 EXPERIMENTAL DETERMINATION OF QUANTUM EFFICIENCY

For the determination of quantum efficiency of a photochemical reaction, we must measure the following:

- the rate of decomposition of the reactants or the rate of formation of the products ; this can be done using any of the methods discussed in Unit 18.
- the number of quanta absorbed in the given time.

In short, we need a method for measuring the amount of light absorbed. If we can devise a method for estimating the intensity of the incident light (I_0) and the intensity of the light transmitted (I) by the reaction mixture, the intensity of the light absorbed (I_a) can be calculated using the relationship ;

$$I_a = I_0 - I$$

For measuring I_0 and I, same cell is used. I_0 corresponds to the measurement of intensity with empty cell (known as blank) and I, to the measurement using the cell containing the reaction mixture.

The experimental set-up used for measuring the intensity of light is shown in Fig. 19.2.

As a source (A) of visible light, a high intensity tungsten lamp or quartz halogen lamp or xenon arc lamp can be used. For obtaining ultraviolet light, hydrogen or deuterium lamps are good sources. The light is first passed through a lens, B (to get a parallel beam of light), and then through a monochromator (C). The monochromator yields a narrow band of light in the desired wavelength. The monochromatic light then passes through the reaction cell (D). The light transmitted by the reaction cell reaches the detector (E).

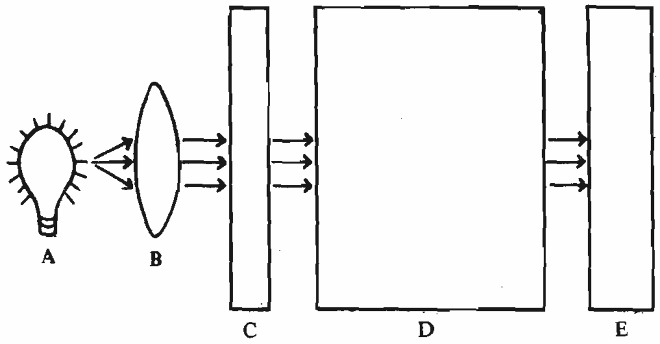

Fig. 19.2 : Measurement of intensity of light during a photochemical reaction.

While using ultraviolet light as a source of radiation, quartz cuvettes (cells) and lenses must be used.

Since pyrex glass absorbs light below 300 nm, it can be used for radiation above 300 nm only.

The visible light has the wavelength region, 800-380 nm. The ultraviolet light has wavelength below 380 nm and above 10 nm.

The detector is used for measuring the intensity of light. The quantitative measurement of light intensity based on energy conversion or on chemical reaction is called **actinometry**. Detectors such as thermopiles and the photoelectric cells function on energy conversion principle. We discuss each of them in brief below :

Thermopile

Thermopile consists of thermocouples connected in series and it generates electricity on heating.

Thermopile (Fig. 19.3) is a device useful for converting light into heat, and then, heat into electricity. It has a set of junctions of different metals having a blackened surface. This black coating is to ensure absorption of all radiation falling on it. The energy so absorbed increases the temperature of the metals. Thermopile converts this temperature increase into a potential difference. Light intensity is related to electricity generated by it. The detector device must be calibrated against a standard light source. Thermopile could be used as a detector for light of any wavelength.

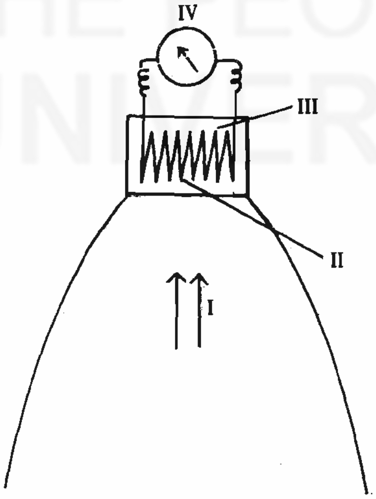

Fig. 19, 3 : Thermopile : I. light radiation, II. blackened surface exposed to radiation; III. unexposed surface at the back; IV galvanometer.

Photoelectric Cells

Photoelectric cell converts light directly into electricity. The current generated is directly proportional to light intensity. Photoelectric cell is an evacuated bulb with a photosensitive cathode. Light radiation results in the emission of electrons from the cathode which get collected at the anode. Thus the flow of current is caused. The photoelectric cell is sensitive to the wavelength of the light used and must be calibrated using a thermopile.

Chemical Actinometers

Light intensity could be estimated by a quantitative estimation of a substance formed or decomposed by light. The photochemical decomposition of $K_3Fe(C_2O_4)_3$ is a widely used chemical method for estimating intensity of light between the wavelength range 250 nm and 577 nm. Light within this wavelength range causes $K_3Fe(C_2O_4)_3$ dissolved in sulphuric acid to react as follows:

$$2\,Fe^{3+} + 2\,e^- \rightarrow 2\,Fe^{2+}$$

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

The concentration of Fe^{2+} is estimated colorimetrically through complex formation with 1,10-phenanthroline. (See Example 1). This complex has a deep red colour. The concentration of the complex is equal to the concentration of Fe^{2+} present before complexation. The following example is worked out to illustrate this method.

Example 3

In a potassium ferrioxalate actinometer, the quantum efficiency for Fe^{2+} production (ϕ_{FS}) at 480 nm wavelength is 0.95. After irradiating the potassium ferrioxalate solution for 20 minutes, it is completely transferred to a 200 cm^3 volumetric flask, mixed with required quantity of 1,10-phenanthroline for complex formation and made up to mark with a buffer solution. For colorimetric estimation, a sample of this complex is taken in a cell of 1.00 cm thickness. The complex has an absorbance value of 0.391 and its ε is $1.11 \times 10^3\ m^2\ mol^{-1}$. Calculate

i) the concentration of the complex,

ii) the number of Fe^{2+} ions formed in the actinometer due to irradiation,

iii) the rate of formation of Fe^{2+} ions (dN_{FS}/dt)

iv) I_a (number of photons absorbed per second).

Assume that one Fe^{2+} ion forms one complex molecule with 1,10-phenanthroline.

Solution

i) Note that the concentration of the complex is same as that calculated in Example 1 using Eq. 19.1; c = concentration of complex = $0.0352\ mol\ m^{-3}$.
Also, concentration of Fe^{2+} ion = concentration of the complex

$$= 0.0352\ mol\ m^{-3}$$

ii)
$$\left\{\begin{array}{l}\text{Number of moles of } Fe^{2+} \text{ ion}\\ \text{present in 200 } cm^3 \text{ of the}\\ \text{solution}\end{array}\right\} = \left\{\begin{array}{l}\text{Concentration}\\ \text{of } Fe^{2+} \text{ ion}\end{array}\right\} \times \left\{\begin{array}{l}\text{volume of the}\\ \text{solution in } m^3\\ \text{unit}\end{array}\right\}$$

$$= 0.0352 \times 200 \times 10^{-6}\ mol$$

$$= 7.04 \times 10^{-6}\ mol \quad \left\{\begin{array}{l}\text{because, } 200\ cm^3\\ = 200 \times 10^{-6}\ m^3\end{array}\right\}$$

$$\left\{\begin{array}{l}\text{Hence the number of moles}\\ \text{of } Fe^{+2} \text{ ion formed in the}\\ \text{actinometer}\end{array}\right\} = 7.04 \times 10^{-6}\ mol$$

The number of Fe^{2+} ions formed in the actinometer $= 7.04 \times 10^{-6} \times 6.022 \times 10^{23}$ ions

$$= 4.24 \times 10^{18}\ \text{ions}$$

iii)
$$\frac{dN_{FS}}{dt} = \frac{\text{Number of } Fe^{2+} \text{ ions formed}}{\text{Time in seconds}} = \frac{4.24 \times 10^{18}}{1200}\ \text{ions second}^{-1}$$

$$= 3.53 \times 10^{15}\ \text{ions second}^{-1}$$

iv) Using Eq. 19.2, $\phi_{FS} = \dfrac{dN_{FS}/dt}{I_a}$

Given that $\phi_{FS} = 0.95$

$$\text{Hence } I_a = \frac{dN_{FS}}{dt} \times \frac{1}{0.95}$$

$$= \frac{3.53 \times 10^{15}}{0.95} \text{ photons second}^{-1}$$

$$= 3.72 \times 10^{15} \text{ photons second}^{-1}$$

The Quantum Efficiencies of Some Reactions

If a photochemical reaction follows Stark-Einstein law, then ϕ ust be unity. Studies on a large number of photochemical reactions indicate that while some of them follow Stark-Einstein law, many others do not. The quantum efficiencies of some photochemical reactions along with their effective wavelengths are given in Table 19.1.

Table 19.1: Quantum Efficiencies and Effective Wavelengths of Some Photochemical Reactions

Reaction	Effective wavelength / nm	ϕ
$2NH_3 \rightarrow N_2 + 3H_2$	<210	0.2
$2NO_2 \rightarrow 2NO + O_2$	<366	0.7
$H_2 + Br_2 \rightarrow 2HBr$	<511	0.01
$H_2S \rightarrow H_2 + S$	<208	1.0
$2HI \rightarrow H_2 + I_2$	<327	2.0
$3O_2 \rightarrow 2O_3$	<175	3.0
$H_2 + Cl_2 \rightarrow 2HCl$	<478	10^6

The photochemical reactions for which quantum efficiency is a small integer are said to follow Stark-Einstein law. Examples are the dissociation of H_2S or ozonisation of oxygen etc. Reactions like the formation of hydrogen chloride or hydrogen bromide do not follow Stark-Einstein law. The quantum efficiency for the former reaction ($H_2 + Cl_2 \rightarrow 2\,HCl$) is very high while it is much low for the latter ($H_2 + Br_2 \rightarrow 2\,HBr$). In order to explain these discrepancies, Bodenstein pointed out that photochemical reactions involve two distinct processes:

i) In the primary process, absorption of one quantum of light results in the excitation of one molecule or an atom (A) to form the excited species, A^*.

$$\underset{\text{Atom or molecule}}{A + h\nu} \rightarrow \underset{\text{Excited species}}{A^*}$$

ii) In the secondary process, the excited species undergoes a chemical change

$$A^* \rightarrow \text{Products}$$

According to Bodenstein, the deviations from Stark-Einstein law are due to the secondary processes.

In the case of reactions having low quantum yields, the number of molecules decomposed by the absorption of one quantum of radiation is less than one. The probable reasons for the low quantum yields are given below:

- The excited species formed at the first step may be deactivated by collisions before the product could be formed. This process is called **quenching**. Sometimes the presence of paramagnetic substances like oxygen or nitric oxide could result in quenching leading to low quantum yield for a chemical reaction.

- One or more of the reactions in the secondary processes may be endothermic. High energy requirement could decrease the reaction rate. In Sec. 19.5, we will see that the quantum yield for the formation of hydrogen bromide is low due to the endothermic nature of the reaction between Br and H_2 (see Example 5 in Sec. 19.5).

- The excited species may recombine to give the reactant molecule. In the hydrogen bromide formation, another reason for the low quantum yield is the recombination of bromine atoms which are formed in the primary step.

In the case of reactions with high quantum yields, the excited species formed in the first step could initiate a series of chain reactions. This causes a large number of molecules to react by absorption of one quantum of light, as in the case of hydrogen chloride formation (see Sec. 19.5).

The following SAQ could be answered correctly, if you have understood the materials in this section.

SAQ 2

The quantum yield for the photochemical formation of hydrogen chloride is high in the absence of oxygen but low when oxygen is present. Explain.

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19.4 PHOTOCHEMICAL DISSOCIATION

In Unit 3 of Atoms and Molecules course, it has been stated that the bond enthalpy gives an estimate of the average energy required to break a particular bond. These bond enthalpies are derived from thermochemical calculations (see Sec. 7.8 of Unit 7 of this course). It is generally seen that the energy required for the dissociation of a particular bond by light absorption is much greater than its bond enthalpy value. In Table 19.2, we illustrate this for some diatomic molecules.

Bond enthalpy of a diatomic molecule indicates the energy requirement for its thermal dissociation.

Table 19.2: Comparison of Photochemical Dissociation Energies and Bond Enthalpies

Dissociating molecule	λ/nm*	(Photochemical dissociation** energy) / kJ mol^{-1}	Bond enthalpy*** kJ mol^{-1}
H_2	84.5	1420	436
Cl_2	478	250	242
Br_2	511	235	193
HI	327	367	299
O_2	176	682	497

* λ value corresponds to maximum wavelength of light required for decomposition by direct irradiation.

** Photochemical dissociation energy for one mole is calculated by substituting for λ in Eq. 19.4.

*** Bond enthalpies except for HI are taken from Table 3.9 of Unit 3 of Atoms and Molecules course.

The reasons for the higher photochemical dissociation energies as compared to bond enthalpies are given below:

- For dissociating a molecule through light absorption, there must be an upper electronic state with appropriate energy levels. There is no such restriction for thermal decomposition.

- During photochemical dissociation, the product species could be in an excited state and / or in ground state. For example, decomposition of bromine by absorption of light of wavelength 511 nm can be shown as below:

$$Br_2 + h\nu \rightarrow Br^* + Br \qquad \lambda = 511 \text{ nm}$$

The atom with asterisk sign indicates excited state. Thus, photochemical decomposition of bromine needs 235 kJ mol^{-1}. But thermal decomposition of bromine needs 193 kJ mol^{-1} only, since both the bromine atoms are formed in ground state.

The photochemical dissociation of molecules is also known as **photolysis.** The photolysis can be understood using potential energy diagrams of the type discussed in Unit 4 of Atoms and Molecules course. In Fig. 19.4, the ground state and the excited state are represented using potential energy diagrams I and II, respectively. The quantised vibrational sublevels in each state are shown by horizontal lines such as AB, EF etc.

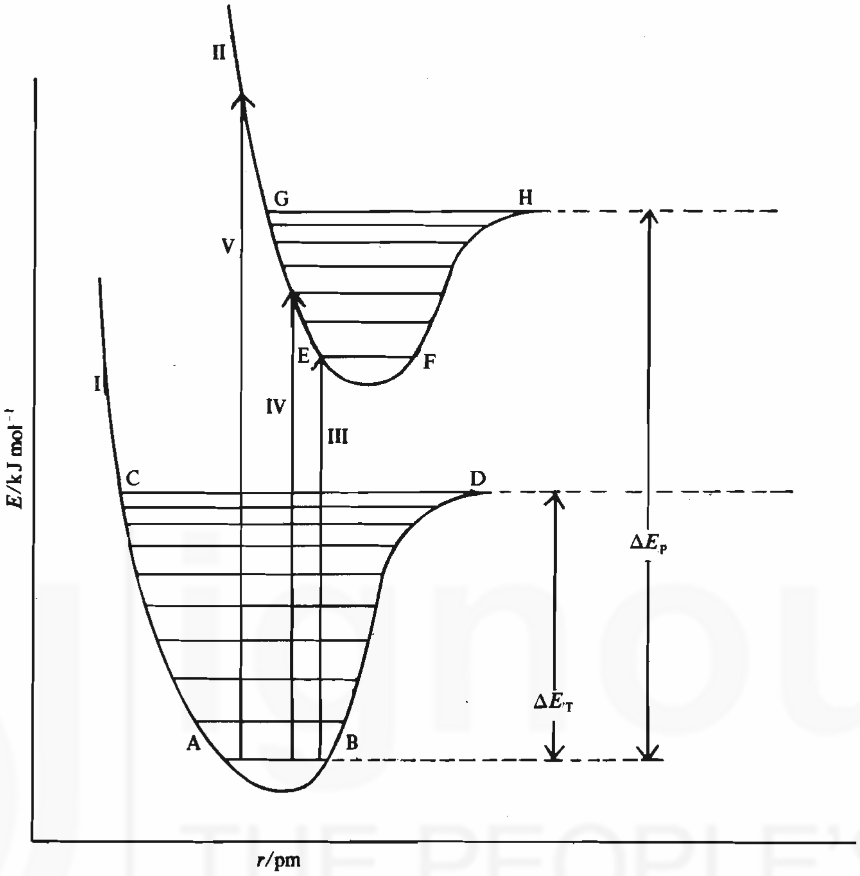

Fig. 19.4: Electronic excitation; E (potential energy) vs r (internuclear distance).

When a molecule is excited from zero vibrational level AB of ground electronic state to any of the vibrational levels **below** GH in the upper electronic state, the resultant electronic spectrum shows an absorption band with vibration — rotation fine structure. The fine structure is due to numerous transitions (such as III, IV etc.) possible from the zero vibrational level (AB) in the lower electronic state to any of the quantised vibrational levels in the upper electronic state. This can further be understood from the fact that each vibrational level has its own rotational sublevels.

When a molecule absorbs sufficient energy such that it is transferred from the ground state to or above GH in the upper electronic state, then the molecule undergoes photochemical dissociation. The spectrum shows a continuum (lack of discrete lines), once the molecule dissociates. The difference in energy between the levels AB and GH (ΔE_P) is the **photochemical dissociation energy. The thermal dissociation energy** (ΔE_T) is equal to the bond enthalpy in the case of diatomic molecules and it is the energy difference between the lowest and uppermost vibrational levels (AB and CD) in the ground state. Note that $\Delta E_P > \Delta E_T$.

We have discussed photolysis in detail so far because it is the initial reaction in many photochemical reactions. The excited atom or radical formed due to photolysis of a molecule often starts a chain reaction. We shall use this principle in the next section in the study of some photochemical reactions. Before studying that, answer the following SAQ which will help you in understanding Example 4.

SAQ 3

In the photochemical dissociation of HI, the first step is given below:

$$HI + h\nu \rightarrow H + I$$

Assume that H atom formed is in excited state while I atom is in ground state. Calculate the excess energy that the excited hydrogen atom carries as (use Table 19.2) compared to a ground state hydrogen atom.

The excess energy ($\Delta E_P - \Delta E_T$) that a photochemical decomposition demands as compared to thermal decomposition is given to one of the atoms formed. This atom is said to be in the excited state.

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19.5 SOME PHOTOCHEMICAL REACTIONS

In this section, we discuss the mechanism of some photochemical reactions and then explain flash photolysis. For the first two reactions given below, we derive rate equations also. You go through these derivations carefully. These two examples could give you an idea as to how the photochemical rate expressions are written.

The first step in both the examples is photolysis. The rate of the photolysis step is expressed as I_a which is the rate of absorption of light (number of quanta absorbed per second). The initial photolysis is followed by thermal (or dark) reactions for which kinetic expressions are similar to those discussed in Unit 18.

Example 4

Photochemical Decomposition of Hydrogen Iodide

Let us derive expressions useful in calculating the rate of decomposition of HI and the quantum efficiency for this reaction. HI undergoes photochemical decomposition below 327 nm. The mechanism is given below:

$$HI + h\nu \rightarrow H + I \qquad \text{Rate of photolysis} = I_a \qquad ..\ (19.7)$$

$$H + HI \xrightarrow{k_2} H_2 + I \qquad ..\ (19.8)$$

$$I + I \xrightarrow{k_3} I_2 \qquad ...\ (19.9)$$

Such steps are written based on energy considerations. If you have answered SAQ in the last section correctly, you could follow why in the second step H atom attacks HI whereas I does not.

While deriving rate expressions, we try to eliminate terms containing active species using steady state principle.

HI is consumed in two ways as per Eqs. 19.7 and 19.8. The rate of disappearance of HI can be written as follows :

$$\frac{-d[HI]}{dt} = I_a + k_2[H][HI] \qquad ...\ (19.10)$$

As per steady state approximation discussed in Unit 18, the concentration of the active species H is constant. In other words, its concentration does not vary with time.

i.e., $$\frac{d[H]}{dt} = 0 = I_a - k_2[H][HI] \qquad ...\ (19.11)$$

Note that H is formed as per Eq. 19.7 and is used as per Eq. 19.8.

or $$k_2[H][HI] = I_a \qquad ...\ (19.12)$$

Using Eqs. 19.10 and 19.12, we get,

$$\frac{-d[HI]}{dt} = 2I_a \qquad ...\ (19.13)$$

Experimentally it has been observed that the quantum efficiency for HI decomposition is 2 (Have you worked out SAQ 1?). It is worth noting that the rate of decomposition of HI depends on the intensity of the absorbed light as per Eq. 19.13.

Example 5

Photochemical Reaction between H_2 and Br_2

Hydrogen and bromine combine at wavelengths below 511 nm to give HBr as per the mechanism given below. Let us calculate the rate of formation of HBr and also the quantum efficiency for this reaction.

$$Br_2 + h\nu \rightarrow Br + Br \qquad \text{Rate of photolysis} = I_a \qquad \text{... (19.14)}$$

$$Br + H_2 \xrightarrow{k_2} HBr + H \qquad \text{... (19.15)}$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br \qquad \text{... (19.16)}$$

$$H + HBr \xrightarrow{k_4} H_2 + Br \qquad \text{... (19.17)}$$

$$Br + Br \xrightarrow{k_5} Br_2 \qquad \text{... (19.18)}$$

The rate of formation of HBr can be written as,

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \qquad \text{.. (19.19)}$$

Note that Br and H are active species and we can apply steady state approximation for these two.

$$\frac{d[Br]}{dt} = 0 = 2I_a - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - 2k_5[Br]^2 \qquad \text{...(19.20)}$$

The coefficient 2 in $2I_a$ and $2k_5[Br]^2$ are due to the formation or disappearance of two bromine atoms in the respective steps.

$$\frac{d[H]}{dt} = 0 = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] \qquad \text{... (19.21)}$$

Adding Eqs. 19.20 and 19.21 and rearranging we get

$$2k_5[Br]^2 = 2I_a \qquad \text{... (19.22)}$$

or

$$[Br] = (I_a/k_5)^{1/2} \qquad \text{... (19.23)}$$

Rearranging Eq. 19.21 and using Eq. 19.23 we get,

$$[H] = \frac{k_2[Br][H_2]}{k_4[HBr] + k_3[Br_2]} = \frac{k_2[H_2](I_a/k_5)^{1/2}}{k_4[HBr] + k_3[Br_2]} \qquad \text{... (19.24)}$$

Using Eqs. 19.19, 19.23 and 19.24,

$$\frac{d[HBr]}{dt} = k_2(I_a/k_5)^{1/2}[H_2] + \{k_3[Br_2] - k_4[HBr]\}\left[\frac{k_2[H_2](I_a/k_5)^{1/2}}{k_4[HBr] + k_3[Br_2]}\right]$$

$$= \frac{2k_2k_3(I_a/k_5)^{1/2}[H_2][Br_2]}{k_4[HBr] + k_3[Br_2]}$$

Dividing the numerator and the denominator of R.H.S by $k_3[Br_2]$,

$$\frac{d[HBr]}{dt} = \frac{2k_2k_5^{-1/2}I_a^{1/2}[H_2]}{1 + k_4[HBr]/k_3[Br_2]} \qquad \text{...(19.25)}$$

i.e.,

$$\frac{d[HBr]}{dt} \propto I_a^{1/2} \qquad \text{... (19.26)}$$

This shows that the rate of hydrogen bromide formation is proportional to the square root of absorbed intensity. This has been proved experimentally.

In the above two cases, we derived rate expressions. Next, we shall study the reaction between H_2 and Cl_2 in a qualitative way, and then, study the principles of flash photolysis.

Hydrogen-chlorine Reaction

The quantum efficiency for the photochemical combination of hydrogen and chlorine is very high. When exposed to light of wavelength 478 nm, the primary process in the photochemical reaction is the decomposition of chlorine,

$$Cl_2 + h\nu \rightarrow 2\,Cl \qquad \text{... (19.27)}$$

This is followed by the following secondary processes:

$$Cl + H_2 \rightarrow HCl + H \qquad \text{... (19.28)}$$

$$H + Cl_2 \rightarrow HCl + Cl \qquad \text{... (19.29)}$$

The reaction between Cl and H_2 (Eq. 19.28) is exothermic and much fast. This results in the propagation of chain reaction with high quantum efficiency. The chain-terminating step is the recombination of chlorine atoms on the walls of the vessel to form chlorine molecule.

$$Cl + Cl \rightarrow Cl_2 \qquad \text{... (19.30)}$$

Next we shall explain briefly the main features of flash photolysis. Flash photolysis is useful in detecting the short-lived intermediates in a reaction sequence. The reaction mechanisms are proposed based on flash photolysis results.

Flash Photolysis

Flash photolysis was developed by Norrish and Porter in 1949. In ordinary photolysis, the steady state concentrations of the intermediates are so small that these cannot be detected by absorption spectrophotometers. In flash photolysis, a high-intensity flash of microsecond duration is used for photolysing the substance and the products are identified using absorption spectrophotometers. The flash duration must match the decay rate of the intermediates. Flash lamps work for a time of around 15 μs. This restricts their use to the study of intermediates of life time around 100 μs. In recent years, laser flash sources have been developed. The flash duration is around 10^{-9} s.

As far as this section is concerned, make sure that you understand the derivations for calculating the rate of decomposition of hydrogen iodide and the rate of formation of hydrogen bromide. This could help you in arriving at the rate expressions for simple photochemical reactions for which reaction sequence (like Eq. 19.14 to Eq. 19.18) is known. You can build up confidence by answering the SAQ given below. The aim of this SAQ is to make you derive expression for the rate of formation of carbon monoxide in the photolysis of acetaldehyde. You are guided through a series of steps with helpful hints. This guidance has added to the length of the problem. Don't mind it!

SAQ 4

Look at the reaction sequence for the photolysis of acetaldehyde:

$$CH_3CHO + h\nu \rightarrow CH_3 + CHO \quad \begin{matrix}\text{Rate of}\\ \text{photolysis}\end{matrix} = I_a \qquad \text{...(1)}$$

$$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO \qquad \text{...(2)}$$

$$CH_3CO \xrightarrow{k_3} CH_3 + CO \qquad \text{...(3)}$$

$$CH_3 + CH_3 \xrightarrow{k_4} C_2H_6 \qquad \text{...(4)}$$

I_a is the absorbed light intensity and it represents the rate of photochemical excitation (as per Eq. (1)).

Using the above mechanism, derive expressions for the following:

i) $\frac{d[CH_3CO]}{dt}$ ii) $\frac{d[CH_3]}{dt}$

(**Hints:** CH_3CO and CH_3 are active species. CH_3CO is formed as per Eq. (2) and consumed as per Eq. (3). CH_3 is formed as per Eqs. (1) and (3), and used up as per Eqs. (2) and (4). The answers for (i) and (ii) are to be arrived at using Eqs. 19.21 and 19.22 as models. Note that as per Eq. (4), two CH_3 radicals are consumed for every molecule of ethane formed).

iii) Derive the combined expression for $\frac{d[CH_3CO]}{dt} + \frac{d[CH_3]}{dt}$

(**Hint:** Add up the expressions you have got as answers for (i) and (ii)).

iv) Find the relationship between $[CH_3]$ and I_a.

(**Hint:** Rearrange the answer for (iii)).

v) State the relationship between $\frac{d[CO]}{dt}$ and $[CH_3CO]$.

(**Hint:** Use Eq. (3)).

vi) Find the relationship between the rate of formation of CO and the absorbed light intensity.

(**Hints:** First combine answers for (v) and (i). Then use the answer for (iv)).

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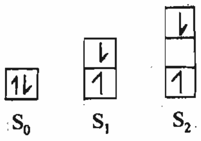
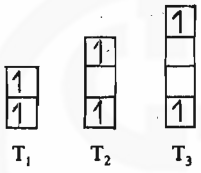
For a 2-electron system, the first three singlet states are represented below :



Note that $E_{S_2} > E_{S_1} > E_{S_0}$, where E stands for the energy of a particular level.

Similarly, the first three triplet states are represented below for a 2-electron system:



$E_{T_3} > E_{T_2} > E_{T_1}$

19.6 PHOTOPHYSICAL PROCESSES

The light absorbed by a molecule is not always used up in producing a chemical reaction. The absorbed energy can be lost through various physical processes also. In this section, we examine such physical processes.

The absorption of ultraviolet or visible light results in the increase of electronic energy from the ground state to the excited state. Usually electronic excitation is also accompanied by an increase in the rotational and vibrational energy levels. In our discussion, for convenience, we depict only transitions between electronic energy levels. In order to understand the nature of electronic transitions, it is essential to know the concept of spin multiplicity. A molecule with electrons paired and with anti-parallel spins is said to be in the singlet ground state (S_o). An excited molecule with **two of its electrons unpaired and, with anti-parallel spins** is said to be in the excited singlet state such as S_1, S_2, S_3, ... etc. An excited molecule with **two of its electrons unpaired, but with parallel spins** is said to be in the excited triplet state such as T_1, T_2, T_3, ... etc.

Normally excitation of a ground state molecule leads only to one of the excited singlet states. But in some specified cases, direct excitation from S_o to a triplet level is possible. We restrict our discussion to $S_o \rightarrow S_1$, $S_o \rightarrow S_2$ etc. transitions only.

Multiplicity of state is given by the expression $2S + 1$, where S (note the italicised type) is the sum of spin values of electrons. This symbol S should not be confused with S (Roman type) for singlet state.

Normally a molecule in the S_o state on absorbing a quantum of light gets two of its paired electrons unpaired and gets transferred to S_1 or S_2 or S_3 .... etc. levels, but not to T_1 or T_2 or T_3 .... etc levels. That is, due to excitation, spin multiplicity is not generally altered. This condition is called the selection rule for electronic transition. In other words, absorption of energy by the molecule in the ground state leads to allowed transition such as $S_o \rightarrow S_1$, $S_o \rightarrow S_2$, $S_o \rightarrow S_3$ and so on. Such excitations and the subsequent energy loss while reaching the ground state are shown by Jablonski diagram (Fig. 19.5). The solid arrows pointing upwards refer to absorption of energy. The solid arrows pointing downwards refer to energy emission as light, known as radiative transitions. The wavy horizontal arrows stand for transition between excited singlet and triplet states without energy loss, while wavy vertical arrows stand for transitions between singlet-singlet or triplet-triplet levels with energy loss as heat (the later is not shown in Fig. 19.5). These wavy arrows stand for nonradiative transitions (transitions without light emission).

Imagine a molecule in the singlet state. It has two electrons with anti-parallel spins (such as $\uparrow\downarrow$). Then, sum of the electron spins

$= S = +\frac{1}{2} - \frac{1}{2} = 0$

Hence multiplicity

$= 2S + 1 = (2 \times 0) + 1 = 1$

In Fig. 19.5, the excitation from the singlet ground state to the excited singlet levels

Thus the singlet state has two electrons with anti-parallel spins and its $(2S + 1)$ value is equal to 1. In the presence of a magnetic field, a singlet state does not split further.

A molecule in the triplet state has two electrons with parallel spins (such as $\uparrow\uparrow$). The sum of electron spins

$$= S = \frac{1}{2} + \frac{1}{2} = 1$$

Hence the multiplicity
$= (2S + 1) = 3$
So, a molecule in the triplet state has two electrons with parallel spins and its $(2S + 1)$ value is equal to 3. In the presence of a magnetic field, a triplet state splits into three energy levels.

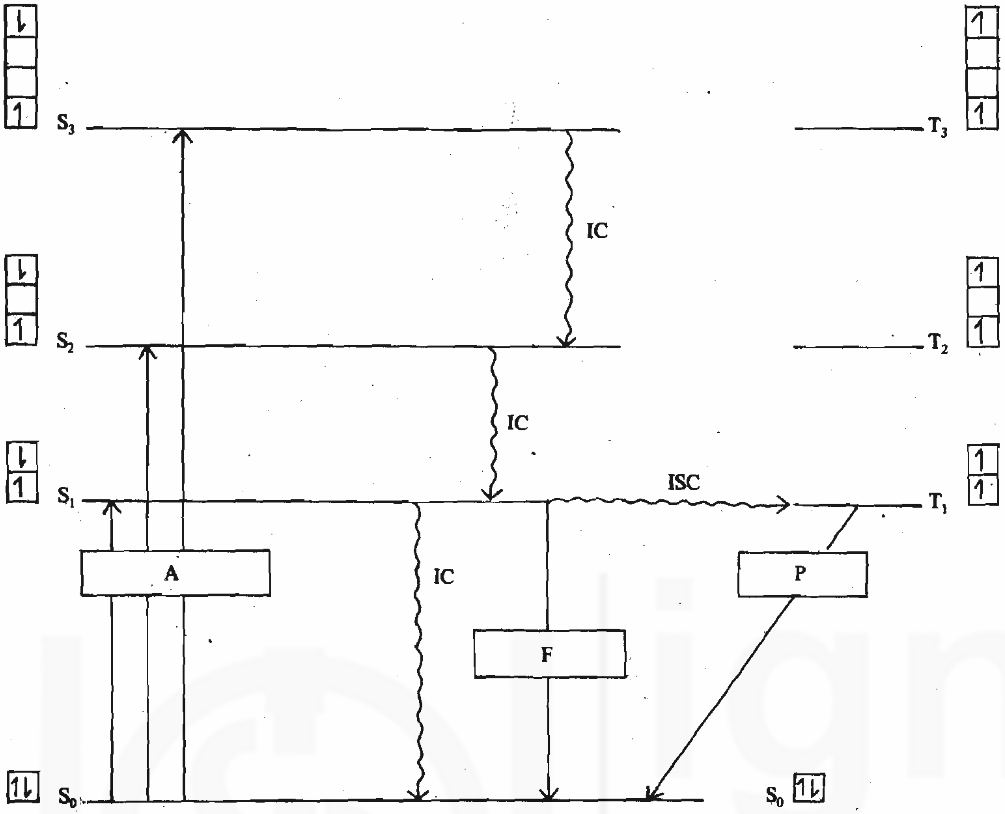


Fig. 19.5: Jablonski diagram

S_1, S_2 and S_3 are shown by vertical arrows marked A. The excited species at S_2 and S_3 have very short lifetimes and these species, quickly lose their energy as heat to the medium in about 10^{-11} second and reach S_1 level. Such a singlet-singlet transition is called an internal conversion (IC). The molecule at S_1 state has a life time of $10^{-8} - 10^{-10}$ second. The system at S_1 may undergo any of the following transitions:

A = **Absorption of quanta leading to excitation to S_1, S_2 and S_3 levels. Note the antiparallel spins at various S levels.**
IC = **Internal conversion from S_3 to S_2, from S_2 to S_1 and from S_1 to S_o.**
F = **Fluorescence; a transition from $S_1 \rightarrow S_o$ with light emission.**
ISC = **Intersystem crossing ; $S_1 \rightarrow T_1$ transition. Note the parallel spins at various T levels.**
P = **Phosphorescence; a transition from $T_1 \rightarrow S_o$ with light emission.**
For clarity, transitions to and fro T_2 and T_3 are not shown.

The name "fluorescence" is derived from the name of the mineral, "fluorite", which emits visible light on exposure to ultraviolet radiation.

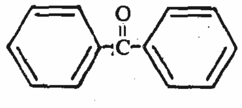
i) Fluorescence

The excited molecule could undergo the transition, $S_1 \rightarrow S_o$, with the emission of light. This phenomenon is called fluorescence (F). Since $S_1 \rightarrow S_o$ transition is allowed by selection rule, it is very fast. In other words, substances fluoresce in the presence of the exciting radiation. Once the exciting radiation is stopped, fluorescence stops.

ii) Internal Conversion

The excess energy may be lost as heat while $S_1 \rightarrow S_o$ transition takes place which is again a case of internal conversion and a radiationless transition.

iii) Intersystem Crossing



Benzophenone

The excited molecule could cross over to the first triplet state through $S_1 \rightarrow T_1$ transition. Such a transition involves spin inversion. For such intersystem crossing (ISC) to be efficient, the energy gap between S_1 and T_1 levels must be low.

Ketones have very low energy gap between S_1 and T_1 levels and have high efficiency for intersystem crossing. Thus benzophenone has 100% efficiency for intersystem crossing. Compared to ketones, aromatic hydrocarbons are less efficient in intersystem crossing and olefins are still less efficient. Let us now study two of the processes by which the molecule in the triplet state could reach the ground state.

1) **Phosphorescence**

An interesting physical process by which an excited species at T_1 level may undergo transition to S_o level is by emitting light ; $T_1 \rightarrow S_o$ transition with emission of light is called **phosphorescence (P).** This is a process with a spin change and is a forbidden transition. Hence, in contrast to fluorescence, light emission during phosphorescence is slow and it lasts even after the removal of exciting radiation.

"Phosphorescene" is derived from "phosphorus" which glows in dark although it is not strictly phosphorescent (see Sec. 19.9).

2) **Energy Transfer**

Another process by which a molecule in the triplet state (called a donor molecule) may lose its excess energy is by energy transfer to an acceptor molecule.This is an instance of **sensitisation** which we shall discuss in Sec. 19.7.

Fluorescence and phosphorescence are exhibited by those substances which do not undergo chemical reaction at the wavelength of radiation.

In this section, we have dealt with some of the important physical processes only. Let us now see some of the applications of the study of the physical processes. Study of fluorescent behaviour of substances has led to the development of fluorescence spectroscopy. Using spectrofluorometers, it is possible to identify several fluorescing substances present in the same solution, provided they have sufficiently different fluorescent spectra. This method is both sensitive and selective. Even substances with a low concentration such as 10^{-9} g/cm^3 could be detected. For example, this method is quite useful in the analysis of drugs, pesticides and atmospheric pollutants which are present in trace amounts. Studies based on fluorescence and phosphorescence provide important data on the properties of excited states such as lifetime, energy and electronic configuration.

On the commercial side, fluorescent lamp is one of the applications of the phenomenon of fluorescence. A fluorescent lamp consists of a glass tube with

- a small amount of mercury,
- two electrodes, and
- a coating of phosphor.

A phosphor is a solid substance which emits fluorescent light when excited by ultraviolet radiation. The electrodes initiate an electric arc which helps in vaporizing and exciting mercury atoms. The excited mercury atoms emit ultraviolet radiation. The phosphor, being excited by ultraviolet radiation, emits fluorescence.

Some other commercial applications of fluorescence are given below:

- Optical brighteners are added to detergents to give extra–brightness to the clothes. Optical brighteners fluoresce in sunlight.
- Fluorescent paints are manufactured using suitable additives.
- TV screens of different colours are produced using phosphors.

Although molecules in the excited singlet and triplet states could show interesting chemical behaviour, their studies are included in Unit 14 of the course on Organic Reaction Mechanisms. In the next section, we shall discuss photosensitisation ; this discussion could make you understand how a substance gains photochemical activity in the presence of another photochemically excited substance. Based on the materials of this section, answer the following SAQ.

SAQ 5

State two differences between fluorescence and phosphorescence.

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19.7 PHOTOSENSITISATION

Photosensitisation is the process of exciting a molecule by energy transfer from an excited molecule. In this process, a donor molecule (D) absorbs a quantum light and forms an excited molecule (D^*). The excited donor molecule then transfers its excitation energy to an acceptor molecule (A) in the ground state in order to excite it. This can be explained using the following reaction sequence:

Light absorption : $D + h\nu \rightarrow D^*$

Sensitisation : $D^* + A \rightarrow A^* + D$

The donor molecule is called the **sensitiser**. In Sec. 19.6, we mentioned about such energy transfer by the excited molecule. The excited acceptor molecule A^* could take part either in chemical reactions or in physical processes which we shall discuss now.

Photosensitised Chemical Reactions

If the excited molecule A^* has obtained sufficient energy, it will get dissociated and start a chemical reaction. The advantage in photosensitised dissociation of a molecule is that it is enough to transfer energy equivalent to its bond enthalpy to dissociate it. It is so since the photosensitised molecule gets dissociated in the ground state. This is in contrast to direct photochemical decomposition for which much higher energy is required due to the necessity of exciting a molecule to upper electronic state (see Sec. 19.4). Thus the energy required for photosensitised dissociation of a molecule is less than that for photochemical dissociation.

Let us consider an example. When irradiated with 253.7 nm light, hydrogen and oxygen react in presence of mercury vapour but not in its absence. Mercury vapour acts as a sensitiser. The reaction sequence is given below:

$$Hg + h\nu \rightarrow Hg^*$$

$$Hg^* + H_2 \rightarrow H + H + Hg$$

$$H + O_2 \rightarrow OH + O$$

The chain reaction continues further. The energy transferred to hydrogen molecule by excited mercury atom is equal to 472 kJ mol^{-1} (as per Eq. 19.4 where $\lambda = 253.7$ nm). This energy is sufficient for thermal dissociation of hydrogen since its bond enthalpy is 436 kJ mol^{-1}(see Table 19.2). Note that excited mercury atom cannot directly dissociate oxygen molecule since its bond enthalpy is higher (497 kJ mol^{-1}). Further in the absence of mercury vapour, light of 253.7 nm (or 472 kJ mol^{-1} energy) cannot photolyse hydrogen or oxygen directly, since the energies needed for their photochemical dissociation are much higher (1420 kJ mol^{-1} and 682 kJ mol^{-1}, respectively). Hence mercury vapour is essential as a sensitiser for H_2–O_2 photochemical reaction at $\lambda = 253.7$ nm.

A well-known photosensitised reaction is photosynthesis. Chlorophyll ("chl") and other plant pigments act as photosensitisers in the synthesis of starch from carbon dioxide and water. A simplified reaction sequence is as follows:

$$\text{chl} + h\nu \rightarrow \text{chl}^*$$

$$\text{chl}^* + CO_2 + H_2O \rightarrow \frac{1}{n}\underset{\text{Starch}}{(CH_2O)_n} + O_2 + \text{chl}$$

Chlorophyll is the name given for a group of compounds with minor variation in structure. Chlorophyll-*a* absorbs effectively in the red region of sunlight; the red light is in abundance in sunlight.

The reaction mechanism is very complex. Energy calculations show that apart from chlorophyll, there must be other coloured light-absorbing materials (pigments) which also provide energy required for the synthesis of starch.

Photosensitisation is frequently used by chemists for preparing compounds which cannot be formed by thermal or direct irradiation methods.

Sensitised Fluorescence

Let us now discuss a physical process which proceeds through sensitisation. Thallium vapour does not give rise to fluorescence when directly irradiated with light of wavelength 253.7 nm. But if mercury vapour is also included in the reaction vessel, thallium exhibits fluorescence. Mercury atoms get excited first and transfer energy to thallium atoms to excite them. The excited thallium atoms emit fluorescence as they go down to the ground level.

Using the ideas learnt in this section, answer the following SAQ.

SAQ 6

Oxalic acid is not decomposed directly by light of wavelength, 335 nm. Irradiation in presence of uranyl (UO_2^+) ion results in the decomposition of oxalic acid to carbon monoxide and carbon dioxide.

i) How do you explain this reaction?

ii) Suggest a reaction sequence.

(**Note:** The above procedure was used in the earlier chemical actinometric method of determining the light intensity. Oxalic acid solution of known concentration was irradiated in presence of uranyl ion and the unreacted oxalic acid was estimated using potassium permanganate solution. From the amount of oxalic acid reacted, the intensity of light was calculated using ϕ for a particular wavelength.)

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19.8 APPLICATIONS OF PHOTOCHEMISTRY

We have earlier indicated the applications of the study of fluorescence, phosphorescence, flash photolysis and photosensitisation. Apart from the above, a few are worth mentioning.

Synthetic organic chemists have increasingly started using photochemical methods for synthesis due to greater efficiency and selectivity as compared to dark reactions. Photochemistry offers a method of conducting reactions which are not possible thermodynamically.

Three common types of cells used for converting light into electricity are given below :

i) Photoelectric cells or photo cells convert light into electricity using photosensitive cathode. (see Sec .19.3).

ii) Photovoltaic cells have two dissimilar silicon (or germanium) crystals in close contact. Irradiation of light causes flow of electrons from one crystal to other. Solar cells used in calculators are photovoltaic cells.

iii) Photogalvanic cells convert light into electricity through chemical reactions.

In the analysis of pollutants, photochemistry plays an important role. For example, photochemical studies have indicated how ozone layer is affected by chlorofluorocarbons (freon) used as refrigerants, solvents and spray- propellants. The simplest freon is CF_2Cl_2. Freon is chemically inert and remains as such for years. But when it reaches stratosphere (10 km to 50 km above the earth's surface), freon decomposes and gives out free chlorine atoms. These chlorine atoms can react with ozone decomposing it. This can cause depletion of ozone layer. It is a matter of serious concern since ozone layer protects our planet from low wavelength portion of sun's rays (290 nm-320 nm wavelength). Irradiation with such high energy radiation could produce skin cancer. As a result of photochemical studies, alternatives are tried for freon.

The present energy crisis has compelled the scientists to look for alternatives. Solar energy, if properly utilised through suitable photochemical reactions, could offer a solution for this energy problem. In this connection we now discuss the functioning of a photogalvanic cell which is helpful for solar energy conversion through chemical reactions.

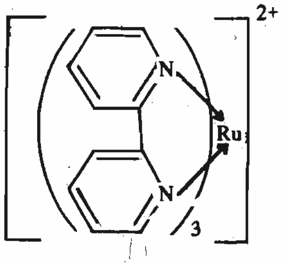
Photogalvanic Cell

A reversible cell which converts light into electricity through an intermediate chemical reaction is called photogalvanic cell. It undergoes cyclic charging and recharging processes as explained below:

Charging in presence of light

Two substances undergo oxidation — reduction in presence of light.

$$OA_1 + RA_2 \xrightarrow{h\nu} OA_2 + RA_1$$



tris - (2, 2′ - bipyridine) ruthenium (II) ion

In this OA_1 and RA_1 refer to oxidised and reduced forms of substance 1, while OA_2 and RA_2 to those of substance 2. In this process, light is used in conducting a chemical reaction. This photochemical reaction is thermodynamically non-spontaneous ($\Delta G > 0$). By the above photochemical process, the cell is charged.

Discharging in the absence of light

In the absence of light, the reaction reverses spontaneously ($\Delta G < 0$).

$$OA_2 + RA_1 \rightarrow OA_1 + RA_2$$

The chemical energy gained during charging is converted into electrical energy and the cell is discharged.

An example of such a system is given below:

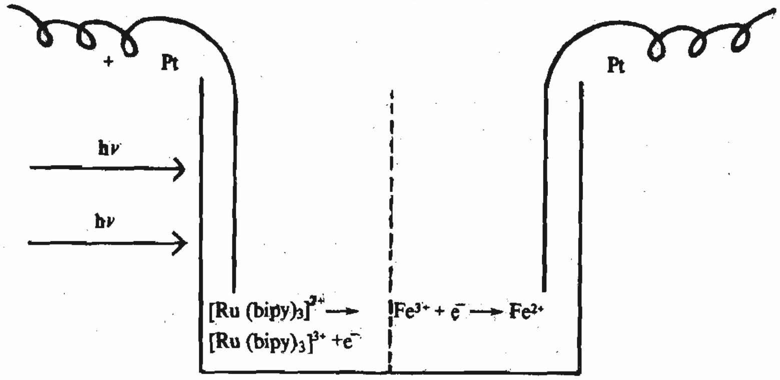


Fig. 19.6: Photogalvanic cell.

$$Fe^{3+} + [Ru(bipy)_3]^{2+} \underset{dark}{\overset{h\nu}{\rightleftharpoons}} [Ru(bipy)_3]^{3+} + Fe^{2+}$$

In this system, tris- (2,2′-bipyridine) ruthenium (II) - tris- (2,2′-bipyridine) ruthenium (III) and iron (II) - iron(III) are the two redox pairs. The platinum electrodes serve as electrical contacts (Fig. 19.6).

In the next section, we shall discuss chemiluminescence, which in a way, is the reverse of photochemical reaction.

SAQ 7

Suggest a basic difference between galvanic cells (discussed in Unit 17) and photogalvanic cells.

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Photochromism is the light induced reversible colour change. The colour change is brought about by reversible reactions. Photochromic sunglasses darken in sunlight and protect the eyes from the excess light. The sunglasses contain Ag^+ and Cu^+ ions and react reversibly as follows :

In presence of sunlight :

$Ag^+ (s) + Cu^+ (s) \rightarrow Ag (s) + Cu^{2+} (s)$

Silver formed is responsible for the darkening of the glasses.

In the absence of sunlight :

$Ag (s) + Cu^{2+} (s) \rightarrow Ag^+ (s) + Cu^+ (s)$

19.9 CHEMILUMINESCENCE

Chemiluminescence is the emission of light as a result of chemical reaction at room temperature. It must be clearly understood that chemiluminescence is not due to any photophysical process like fluorescence or phosphorescence. Some examples of chemiluminescence are given below :

- Glow of phosphorus is due to slow oxidation ; it is not due to phosphorescence as name suggests.
- Oxidation of Grignard compounds by air or oxygen results in greenish-blue luminescence.
- *Will-o-the-wisp* (mistaken as light produced by evil spirits) is the glow caused by the oxidation of decaying wood in marshy places.
- Emission of light by firefly is due to oxidation of some proteins in its body (this is also called bioluminescence).

19.10 SUMMARY

In this unit, we have discussed the physical and chemical processes accompanying light absorption.

- The laws of photochemistry have been stated and explained.
- Quantum yield has been defined and the method of determining it has been explained.
- The variation in energy requirements for photochemical and thermal dissociation has been discussed.
- The rate expressions have been derived for some photochemical reactions.

- The photophysical processes have been explained. The applications of fluorescence and phosphorescence have been stated.
- Photosensitisation has been explained with examples.
- Applications of photochemical studies have been listed.
- Chemiluminescence has been defined.

19.11 TERMINAL QUESTIONS

1) State two differences between a chemical reaction and a photochemical reaction.

2) If 10% of the energy of a 100 W incandescent bulb generates visible light having average wavelength 600 nm, how many quanta of light are emitted in 10 minutes?

$$(1\ \text{W} = 1\ \text{J s}^{-1})$$

(Hint : A tungsten filament bulb is an example of incandescent bulb. Incandescence is light emission due to intense heat.)

3) The extinction coefficient (ε) value of a substance is 4.66 $\text{m}^2\ \text{mol}^{-1}$. Calculate the concentration of its solution (in molarity) which has $\frac{I}{I_0} = 0.2$. The thickness of the cell is 1.00 cm.

4) At 478 nm, hydrogen and chlorine combine to give hydrogen chloride with a quantum efficiency of 1.00×10^6. If the absorbed intensity is $2.50 \times 10^{-3}\ \text{J s}^{-1}$, calculate the amount of hydrogen chloride formed in 10 minutes.

(Hint: The unit for amount is mole.)

5) State some of the applications of fluorescence and phosphorescence studies.

6) In the photochemical reaction between hydrogen and bromine at 511 nm wavelength, the first step is the photolysis of bromine but not of hydrogen. Why?

(Hint: Use Table 19.2.)

7) Fill in the blanks:

   i) Light emission through $S_1 \rightarrow S_0$ transition is called ....

   ii) Light emission through $T_1 \rightarrow S_0$ transition is called ....

   iii) The energy required for photolysis of bromine is ...... than its bond enthalpy.

8) Suggest a condition that should be fulfilled in order to photolyse a molecule using a sensitiser.

19.12 ANSWERS

Self-assessment Questions

1) Energy absorbed per photon $= \dfrac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{250 \times 10^{-9}}$ joule photon^{-1}

$$= 7.95 \times 10^{-19} \text{ joule photon}^{-1}$$

Assume that the reaction is conducted for t seconds.

$$\text{Hence, } I_a = \frac{\text{Intensity in joule second}^{-1}}{7.95 \times 10^{-19} \text{ joule photon}^{-1}}$$

$$= \frac{4.18 \times 10^{3} \text{ joule}/t \text{ second}}{7.95 \times 10^{-19} \text{ joule photon}^{-1}}$$

$$= \frac{5.26 \times 10^{21}}{t} \text{ photon second}^{-1}$$

Amount of HI decomposed in 1 second $= \dfrac{1.85 \times 10^{-2} \text{ mol}}{t \text{ second}}$

$$\frac{-dN_{HI}}{dt} = \frac{1.85 \times 10^{-2}}{t} \times 6.022 \times 10^{23} \text{ molecule second}^{-1}$$

$$= \frac{1.114 \times 10^{22}}{t} \text{ molecule second}^{-1}$$

Using Eq. 19.3, $\phi_{HI} = \dfrac{-dN_{HI}/dt}{I_a} = \dfrac{1.114 \times 10^{22}/t}{5.26 \times 10^{21}/t}$

$$= 2.12$$

2) Oxygen molecules could quench the excited species. Hence in presence of oxygen, ϕ_{HCl} is low.

3) For HI, the difference between photochemical dissociation energy and bond enthalpy is 68 kJ mol^{-1} and the excited hydrogen atom carries this excess energy.

4) i) $\dfrac{d[CH_3CO]}{dt} = 0 = k_2[CH_3][CH_3CHO] - k_3[CH_3CO]$

ii) $\dfrac{d[CH_3]}{dt} = 0 = I_a - k_2[CH_3][CH_3CHO] + k_3[CH_3CO] - 2k_4[CH_3]^2$

iii) $\dfrac{d[CH_3CO]}{dt} + \dfrac{d[CH_3]}{dt} = 0 = I_a - 2k_4[CH_3]^2$

iv) $[CH_3] = \left(\dfrac{I_a}{2k_4}\right)^{½}$

v) $\dfrac{d[CO]}{dt} = k_3\ [CH_3CO]$

vi) $\dfrac{d[CO]}{dt} = k_2\ [CH_3][CH_3CHO]$

$$= k_2 \left(\frac{I_a}{2k_4}\right)^{½} [CH_3CHO]$$

5) The light emission during fluorescence is due to $S_1 \rightarrow S_o$ transition. Fluorescence, being due to an allowed transition, is quite fast and stops as soon as exciting source is removed.

The light emission during phosphorescence is due to $T_1 \rightarrow S_o$ transition. Since this transition is forbidden, it is slow and it persists even if the exciting source is removed.

6) i) UO_2^{+} ion acts as a photosensitiser and facilitates the decomposition of oxalic acid.

ii) $UO_2^{+} + h\nu \rightarrow (UO_2^{+})^*$

$(UO_2^{+})^* + H_2C_2O_4 \rightarrow UO_2^{+} + H_2O + CO + CO_2$

7) In a galvanic cell, the potential difference is due to conversion of chemical energy into electrical energy.

In a photogalvanic cell, light energy is converted into chemical energy, which is then, converted into electrical energy.

Terminal Questions

1) A photochemical reaction could take place even if ΔG is positive. For a chemical reaction to take place, ΔG must be negative at a given temperature and pressure.

In a photochemical reaction, the reacting molecules get the excitation energy through light absorption. In a chemical reaction, the reacting molecules get the activation energy through collisions.

2) A 100 W bulb emits 100 J s^{-1} of which 10 J s^{-1} comes out as light.

$$\text{Energy per quantum} = \frac{6.626\times10^{-34}\times3\times10^{8}}{600\times10^{-9}}\ \text{joule photon}^{-1}$$

$$= 3.31\times10^{-19}\ \text{joule photon}^{-1}$$

$$\left\{\begin{array}{l}\text{Number of quanta}\\ \text{emitted per second}\end{array}\right\} = \frac{\text{Energy emitted per second}}{\text{Energy per photon}}$$

$$= \frac{10\ \text{joule second}^{-1}}{3.31\times10^{-19}\ \text{joule photon}^{-1}}$$

$$= 3.02\times10^{19}\ \text{photons second}^{-1}$$

$$\left\{\begin{array}{l}\text{Number of quanta emitted}\\ \text{in 10 minutes}\end{array}\right\} = 3.02\times10^{19}\times600\ \text{photons}$$

$$= 1.81\times10^{22}\ \text{photons}$$

3) $I/I_o = 0.2$; so, $\frac{I_o}{I} = 5$

$$A = \log I_o/I = 0.699 = \varepsilon c l$$

$$c = \frac{0.699}{\varepsilon l} = \frac{0.699}{4.66\times1.00\times10^{-2}\ \text{m}^3\ \text{mol}^{-1}}$$

$$= 15\ \text{mol m}^{-3}$$

$$= 15\times10^{-3}\ \text{mol dm}^{-3} = 0.015\ \text{M}$$

1 M = 1 mol dm^{-3} and
1 m^{-3} = (10 dm)$^{-3}$
= 10^{-3} dm^{-3}

4) $$\text{Energy per quantum} = \frac{6.626\times10^{-34}\times3\times10^{8}}{478\times10^{-9}}\ \text{joule photon}^{-1}$$

$$= 4.16\times10^{-19}\ \text{joule photon}^{-1}$$

$$I_a\left(\begin{array}{l}\text{Number of quanta}\\ \text{per second}\end{array}\right) = \frac{\text{Intensity in joule second}^{-1}}{\text{Energy per photon}}$$

$$= \frac{2.50\times10^{-3}\ \text{joule second}^{-1}}{4.16\times10^{-19}\ \text{joule photon}^{-1}}$$

$$= 6.01\times10^{15}\ \text{photons second}^{-1}$$

$$\phi_{\text{HCl}} = \frac{\frac{dN_{\text{HCl}}}{dt}}{I_a};\ \text{hence,}\ \frac{dN_{\text{HCl}}}{dt} = \phi_{\text{HCl}}\cdot I_a$$

$$\text{i.e.,}\ \frac{dN_{\text{HCl}}}{dt} = 6.01\times10^{15}\times1.00\times10^{6}\ \text{molecules second}^{-1}$$

$$= 6.01\times10^{21}\ \text{molecules second}^{-1}$$

$$\left\{\begin{array}{l}\text{Number of molecules of HCl}\\ \text{formed in 10 minutes}\end{array}\right\} = 6.01\times10^{12}\times600\ \text{molecules}$$

$$= 3.61\times10^{24}\ \text{molecules}$$

$$\left\{\begin{array}{l}\text{Amount of HCl formed}\\ \text{in 10 minutes}\end{array}\right\} = \frac{3.61\times10^{24}}{6.022\times10^{23}}\ \text{mole}$$

$$= 5.99\ \text{mole.}$$

5) See Sec. 19.6.

6) Light of wavelength 511 nm is just sufficient to photolyse bromine molecule. To photolyse hydrogen molecule directly, light of higher energy is required.

7) i) fluorescence ii) phosphorescence
iii) higher

8) The energy emitted by the excited sensitiser during its return to ground state should be atleast equal to the energy required for the thermal decomposition of the molecule.

UNIT 20: COLLOIDS AND MACROMOLECULES

Structure

20.1 INTRODUCTION

In unit 10 of this course we have discussed the properties of solutions. In a true solution, the solute particles are homogeneously distributed and are of the same molecular dimension as solvent particles. For example, a sugar solution contains sugar and water molecules homogeneously distributed over the whole volume. Such solutions are called **molecular solutions** in order to distinguish them from solutions of macromolecules (i.e., molecules having large molar masses). On the other hand we have **coarse suspensions**; these are formed from substances which do not dissolve in the solvent but form two or more distinct phases with the solvent. An example is adding $CaCO_3$ to water. However, there does exist a third possibility where the size of the solute particle is much bigger than that of the solvent molecule, but is not large enough to be seen with naked eyes. Such a dispersion of particles of one material in another is called **Colloid**. In the early days, colloids were defined as a suspension of small particles in a continuous medium. However, we define a system to be in the colloidal state if particles of one or more of its components have dimensions in the range of 1 to 1000 nm. These are classified into three categories:

1) Colloidal dispersions,

2) Associated colloids, and

3) Solutions of macromolecules.

We shall discuss each of the above in this unit. Further we shall study the preparation of colloids, their properties and uses.

Objectives

After studying this unit, you should be able to

- define colloids and distinguish them from true solutions and coarse suspensions,
- describe methods for the preparation and purification of colloids,
- explain the characteristic properties of colloids,
- discuss factors responsible for the stability of colloids,
- describe various methods for the determination of the molar masses of polymers, and
- state some applications of colloids.

20.2 DIFFERENCES AMONG THE COLLOIDS, SOLUTIONS AND COARSE SUSPENSIONS

The colloidal systems differ from coarse suspensions and true solutions in a number of ways. The following discussion will make the differences clear.

i) Size

As mentioned earlier, the particle size of one of the phases in a colloid lies in the range 1 to 1000 nm. In the coarse suspensions, the size of the suspended particles is always larger than 1000 nm, whereas the dimensions of solute molecules in true homogeneous solutions are less than 1 nm.

ii) Filterability

Coarse suspensions can be easily filtered using ordinary filter papers so as to separate into two phases. The colloidal system cannot be filtered using ordinary filter papers but need special ultrafilter papers (See Subsec. 20.3.2). Molecular solutions pass even through ultrafilter papers.

iii) Appearance

Coarse suspensions appear heterogeneous even to the naked eye whereas colloidal systems and molecular solutions appear clear and homogeneous (See Subsec. 20.6.3).

iv) Diffusibility

Membranes are thin, soft layer of animal or plant tissue or synthetic polymer.

Solute molecules in molecular solutions diffuse through membranes rather rapidly, while the particles in a coarse suspension or in a colloidal system diffuse very slowly.

In the next section, we shall discuss different types of colloidal dispersions.

20.3 COLLOIDAL DISPERSIONS

A colloidal dispersion is a heterogeneous system in which the colloidal particles (the dispersed phase) are dispersed in a continuous phase (the dispersion medium). The colloidal dispersions can be further classified on the basis of the state of matter in which the two phases exist. Table 20.1 lists the colloidal dispersions of various types with their common names and suitable examples.

Some gas mixtures show inhomogeneous regions at extremely high pressures.

It may be noted that due to the mutual solubility of all gases in all proportions, it is not possible to have a colloidal dispersion of one gas in another gas.

In some cases where the dispersion medium is either a liquid or gas, the colloidal dispersions are called sols. The dispersion medium is characterised by the addition of a prefix to the word, sol. Some examples are hydrosol, aerosol and alcosol.

Table 20.1 : Various Types of Colloidal Dispersions

Dispersed phase	Dispersion medium	Common name	Example
Liquid	Gas	Aerosol (of liquid particles)	Mist
Liquid	Liquid	Emulsion	Cream
Liquid	Solid	Solid Emulsions and Gels	Jellies
Solid	Gas	Aerosol (of solid particles)	Smoke
Solid	Liquid	Sol	Hydrosol of $Fe(OH)_3$
Solid	Solid	Solid suspensions	Precious stones
Gas	Liquid	Foam	Whipped Cream
Gas	Solid	Solid foam	Polystyrene

In most cases, the lyophilic colloids are called gels. A gel is a semisolid mass of lyophilic sol in which all the solvent has been absorbed by the particles.

Based on the interaction between the colloidal particles and the medium, the solid-liquid sol could be further classified as (1) lyophilic and (2) lyophobic. "Lyophilic" literally means solvent loving. The lyophilic colloids are dispersions of polymeric molecules. There is a strong interaction between the dispersed particles and the dispersion medium.

Examples

Starch in water, rubber in benzene, cellulose nitrate (collodion) in acetone, etc.

The word "lyophobic" means solvent hating. The lyophobic colloids are prepared by dispersing insoluble substances in a solvent. The lyophobic colloids are a collection of small molecules or formula units (where it is difficult to classify as a molecule).

Examples

Sols of gold, sulphur, ferric hydroxide, silver iodide, etc. Let us now discuss the methods of preparation of lyophilic and lyophobic sols.

20.3.1 Methods of Preparation

The preparation of lyophilic colloidal dispersions are quite straightforward. Generally, vigorous shaking of the dispersed phase with the dispersion medium results in lyophilic sols. Lyophobic sols, due to their low stability, present greater difficulty in their preparation. Such sols are usually prepared by the following methods:

A) **Condensation methods**

In these methods, small particles are coalesced together so as to produce particles of colloidal dimensions. Let us consider some examples.

1. **Bredig's Arc Method**

This is particularly suitable for the preparation of colloidal sols of metals. Two rods of the same metal (say, gold, or platinum)are placed in a suitable liquid (water or an organic solvent) containing small amount of alkali (Fig. 20.1).

From metal sols,it is possible to precipitate metals by suitable methods (Sec. 20.6). The metals thus precipitated are in a finely divided state. In such a finely divided state, the metallic particles have a large surface area and are effective catalysts. (See Sec. 20.10)

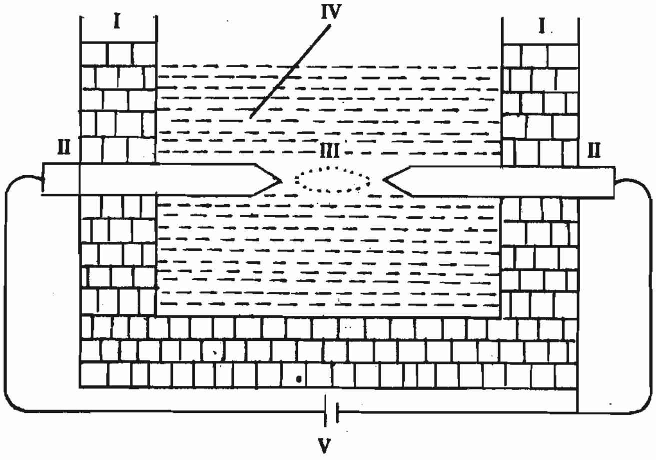


Fig. 20.1 Bredig's arc method: I. ice ; II. electrodes ; III. arc ; IV. solvent + alkali; V. power supply.

An electric arc is struck between them. The heat produced by the arc converts metal into vapours. These vapours condense into liquid to give the required colloidal sol.

2. Through Chemical Reactions

Many molecules produced in a chemical reaction aggregate to give particles of colloidal dimensions. For example, sulfur sols can be prepared by the oxidation of hydrogen sulphide:

$$2\,H_2S + O_2 \rightarrow 2\,S + 2\,H_2O$$

The gold sol can be prepared by the reduction of $HAuCl_4$ ($AuCl_3 + HCl$) using reducing agents like formaldehyde or hydrazine. Metal sols and metal hydroxide sols, which are found to be very useful in many industries, are normally prepared by this method.

3. Use of a Second Solvent

A substance may form a molecular solution in one liquid but may be insoluble in another liquid. If the saturated solution of a substance is diluted with another liquid in which it is insoluble, it may lead to the formation of colloidal sol. The two liquids, however, should be miscible. Thus when a saturated solution of sulphur in alcohol is diluted with water, we get sol of sulphur in water.

B) Dispersion Methods

In this method, larger particles are broken down into smaller particles of colloidal dimensions. This can be achieved either by mechanical means or by the use of some reagents known as peptizing agents.

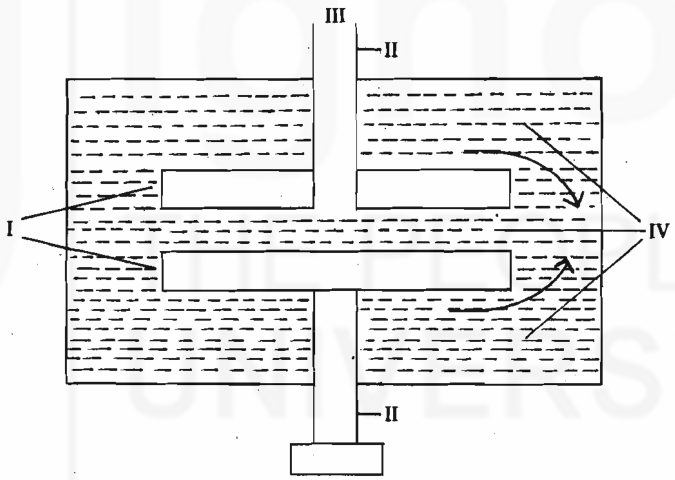


Fig. 20.2: A colloidal mill : I. heavy discs ; II. axle ; III. inlet for introducing the suspension of solid in the dispersion medium ; IV. sol ; the two arrows denote motion in the opposite directions.

1. Mechanical Method

The material to be converted into colloidal particles is introduced into a colloidal mill in which two discs rotate rapidly in opposite directions on a common axle (Fig. 20.2). The size reduction takes place due to the large force between the two discs. Many commercial colloids like printing ink and paints are prepared by this method.

2. Peptization

In this process, a precipitate is converted into colloidal dispersion by the addition of an electrolyte to the dispersion medium. The adsorption of suitable ions from the electrolyte causes the stabilisation of the colloidal particles. The electrolyte is called the peptizing agent. For example, in the preparation of ferric hydroxide sol, the freshly prepared precipitate of ferric hydroxide is taken in a beaker containing water and very small amount of peptizing agent, ferric chloride. The ferric ions, arising from the ionisation of ferric chloride, are preferentially adsorbed on the surface of the $Fe(OH)_3$ particles. The positively charged particles of ferric hydroxide repel each other and are easily dispersed throughout the medium giving colloidal sol of ferric hydroxide. Similarly the addition of a common ion to precipitates of many other substances can lead to the formation of colloidal sols.

20.3.2 Methods of Purification

Any impurities present in a colloidal sol renders it unstable and therefore it is necessary to purify it before undertaking any studies on it. The following methods are generally used for the purification of sols.

1. Ultrafiltration

We know that a colloidal system cannot be filtered using ordinary filter papers but need special ultrafilter papers which can be prepared by reducing the pore size of ordinary filter papers or other porous materials. It is achieved by impregnating the filter paper with a solution of gelatin or collodion. Colloidal systems can then be filtered through ultrafilters and the process is known as ultrafiltration.

Gelatin : Animal protein which could form gel.

Collodion : Cellulose nitrate.

A pure sol is obtained by passing the impure sample through ultrafilters which allow the soluble impurities to pass but not the colloidal particles. However, the method is very slow and not always successful.

2. Dialysis

A much better method of purification is dialysis. It is seen that colloidal particles cannot pass through certain semipermeable membranes like **parchment bag** while smaller particles or ions pass through them. In dialysis, we use such a membrane to separate the smaller particles from the colloidal particles. The method is illustrated in Fig. 20.3.

Parchment : The skin of a sheep, goat or other animal prepared for writing.

A bag of a suitable membrane containing the sol is suspended in a container through which fresh liquid is passed continuously. The ions or smaller molecules inside the bag diffuse out leaving the pure sol behind. The process of diffusion is made faster by using hot water instead of cold water in the process. It must however be kept in mind that excessive dialysis can lead to destabilisation of the sol and a precipitate may be obtained.

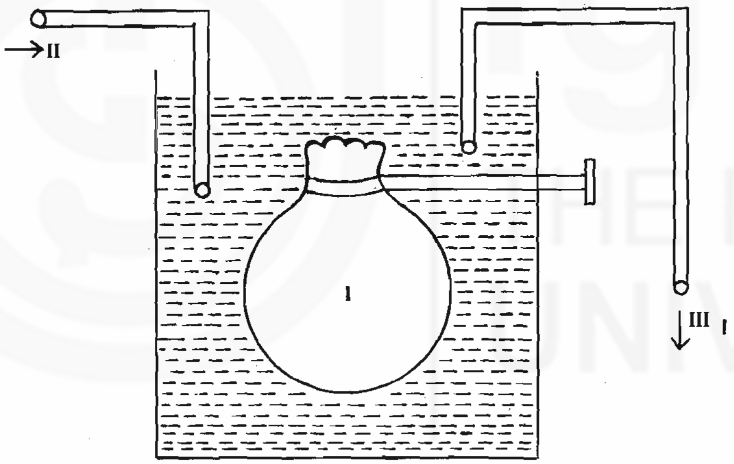


Fig. 20.3: Dialysis apparatus: I. sol in parchment bag ; II. water inlet; III. water outlet .

3. Electrodialysis

This modification of the process of dialysis is specially used when the impurities are ionic. The apparatus is shown in Fig. 20.4.

A parchment bag containing the sol is kept immersed in a liquid (generally water). Two electrodes are dipped in this liquid. When an electric field is applied across the electrodes,the positive ions move towards the cathode and the negative ions towards the anode through the membrane in the liquid. The rate of diffusion is considerably increased by the application of electric field and the process is quite quick.

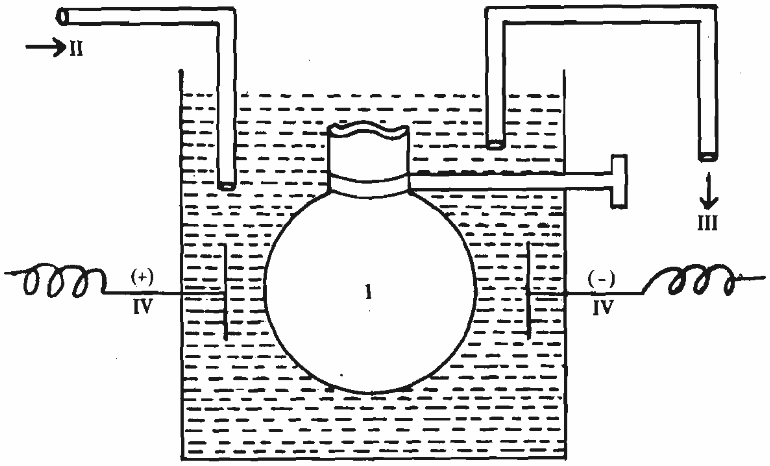


Fig. 20.4: Electrodialysis apparatus : I. sol in parchment bag; II. water inlet; III. water outlet; IV. electrodes.

SAQ 1

In order to prepare platinum in a finely divided state, a platinum sol is prepared using $1.00 \times 10^{-6}\ \text{m}^3$ of platinum. Assuming that each platinum particle in the dispersion is a sphere of radius 50 nm., calculate the total surface area of all the platinum particles in the sol in cm^2 unit.

Hints : i) Volume of each platinum particle is given by the formula, $4/3\ \pi r^3$.

ii) Calculate the number of particles that could be formed from $1.00 \times 10^{-6}\ \text{m}^3$ platinum

$$\left(= \frac{1 \times 10^{-6}}{4/3\ \pi r^3} = n\ (\text{say}) \right)$$

iii) Surface area of each platinum particle is given by the formula, $4\pi r^2$

iv) Total surface area of all the platinum particles in the sol $= 4\pi r^2 n$

Finally change the unit into cm^2.

....

....

....

SAQ 2

Suggest a peptizing agent useful in preparing silver chloride sol from solid silver chloride.

....

....

....

20.4 ASSOCIATED COLLOIDS

The molecules of certain substances (soaps, dyes etc.) on dissolution in a solvent have strong tendency to aggregate (or associate). The size of these aggregates lies in the colloidal range. These aggregates are called micelles. The systems in which the solute molecules aggregate to give particles of colloidal dimensions are called associated colloids. The molecules of associated colloids have both lyophobic and lyophilic groups. Let us consider one example in detail. Soap molecules have a general formula, $RCOO^- \ M^+$, where R is a straight chain of 10 to 20 carbon atoms and M^+ is Na^+ or K^+. We find that many properties of soap solutions such as surface tension, electrical conductivity and osmotic pressure show abrupt changes at a particular concentration of soap. This concentration is called critical micelle concentration (CMC). These observations have been explained by assuming that above the CMC, a substantial portion of the solute ions ($RCOO^-$) aggregate to form particles of colloidal dimension, called micelles. Experiments have confirmed the formation of micelles which usually contain 20 to 100 units depending on the concentration of soap and other substances in solution. The structure of soap micelle is shown in Fig. 20.5.

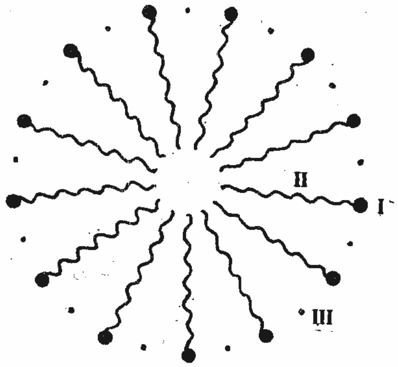


Fig. 20.5: Structure of a micelle: I. polar group; II. nonpolar group; III. counter ion.

A soap micelle has a spherical structure with the nonpolar hydrocarbon part inside the sphere and the polar RCOO$^-$group on its surface. The polar group strongly interacts with the water molecules. A number of M$^+$ ions are bound to the surface of the micelle as counter ions and this helps in reducing its charge considerably.The formation of micelle is reversible. The formation of micelle reduces the electrical conductivity of the electrolyte as well as the osmotic pressure of the solution. The soap solution acts as a solvent for hydrocarbons (grease) by incorporating the molecules of hydrocarbons into the interior of the micelle. The action of soap as a cleanser depends on this property of soap. We shall discuss this in Sec. 20.7.

These days **reverse micelles** are of great help in the study of enzyme–catalysed reactions. As their name implies, the polar part is inside (Fig.20.6) dipping in a small part of water and the nonpolar part is surrounded by an organic phase.

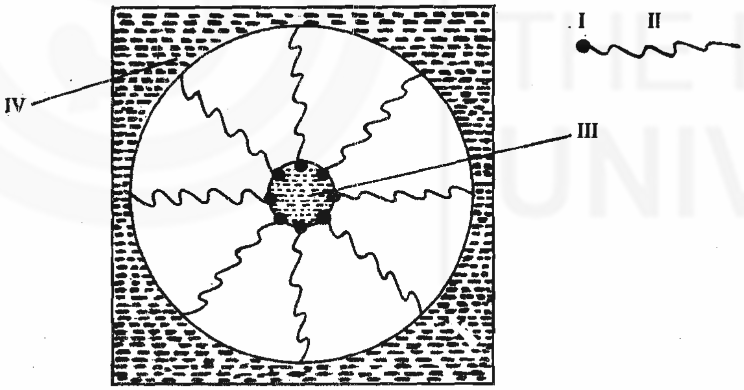


Fig. 20.6: Structure of a reverse micelle: I. polar group ; II. nonpolar group; III. water pool ; IV. organic phase.

The reverse miscelles have structural similarities to a cell in a living system.

The following SAQ is based on the charge calculation of a micelle. Try it.

SAQ 3

Imagine that initially there are 100 Na$^+$ ions and 100 RCOO$^-$ ions and that all the RCOO$^-$ ions aggregate into a micelle which binds 80 Na$^+$ ions on the surface as counter ions.

i) What is the charge on the micellar ion ?

Hint : Charge on the micellar ion

= Charge due to all the RCOO$^-$ ions– Charge due to Na$^+$ ions present as counter ions.

During the formation of the micellar ion, charge due to all the RCOO$^-$ ions is decreased by the counter ions .

ii) Calculate the number of ions present after micelle formation

Hint : Count the aggregate of $RCOO^-$ ions and the counter ions as one ion only.

iii) Can you explain the fact that micelle formation leads to decrease in electrical conductivity and osmotic pressure ?

....

....

....

20.5 MACROMOLECULAR SOLUTIONS

In addition polymerisation, the repeating unit has the same chemical composition as the monomer.

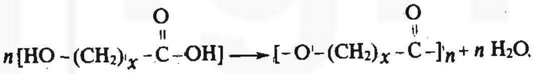
In condensation polymerisation, the repeating unit is different in chemical composition from the monomer. Water or a small molecule is eliminated during the formation of condensation polymer.

When a component in a true solution has molecules large enough (e.g., the molecule of a protein) to be in the colloidal range, even this is considered a colloidal solution. The reason is that the solutions of such macromolecules have properties similar to colloidal dispersions and same techniques are used to study them. Some of the naturally occurring macromolecules are starch, protein, rubber, cellulose, silicates, polyphosphates, plastic sulphur—just to name a few out of a large number. In addition, there is a large variety of macromolecules which are prepared synthetically. These macromolecules are commonly called polymers implying thereby that they are multiples of a monomeric unit. Generally, such molecules are formed by the polymerisation of a single monomer by the addition reaction as shown below :

$$n\ CH_2 = CHCl \rightarrow (-CH_2CHCl-)_n$$

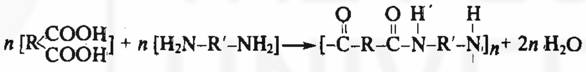
Vinyl chloride   Polyvinyl chloride or PVC

However, some of the polymers are formed by condensation process e.g.,



$$n[HO-(CH_2)_x-\overset{\overset{O}{\|}}{C}-OH] \longrightarrow [-O-(CH_2)_x-\overset{\overset{O}{\|}}{C}-]_n + n\ H_2O$$

Hydroxy acid   Polyester



$$n\left[R\begin{smallmatrix}COOH\\COOH\end{smallmatrix}\right] + n[H_2N-R'-NH_2] \longrightarrow [-\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R'-\overset{\overset{H}{|}}{N}]_n + 2n\ H_2O$$

Dicarboxylic acid   Diamine   Nylon (a polyamide)

The purpose of including polymers here is just to indicate that their behaviour in solution is similar to colloids but we will not study them in detail. The properties of macromolecular solutions depend to a great deal on the size and distribution of macromolecules in a sample. In the synthesis of polymers we get macromolecules with different molar masses depending on the reaction conditions. Thus, the determination of average molar mass becomes important in the studies of polymers. The average molar mass can be defined in different ways and experimentally obtained values depend on the method of determination. The two most commonly used ways to define the average molar mass are discussed below.

20.5.1 The Number Average Molar Mass

The average molar mass of the a polymer can be defined in a number of ways and even the experimentally obtained average molar mass values depend on the method of determination.

Let us assume that a sample contains many species of polymers where N_1, N_2, N_3 ...., are the number of polymer molecules of molar masses M_1, M_2, M_3 ....., respectively. Then the total mass of the sample is $N_1M_1 + N_2M_2 + ...$ and the total number of molecules is $N_1 + N_2 + N_3$ .... We define the number average molar mass, $\overline{M}_n$, of the sample as:

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + ...}{N_1 + N_2 + N_3 + ...} = \frac{\sum_i N_iM_i}{\sum_i N_i} \qquad ...(20.1)$$

where N_i is the number of molecules of the i^{th} species having molar mass M_i. If we divide each term in numerator and denominator by Avogadro number (N_A) we can write

In Eq. 20.2, N_i/N_A is the number of moles of *i*th polymer species.

$$\overline{M}_n = \frac{\sum_i \frac{N_i}{N_A} M_i}{\sum_i \frac{N_i}{N_A}} = \frac{\sum_i n_i M_i}{\sum_i n_i} \qquad \ldots (20.2)$$

where $n_i = N_i/N_A$ is the amount (number of moles) of a species having molar mass, M_i. Thus $\overline{M}_n$ is equal to the total mass of the sample divided by the total number of moles, n, of the sample or

$$\overline{M}_n = \frac{\sum_i n_i M_i}{n} = \sum_i \frac{n_i M_i}{n_i} = \sum_i x_i M_i \qquad \ldots (20.3)$$

where $n = \sum_i n_i$ and

$$x_i = \frac{n_i}{n}$$

= the mole fraction of the molecules for which molar mass is M_i.

This should become clear from the following example :

Example 1

Determine the number average molar mass of a polymer sample with the following distribution of molar masses :

N_i	5	5	10	10	5	5
$\frac{M_i}{\text{kg mol}^{-1}}$	1.000	2.000	50.000	10.000	12.000	20.000

Solution

Using Eq. 20.1 we get,

$$\overline{M}_n = \frac{(5 \times 1.000) + (5 \times 2.000) + (10 \times 50.000) + (10 \times 10.000) + (5 \times 12.000) + (5 \times 20.000)\ \text{kg mol}^{-1}}{5 + 5 + 10 + 10 + 5 + 5}$$

$$= 19.375\ \text{kg mol}^{-1}$$

The number average molar mass is sensitive to the species having low molar mass. The presence of such species as impurities can lead to very low estimates of average molar mass. The experimental determination of average molar mass is given in Sec. 20.9.

20.5.2 The Mass Average Molar Mass

Some methods for the determination of the molar mass depend on the effect produced by the masses of the polymer molecules instead of their numbers. Therefore, in the averaging process, the molar mass (M_i) of any particular molecule (i) is multiplied by its mass (w_i). The sum, $\sum_i w_i M_i$, for all the molecules is then divided by the total mass of the sample $\left(\sum_i w_i\right)$. Thus the mass average molar mass ($\overline{M}_w$) is given by

$$\overline{M}_w = \frac{\sum_i w_i M_i}{\sum_i w_i} \qquad \ldots (20.4)$$

But $w_i = n_i M_i$ $\qquad \ldots (20.5)$

where n_i is the number of moles of the i^{th} species.

$$\overline{M}_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \qquad \ldots(20.6)$$

$$\text{or } \overline{M}_w = \frac{n_1 M_1^2 + n_2 M_2^2 + \ldots}{n_1 M_1 + n_2 M_2 + \ldots} \qquad \ldots(20.7)$$

where n_1, n_2, ... are the number of moles of species with molar mass M_1, M_2 ...., respectively in the polymer sample.

We can multiply the numerator and denominator in the R.H.S. of Eq.20.6 by Avogadro number, and get,

$$\overline{M}_w = \frac{\sum_i n_i N_A M_i^2}{\sum_i n_i N_A M_i} \qquad \ldots(20.8)$$

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \qquad \ldots(20.9)$$

The transformation from Eq. 20.8 to Eq. 20.9 uses the following relationship :

$$n_i = \frac{N_i}{N_A}$$

or

$$N_i = n_i N_A$$

where N_i is the number of molecules of i^{th} type.

Example 2

Calculate the mass average molar mass from the data given in Example 1.

Solution

Using Eq. 20.9,

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

$$= \frac{5(1.000)^2 + 5\,(2.000)^2 + 10\,(50.000)^2 + 10\,(10.000)^2 + 5\,(12.000)^2 + 5\,(20.000)^2}{(5 \times 1.000) + (5 \times 2.000) + (10 \times 50.000) + (10 \times 10.000) + (5 \times 12.000) + (5 \times 20.000)} \text{ kg mol}^{-1}$$

i.e., $\overline{M}_w = 37.09 \text{ kg mol}^{-1}$

It can be seen that $\overline{M}_w$ is larger than $\overline{M}_n$. The ratio of $\overline{M}_w/\overline{M}_n$ is known as polydispersity index. In the next section,we shall discuss some of the properties of colloidal dispersions.

In addition to the above two molar mass equations, we sometimes use the following relationships also which we are not going to discuss in detail:

$$M_{\text{rms}} = \text{Root mean square molar mass} = \frac{\sum_i n_i M_i^2}{\sum_i n_i} \qquad \ldots(20.10)$$

$$\overline{M}_v = \text{Viscosity average molar mass} = \left(\frac{\sum_i n_i M_i^{(1+\alpha)}}{\sum_i n_i M_i} \right)^{1/\alpha} \qquad \ldots(20.11)$$

where α is a constant lying between 0.5 and 0.8.

Before proceeding to the next section, try to solve the following SAQ's.

SAQ 4

When will the polydispersity index be equal to one?

....

....

....

SAQ 5

Show that $M_{\text{rms}} = \overline{M}_n \times \overline{M}_w$.

....

....

....

20.6 PROPERTIES OF COLLOIDAL SYSTEMS

As mentioned earlier, colloidal systems show some characteristic properties which are different from true solutions and coarse dispersions. These properties can be classified as (1) physical (2) optical and (3) electrical. We shall study each of them separately.

20.6.1 Physical Properties

1. **Sedimentation**

Colloidal dispersions are usually quite stable and, do not settle easily. The rate of sedimentation can be increased by the use of an ultracentrifuge. The ultracentrifuge consists of a cylinder provided with a rotor that can be driven at a high speed. The rotational motion of the cylinder about its axis causes the particles to settle. The centrifugal force on the particles is generated by the rotational motion which is opposed by the frictional force. Due to these forces, the colloidal particles move outwards causing more concentration of the particles near the edge of the cylinder compared to the centre. The rate of sedimentation depends upon the size and shape of the particles.

Sedimentation : Deposition of an undissolved material

2. **Diffusibility**

We have already discussed in Sec. 20.2 that particles in a colloidal suspension diffuse very slowly through a membrane. Note that the colloidal particles cannot pass through ultrafilter papers or semipermeable membranes (like parchment bag) as mentioned in Sec. 20.3.

3. **Viscosity**

The viscocity of a solution containing macromolecules is high even at low concentrations. The measurement of viscosity of such a solution provides us a way of obtaining the molar mass of macromolecules (See Sec. 20.9).

4. **Colligative Properties**

Colloidal dispersions also show colligative properties just like a true solution. Out of the four colligative properties namely (i) the lowering of vapour pressure (ii) the depression of freezing point (iii) the elevation of boiling point, and (iv) the osmotic pressure, only the last one gives measurable values. The other three give too small a change to be usefully employed (See Sec. 20.9).

20.6.2 Kinetic Properties

Brown in 1827 observed that pollen grains suspended in water show continuous random motion. This motion is along short straight paths of different lengths and directions, as shown in Fig. 20.7.

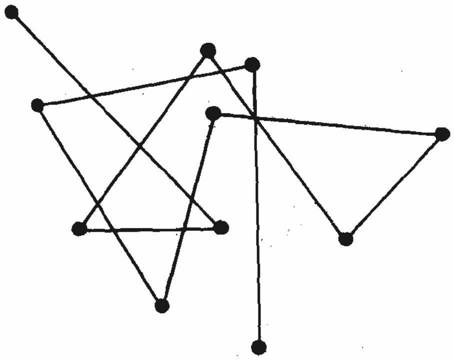


Fig. 20.7 : Brownian motion.

This type of motion is called Brownian motion in recognition of its discoverer. With proper lighting, Brownian motion of colloidal particles can also be viewed. This motion is not due to convection current in the fluid.

The Brownian motion of a colloidal particle is due to its bombardment by the molecules of the medium. A colloidal particle will acquire the same average kinetic energy (= 3/2 kT) as all other molecules in such motion. But due to its heavy mass, its speed will be much less compared to those of the molecules of the medium.

Example 3

Compare the root mean square speed of a water molecule with that of a colloidal particle having mass, 1.00×10^{-23} kg.

Solution

$$\text{Mass of water molecule } (m_1) = \frac{\text{Molar mass}}{\text{Avogadro constant}}$$

$$= \frac{0.018 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$= 2.99 \times 10^{-26} \text{ kg}$$

$$\text{Mass of colloidal particle } (m_2) = 1.00 \times 10^{-23} \text{ kg}$$

From kinetic theory, we know

$$\frac{1}{2} m_1 \overline{u_1^2} = \frac{1}{2} m_2 \overline{u_2^2}$$

You could recollect that we derived the relationship between u_{rms} and the molar mass in Eq. 2.43 of Unit 2 of this course, although it was meant for gases.

where $\overline{u_1^2}$ and $\overline{u_2^2}$ are the mean square speeds of water molecules and colloidal particles respectively. Then their respective root mean square speeds (u_{rms1} and u_{rms2}) can be written as,

$$\sqrt{\frac{\overline{u_1^2}}{\overline{u_2^2}}} = \frac{u_{rms1}}{u_{rms2}} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{1.00 \times 10^{-23}}{2.99 \times 10^{-26}}} = 18.3$$

Thus the root mean square speed of water molecules is about 18.3 times that of the colloidal particles.

20.6.3 Optical Properties

When a beam of light is passed through a clear solution and viewed from a direction at right angles to the direction of the beam of light, it appears completely dark. However, in the case of a colloidal sol we observe bright spots of light against this dark background. This is due to the scattering of light by the colloidal particles and is known as Tyndall effect. Although the phenomenon is also prevalent in most gases, liquids and solutions, the intensity of the scattered light is negligible. This is attributed to the small size of the particles in these cases. However, colloidal particles are large enough to cause considerable scattering of light. It is observed that spots of light keep on continuously changing which indicates the heterogeneous character of the sol and the continuous motion of the particles.

A very common example of Tyndall effect can be seen in a cinema hall. You can see clearly the projection beam all the way from the projector to the screen due to scattering of light by the suspended dust particles in the cinema hall.

The Tyndall effect depends on the refractive indices of both the dispersed phase and the dispersion medium. It is best observed when the refractive indices of the two differ appreciably from each other and the size of the particles is in the same region as the wavelength of light used.

The Tyndall effect has been put to a number of practical uses, one of which is the construction of ultramicroscope (Fig. 20.8).

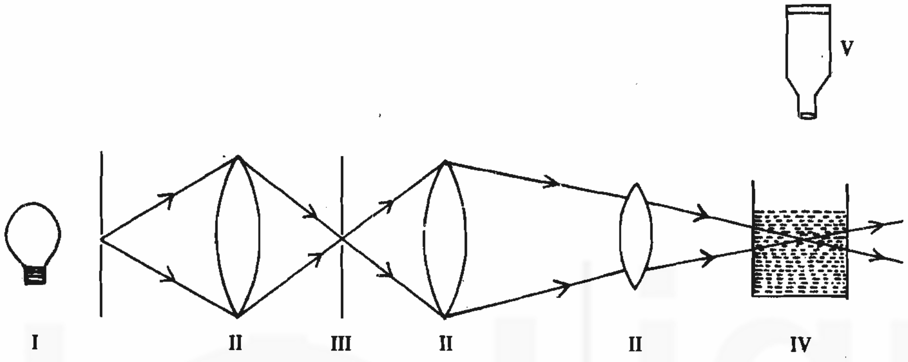


Fig. 20.8: Ultramicroscope: I. light source; II. lens ; III. slit ; IV. sol; V. microscope.

When a narrow beam of light is observed at right angles to its path through a sol, the particles can be viewed in the form of blocks of light moving continuously in all directions. Using ultramicroscope, we can distinguish the different colloidal particles on the basis of light scattered by them.

20.6.4 Electrical Properties

Colloidal particles in a dispersion medium carry charges on their surfaces. These charges can be positive (as in the case of ferric hydroxide sol) or negative (as in the case of arsenious sulphide sol). The total charge on the colloidal particles is, however, fully balanced by the charge on the particles of the dispersion medium thus preserving the electrical neutrality of the sol. The origin of charge can be traced mainly to two causes:

1. **Direct ionisation of surface groups**

Proteins contain many acidic and basic groups and, these groups are ionisable. Depending on the acidity of the medium, the particles in a protein sol may acquire a positive or negative charge. Similarly in the cases of associated colloids like soaps and detergents, the ionised molecules associate to give micelles whose outer surface will be charged (See Sec.20.4).

2. **Adsorption**

In certain cases positive or negative ions present in the medium are specifically adsorbed on the surface of the colloidal particles. For example, in silver iodide sol, the particles adsorb the iodide ions from the solution and, acquire a negative charge.

Similarly, some molecules may get adsorbed on the surface of the colloidal particles, dissociate and leave a charge on the surface. Arsenious sulphide sol adsorbs H_2S molecules which dissociate leaving a negatively charged sol.

3. **Electrical double layer**

The charges on the colloidal particles will affect the charge distribution in the dispersion medium. Thus the charges on the colloidal particles will attract ions of opposite charges (counter ions) and repel the ions having similar charge (coions).

This is the basis of the formation of double layer of charges. In the vicinity of the colloidal particles, there would be a higher concentration of counter ions compared to that of coions. The concentration of counter ions starts decreasing gradually at greater distances, till the concentration of counter ions and coions becomes equal.

In Fig. 20.9, the double layer around a colloidal particle (I) with positively charged adsorbed ions is shown. The double layer consists of,

i) a compact layer (II) made up of excess of counter ions,

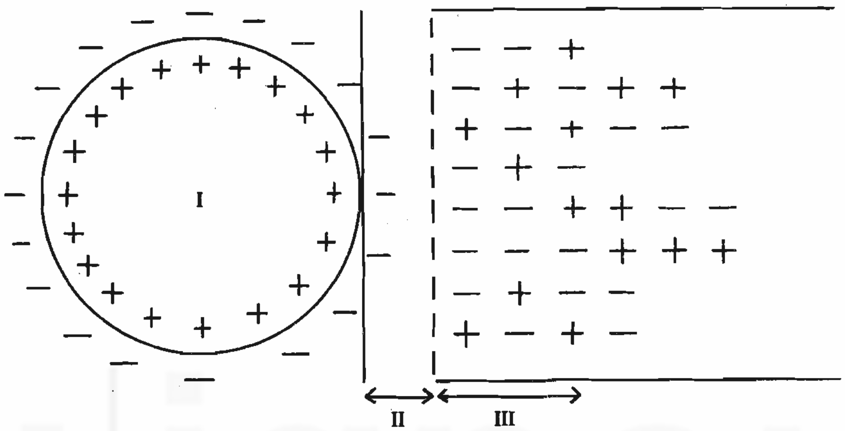


Fig. 20.9 : The double layer around a colloidal particle with positively charged adsorbed ions.

ii) a diffused layer (III) consisting of increasing concentrations of coions, as distance increases. At a particular distance, the concentration of coions and counter ions becomes equal. The diffused layer is loosely held and is therefore mobile.

Although the double layer theory could help us in explaining,

- electrophoresis,
- electro-osmosis and
- stability of lyophobic sols,

We give only a simple description of these phenomenon.

4. **Electrophoresis**

Due to the charge on the colloidal particles they move towards the suitable electrode when

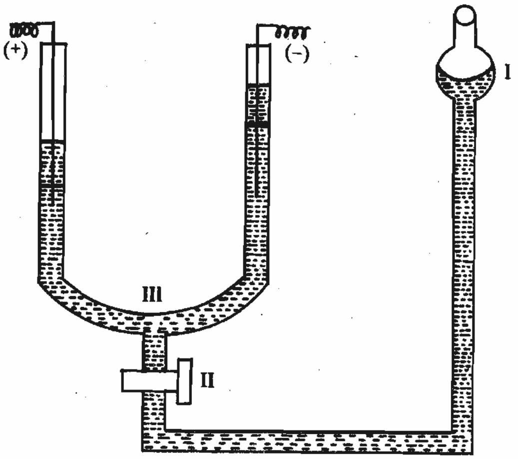


Fig. 20.10 : Apparatus for electrophoresis : I. reservoir of sol ; II. stopcock ; III. water; note the rise in level in the cathode section; the colloidal particles are positively charged.

an electrical potential is applied. This migration of colloidal particles towards either cathode or anode under the influence of an electrical field is known as electrophoresis. Electrophoresis can be observed in a U-tube fitted with a stopcock and connected to a reservoir of sol (Fig. 20.10).

Two platinum electrodes are fitted, one in each limb of U-tube. The U-ube is partially filled with the solvent. The sol is gently introduced from the reservoir into the U-tube through the stopcock. The electrodes should be dipping in the solvent. A direct current voltage in the range of 50 V to 250 V is applied across the electrodes. If the colloidal particles have a positive charge on their surface, they will move towards the cathode and the level in the cathodic limb will rise whereas the level in the anodic limb will correspondingly move downwards. On the other hand, if the particles are negatively charged, movement will take place in the opposite direction in the two limbs.

Potential gradient is defined in Sec. 16.7 of Unit 16 of this course.

From the direction of the movements in the two limbs we can find whether the particles are positively or negatively charged. The velocity with which the particles move depends on the applied voltage. We can find out the speed of the particle under unit potential gradient which is called the 'electrophoretic mobility'.

Electrophoresis has been used for the separation of various types of colloidal particles from a mixture. Since different particles move with different velocities, their separation becomes easy.

5. **Electro-osmosis**

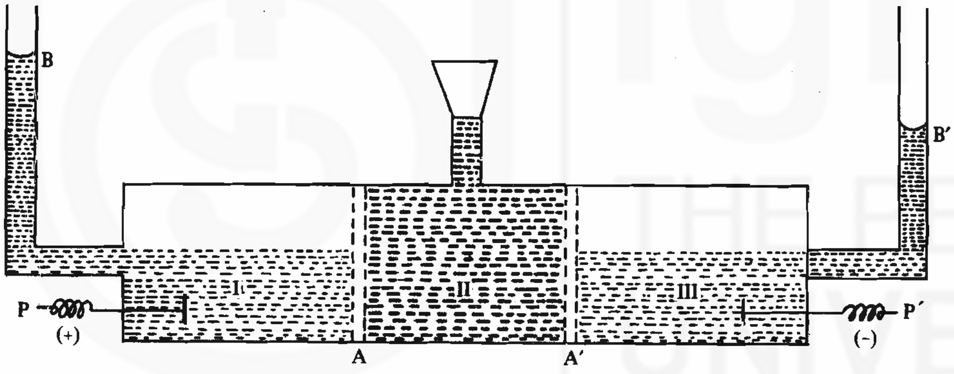


Fig. 20.11 : Apparatus for electro-osmosis : note the solvent level rise in anode compartment ; the colloidal particles in the sol (kept in compartment II) are positively charged.

If the colloidal particles are not allowed to move under the influence of an electrical field due to certain physical barriers, then the dispersion medium itself moves. This phenomenon is known as electro-osmosis. It can be studied by using a simple apparatus shown in Fig. 20.11.

It consists of a vessel divided into three compartments I, II and III by means of semipermeable membranes A and A′. The two outer compartments I and III are fitted with capillary tubes B and B′ and platinum electrodes P and P′. The compartments I and III are filled with the solvent. On passing electricity through P and P′, solvent level rises in one tube and falls in the other. The difference in the levels of the solvent in these tubes is a measure of the motion of the dispersion medium under the influence of the electrical field. If the colloidal particles are positively charged, the dispersion medium will be negatively charged and the level will rise in the tube connected to the anode compartment. Similarly, if the colloidal particles are negatively charged, the level will rise in the tube connected to the cathode compartment.

20.6.5 Stability of Colloids

Sometimes we want to separate colloidal particles from the dispersion medium. This is usually done by the formation of bigger particles due to aggregation. This process is known as coagulation. However, at times, we want to preserve the colloidal sol and prevent its coagulation. This is done by the protection of colloids. Let us study these two processes separately.

1. Coagulation

Let us study the coagulation of lyophilic and lyophobic sols separately.

Lyophilic Sols

Lyophilic sols are more stable than lyophobic sols. In lyophilic sols there is a strong interaction between the colloidal particles and the molecules of the dispersion medium. As a result, lyophilic sols contain highly solvated particles. In order to bring about the coagulation in such a system, we must remove the solvent molecules which surround the particles so that the particles can come near each other. This is done by introducing a competing agent for the solvent molecule. There are two ways of doing it--either by using a second solvent or by adding an electrolyte.

i) Introduction of a Suitable Solvent

If a second solvent, which interacts strongly with the dispersion medium, is added to lyophilic sol, coagulation takes place. Thus protein--in water sol can be coagulated by the introduction of alcohol. The water molecules interact strongly with alcohol molecules and the protein molecules are desolvated (i.e., surrounding solvent molecules are removed).

ii) Introduction of Electrolytes

When electrolytes are added to lyophilic sols, the ions of the electrolyte compete for the solvent molecules. If sufficient amount of electrolyte is added, the sol coagulates. This is called the salting out of the sol.

It has been stated in Sec. 20.3 that lyophobic colloids are made up of substances insoluble in the dispersion medium. If the double layer were absent, you can expect the particles of insoluble material to come close because of attraction due to van der Waals forces. This would have destabilised the lyophobic colloid and resulted in the precipitation of the colloid. The presence of double layer causes repulsion between particles. This is helpful in avoiding precipitation and in stabilising the lyophobic colloids.

Lyophobic sols

Lyophobic sols differ in stability from lyophilic sols. The stability of lyophobic sols is due to the electrical double layer and, their coagulation will thus involve the depletion or the complete removal of this double layer.

One way of doing this is the mixing together of two sols which have particles carrying opposite charges when both the sols are coagulated. For example, the mixing of ferric hydroxide sol with arsenious sulphide sol results in the neutralisation of the charges on both the sols and both of them are coagulated.

The other method involves, once again, the addition of electrolytes but here the mechanism of coagulation is different. In this case,the ions of the electrolyte are taken up by the colloidal particles. This results in the neutralisation of the charge on the particles and the reduction of the repulsion between different colloidal particles. The coagulation of colloidal particles is sometimes also referred to as flocculation. The capacity of an electrolyte to cause flocculation is given by its flocculation value. It is defined as the concentration of an electrolyte in millimoles per litre (or cubic decimeter) which is required to flocculate a sol. **The flocculation values of some common electrolytes for arsenious sulphide and ferric hydroxide** sols are given in Table 20.2.

Table 20.2: The Flocculation Values of Some Common Electrolytes for Arsenious Sulphide and Ferric Hydroxide Sols.

Arsenious sulphide (negatively charged)		Ferric hydroxide (positively charged)	
Electrolyte	(Flocculation value) (10^{-3} mol dm^{-3})	Electrolyte	(Flocculation value) (10^{-3} mol dm^{-3})
NaCl	51	NaCl	9.0
KNO_3	50	KCl	9.0
KCl	50	KNO_3	12.0
$CaCl_2$	0.65	K_2SO_4	0.21
$Al(NO_3)_3$	0.095	Tl_2SO_4	0.22

The effect of the charge of the counter ions on the flocculation value is given by Schulze-Hardy rule. This rule states that the counter ions having a higher charge have a greater power to cause flocculation of a sol. According to this law, the flocculation value of an electrolyte is inversely proportional to the sixth power of the valency of the counter ions. For arsenious sulphide sol (a negatively charged sol), for example, the flocculation value of sodium chloride solution is 51×10^{-3} mol dm^{-3} and that of potassium chloride solution is 50×10^{-3} mol dm^{-3}. These values are more or less the same since the charges on the counter ions, Na^+ and K^+, are the same. But if calcium chloride solution is used as the electrolyte for the flocculation of the arsenious sulphide sol, the flocculation value is much less (0.65×10^{-3} mol dm^{-3}) ; it is so since the charge on the counter ion, i.e., calcium ion, is +2 which thereby is more effective than the unipositive ions, K^+ or Na^+, in the flocculation of the negatively charged sol of arsenious sulphide. Many of the electrolytes follow this rule as seen from Table 20.2. Only in a few cases, it is not followed and in these cases, both the ions of the electrolytes determine the flocculation value.

2. Protection of Colloids

It has been observed that lyophobic sols, in contrast to lyophilic sols, are easily flocculated on the addition of a small amount of electrolyte. The relatively higher stability of lyophilic sols is due to the attraction between the dispersed particles and the dispersion medium. Some lyophilic sols are so stable that their addition to lyophobic sols increases the stability of even lyophobic sols. Such lyophilic sols are called protective colloids. Their stabilising action towards the lyophobic colloids is called protective action. The stabilisation is due to adsorption. In other words, lyophilic colloidal particles get adsorbed on the surface of lyophobic colloidal particles. This increases their capability to interact with the dispersion medium. Usually macromolecules like gelatin, starch etc. are used as protective colloids. The protection of colloids is of great industrial importance. The protective power of a colloid is given in terms of gold number. It is defined as "the number of milligrams of the protective colloid which prevents the coagulation of 10 ml of a gold sol on adding 1 ml of a 10% solution of sodium chloride". The start of the flocculation is taken as the point at which the colour of the gold sol changes from red to blue. The size of the gold particles is smaller in red sol and bigger in the blue sol. Formation of blue colour means partial flocculation. It is clear that smaller the gold number of a colloid, larger will be its protective power. The values of gold number for a few hydrophilic ("water loving") sols are given in Table 20.3.

Table 20.3 Gold number of Some Hydrophilic Sols

Sol	Gold number
Gelatin	0.005 — 0.010
Egg albumin	0.08 — 0.10
Gum arabic	0.10 — 0.15
Soluble starch	10 — 15

Egg albumin : A water soluble protein found in egg

Gum arabic : A gum obtained from a particular type of trees.

Soluble starch: Starch is composed 75% of water-soluble portion known as amylopectin. It has a branced chain structure in which many glucose units are connected.

So far we studied the properties of sols. In the next section, we shall study the formation and the characteristics of emulsions. Before proceeding to the next section, answer the following SAQ's.

SAQ 6

Differentiate between electrophoresis and electro-osmosis.

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SAQ 7

Addition of sodium chloride solution to gold sol results in its coagulation. But if this reaction is carried out in presence of a certain amount of soluble starch, precipitation of gold does not take place. Explain.

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20.7 EMULSIONS

Emulsions are colloidal systems in which both the dispersed phase and the dispersion medium are liquids.

Emulsions can be formed between any two immiscible liquids but normally we come across those which are composed of water and an oil. They can be either oil-in-water type, in which the dispersion medium is water or water-in-oil type in which the dispersion medium is oil. The two types can be distinguished by any of the following methods:

1. A small amount of an oil-soluble dye is added to the emulsion and observed under microscope. If the whole background is coloured,then it is water-in-oil type but if you observe only coloured drops, then it must be oil-in-water type.
2. Oil-in-water type emulsions generally have high conductivity as compared to those of water-in-oil type. This is so because organic liquids have much lower conductance than water.
3. Oil-in-water emulsions will not spread on an oily surface whereas water-in-oil will do so, and hence, a distinction can be made.

In an emulsion, globules of one liquid are found suspended in the other liquid. However, in majority of cases, these globules are unstable and the system separates into two liquid layers. In order to stabilise emulsions we have to add substances known as emulsifiers or emulsifying agents. These are generally long hydrocarbon chain molecules having a polar group at one end. Thus, soaps, proteins, long chain sulphonic acids etc. act as emulsifiers. The stabilisation of an emulsion by means of the addition of an emulsifier is known as emulsification. The emulsifier is first shaken with one of the liquids and then, the other liquid is added.

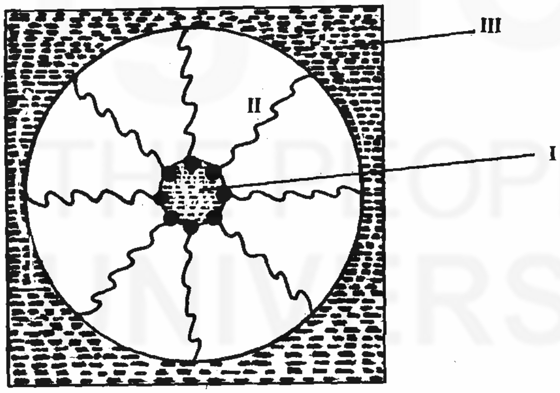

Fig.20.12: Orientations of an emulsifier: I. water ; II. emulsifier molecules with the polar group towards water and nonpolar group towards oil ; III. oil.

The role of an emulsifier is primarily to lower the interfacial tension between the two liquids so as to promote greater interaction between them. The interfacial tension is lowered because of the adsorption of the emulsifier at the interface. This is followed by the preferential orientation of the emulsifier molecules with their polar groups towards water and the long hydrocarbon chain towards the oil as shown in Fig. 20.12.

Emulsions are often used in pharmaceutical preparations, disinfectants etc. Emulsification of greasy material by soap solutions is the mechanism on which the cleansing action of soap depends. The stability of the emulsions can be reduced by adding a substance which destroys the emulsifier. Sometimes centrifuging or freezing may also help in destabilising an emulsion.

Cleansing Action of Soaps and Detergents

$$\underbrace{CH_3-(CH_2)_{16}}_{\text{(Nonpolar hydrocarbon tail)}}-\underbrace{COO^-}_{\text{(Polar head)}}\ Na^+$$

(Sodium stearate)

As explained in Sec. 20.4, soaps are salts of long-chain fatty acids, the most common example being sodium stearate, $C_{17}H_{35}COO^- Na^+$.

Let us now discuss the cleansing action of soaps.

The dirt particles that cling to the textile fibres are generally covered by a layer of oil molecules, called grease. These oil molecules are nonpolar and, so repel water. Hence, water cannot wash such dirt particles out of cloth by itself.

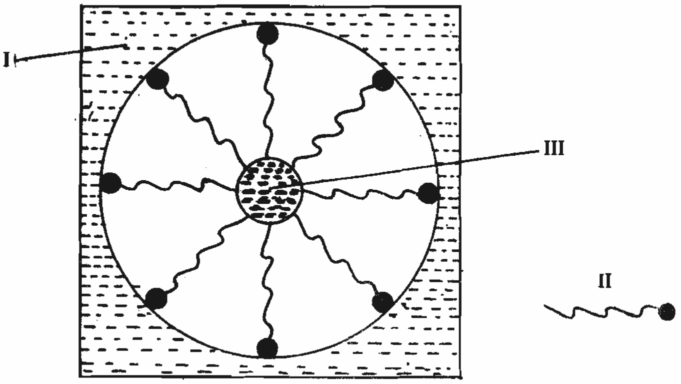

Fig. 20.13 : Soap micelles interacting with grease : I. water ; II. stearate anion ; III. grease molecules attached to the nonpolar tail of the stearate anion.

On the addition of soap, (i) grease molecules get attached to the nonpolar hydrocarbon tail of the stearate anion (due to London forces) and (ii) the polar head of the stearate anion is directed towards water (due to ion-dipole interaction). This results in the lowering of interfacial tension between grease and water. Because of this emulsifying action of soap, grease and hence, dirt is washed out of clothes (Fig. 20.13).

Because of the ability to assist water in wetting and suspending the nonpolar (grease) molecules by lowering the interfacial tension, soaps and detergents are called wetting agents or surfactants.

Soaps are not effective as cleansers when used in hard water. This is because the calcium and magnesium ions present in hard water form a precipitate of calcium and magnesium stearates. This results in

- the loss of cleansing action of soap due to decrease in stearate ion concentrations in water,
- increase of binding of the grease to the cloth, giving it a dull colour.

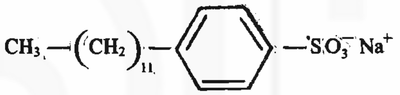

Fig. 20.14 : A linear alkylbenzene sulphonate (sodium salt).

To solve this problem of hard water, detergents are used in the place of soaps. Detergents are of two types–anionic and cationic. The anionic detergents are generally the sodium salts of linear alkylbenzene (LAB) sulphonic acids (Fig. 20.14).

The cationic detergents are generally quaternary ammonium salts of the type,

$$(CH_3)_3RN^+Cl^-$$

where R is a long chain of alkyl groups containing between 12 and 18 carbon atoms.

As far as cleansing action is concerned, detergents, like soaps, act as emulsifiers between grease and water. Further in presence of hard water, detergents do not form precipitates. For example, calcium or magnesium salts of LAB sulphonates are soluble in water. Hence detergents can be used even in hard water.

Your study of this section could help you in answering the following SAQ. In the next section, we shall discuss the characteristics of gels.

SAQ 8

Explain the detergent action of linear alkylbenzene sulphonates (RSO_3^-).

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....

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20.8 GELS

Hot solutions of some substances, when cooled, form a semisolid mass. These are the substances which normally form lyophilic sols. As the solution cools, the molecules of the solute tend to come together to form bigger aggregates. In doing so, they form a network with much open space between the aggregates. Solvent gets trapped in these small spaces of the network. These gels can be of two types: In one case, the gels on standing may lose water and become a solid. However, this solid on mixing water can again turn into a gel. Such substances are called elastic gels. A common example of elastic gel would be the gum or glue we use for pasting paper. The other kind of gel on dehydration gives a powder which cannot be converted back into gel again. These are known as nonelastic gels. So far in this unit, we discussed the characteristics of some colloidal dispertions.

In the next section, we shall discuss the methods of determination of molar mass of macromolecular systems. These methods are based on the characteristics of colloidal dispersions.

20.9 METHODS FOR THE DETERMINATION OF MOLAR MASS

It has been pointed out in Sec. 20.5 that in macromolecular solutions, the distribution of macromolecules is not uniform. Hence, some kind of average molar mass value is obtained experimentally. For these measurements we use such a property of the sample which is directly related to the molar mass. We shall discuss a few of these methods in the present section.

1. **Viscosity Method**

The macromolecular solutions show high viscosities even when the concentrations are low. This may be due

- either to the high solvation of the solute molecules which do not allow the solvent to move freely, or,
- to the macromolecules getting entangled with each other due to their large size and thus restricting the movement of the solvent.

Relative molecular mass is commonly known as molecular weight.

Molar mass

$$= \frac{(\text{Relative molecular mass})}{1000}\ \text{kg mol}^{-1}$$

Due to the simplicity of the measurement of viscosity, this method is widely used in determining the molar masses of the polymers. The first step involves the determination of the viscosities of polymer solutions of different concentrations. From these measurements,we derive the value of intrinsic viscocity which is defined below:

$$\text{Intrinsic viscosity } [\eta] = \underset{d \to o}{Lt}\left[\frac{(\eta - \eta_0)}{d\,\eta_0}\right] \qquad \text{...(20.12)}$$

where η and η_0 are the viscosities of the solution and of the solvent, respectively and d is the concentration of the polymer solution (expressed as mass of the polymer per given volume of the solution).

In order to obtain the value of $[\eta]$ a graph is plotted with $\frac{\eta - \eta_0}{d\eta_0}$ against d which gives a straight line. The line is extrapolated to zero concentration so that the intercept gives the value of intrinsic viscocity. The intrinsic viscosity is related to the relative molecular mass (M) by the following equation:

$$\left.\begin{array}{l} [\eta] = KM^{\alpha} \\ \text{or } [\eta] = \log K + \alpha \log M \end{array}\right\} \qquad \text{...(20.13)}$$

where K and α are constants which depend on the nature of the polymer, solvent and the temperature. For the determination of K and α values, we first take solutions of a polymer of known relative molecular mass, and draw a graph between log $[\eta]$ and log M values for this polymer. The slope of the line gives α and the intercept gives log K. Using these values of K and α we can determine the relative molecular mass for a similar polymer.

This gives us the viscosity average molar mass $\overline{M}_v$ of the polymer. Let us study an example.

Example 4

The intrinsic viscosity of a given polymer sample is 0.96 $dm^3\ kg^{-1}$. If the value of K and α are $1.2 \times 10^{-4}\ dm^3\ kg^{-1}$ and 0.75, respectively, find the relative molecular mass of the polymer.

Solution

$$[\eta] = KM^{\alpha}$$

$$0.96\ dm^3\ kg^{-1} = 1.2 \times 10^{-4}\ dm^3\ kg^{-1}\ M^{0.75}$$

$$M^{0.75} = \frac{0.96}{1.2 \times 10^{-4}} \text{ or } M = \left(\frac{0.96}{1.2 \times 10^{-4}}\right)^{\frac{4}{3}}$$

or

Relative molecular mass = 1,60,000

or

Molar mass = 160 kg mol^{-1}

2. **Osmotic Pressure Method**

The osmotic pressures produced by solutions of even low molarity are easily measurable and, this method is widely used for the determination of molar masses of polymers. For dilute solutions, we can write the relationship between the osmotic pressure and the molar mass of the polymer based on Eq. 12.49 as follows:

Eq. 12.49 was derived in Unit 12 for correlating the molar mass of a nonvolatile solute with the osmotic pressure of the solution.

$$\Pi = \frac{wRT}{MV} \qquad \ldots (20.14)$$

$$\Pi = \frac{wRT}{VM} \qquad \ldots (20.15)$$

w and M are the mass and molar mass of the polymer, R is gas constant, T is temperature, V is the volume of the solution and Π is its osmotic pressure.

Replacing w / V by d we can rewrite Eq. 20.15 as,

$$\Pi = \frac{dRT}{M} \qquad \ldots (20.16)$$

or

$$\frac{\Pi}{d} = \frac{RT}{M} \qquad \ldots (20.17)$$

where d is the concentration of a solution given in kg m^{-3} units.

This equation is applicable only to dilute solutions which do not show deviation from normal behaviour. Such cases are represented using the limiting condition, $d \rightarrow 0$, i. e., the concentration of the solution approaches zero,

$$\underset{d \rightarrow 0}{Lt} \frac{\Pi}{d} = \frac{RT}{M} \qquad \ldots (20.18)$$

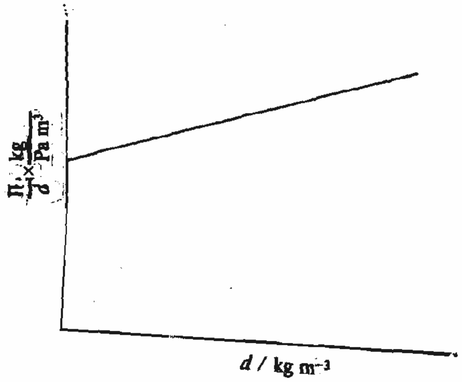

Fig. 20.15 : Plot of Π/d vs. d

The polymer solutions of measurable concentration exibit deviation from ideal behaviour and a correction term, Bd, is to be included in Eq. 20.17, where B depends on the polymer-solvent system and the extent of interaction between the two.

Hence,

$$\frac{\Pi}{d} = \frac{RT}{M} + Bd \qquad \dots (20.19)$$

The method of measurement of osmotic pressure has been discussed in Unit 12. A graph is plotted between Π/d and d which gives a straight line (Fig. 20.15).

By extrapolating the line to zero d value, the intercept, which is equal to L.H.S of Eq. 20.18 and also to RT/M, is obtained. From this, we get the value of M, the number average molar mass of the polymer.

3. Light Scattering Method

In the case of pure fluids light scattering takes place due to local changes of density from time to time. This results in fluctuations in the refractive index of the medium. In case of solutions, these fluctuations are of higher magnitude. Thus, when a ray of light enters the solution, it suffers scattering in all directions thereby giving the solution a turbid appearance. The turbidity (τ) is related as per Eq. 20.20 to the intensity of incident light (I_0) the intensity of scattered light (I) and the distance(x) through which light has passed in the solution:

$$I = I_0 \, e^{-\tau/x}$$

or

$$\frac{I}{I_0} = e^{-\tau/x} \qquad \dots (20.20)$$

Also, I/I_0 value is related to the refractive index of the solvent, angle of scattering, the change in the refractive index of the solution with concentration, wavelength of the incident light etc. Without going into the derivation, we can write the following relationship:

$$\tau = HMc \qquad \dots (20.21)$$

where H includes all the factors mentioned above for which values are known, M is the molar mass and c the concentration of the polymer. This expression has been derived for highly idealised systems and for its application to real systems, we must add another concentration term giving,

$$\frac{Hc}{\tau} = \frac{1}{M} + 2\,Bc \qquad \dots (20.22)$$

where B is a constant.

By plotting Hc/τ against the concentration, we get a straight line which when extrapolated to zero concentration, gives an intercept equal to $1/M$. The scattering method is suitable for the determination of very high molar masses. The apparatus for measuring turbidity are commercially available these days. By this method, we obtain the mass average molar mass.

4. Sedimentation Method

When a polymer or a colloidal sol is left in a vessel,the colloidal particles settle to the bottom under the force of gravity. This process can be accelerated by subjecting the sol to a very high gravitational force by putting the cell containing the sol in an ultracentrifuge and subjecting to high speed of rotation. In analytical centrifuges there is optical arrangement for the determination of the concentration of the polymer molecules at different depths of the cell. The use of ultracentrifuge for the determination of molar mass of a polymer is done either by sedimentation velocity method or sedimentation equilibrium method. However, we shall not discuss these methods in detail.

If you have understood the osmotic pressure method of determining the molar mass of a polymer, you could answer the following SAQ.

SAQ 9

1.00 m^3 of a solution containing 2.50 kg of a polymer has an osmotic pressure of 250 Pa at 298 K. Assuming that the solution does not deviate from ideal behaviour, calculate the molar mass of the polymer.

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20.10 APPLICATIONS

There are many applications of colloids in day to day life and in industry. Some important applications are given below:

Food : The study of colloidal systems has helped in the processing of milk, butter, starch, proteins, curd, ice-cream and cheese.

Medicine : Many medicines are emulsions and colloidal sols. Their preparation and stabilisation require a knowledge of colloidal science. Most biological fluids like blood etc are colloidal dispersions.

Agriculture : Soil is a mixture of clay, organic materials, and salts which shows colloidal behaviour. The study of colloids becomes important in understanding the nature of soil, its moisture adsorption properties, formation of protective colloid by humus, exchange of ions etc.

Rubber : Rubber latex is a colloidal suspension. Since the rubber particles are negatively charged, they can be directly deposited on a mould of any size or shape by making it the anode in an electrophoretic process.

Water Treatment : Water from rivers, lakes etc. contain large amounts of colloidal impurities which are usually purified by the addition of alum which coagulates the colloidal particles.

Sewage disposal : Water in the sewage contains dust, garbage and other impurities as a colloidal suspension. The sewage disposal tanks are fitted with charged electrodes. The colloidal particles move towards the suitable electrode and get discharged. Thus these particles coagulate at the electrodes. The sewage sludge after further treatment can be used as manure. Clear water from the tanks is used for irrigation purposes.

Smoke removal : Industrial towns are saved from smoke pollution to a large extent by fitting Cottrell's apparatus at the chimney of the factories. This apparatus consists of two electrodes, (one being cylindrical and the other being a co-axial pointed rod). These electrodes are maintained at a very high potential difference (50,000 volts). The smoke particles while passing between the electrodes are precipitated on a suitable electrode from where they are scrapped down and removed.

Preparation of catalysts : Catalysts, we know, are most effective when used in the form of finely divided particles (See SAQ 1). These are first obtained in a colloidal state from which they are coagulated on a suitable supporting material.

Hide : Skin removed from a dead animal.

Tanning : Changing hide into leather by chemical treatment.

Chrome-tanning: Tanning by using chromium compounds.

Leather Industry: Hides contain proteins in colloidal state which are precipitated in the tanning process. Leather is usually chrome-tanned by allowing the positively charged particles of hydrous chromic oxide into the animal hides.

Soaps, Detergents and Dyes : The colloidal chemistry of soaps and detergents is important in understanding their cleansing property. They are also used as emulsifiers. Many dyes form associated colloids.

Other Industries : Many industrial products like paints, varnishes, printing inks, gums, resins and adhesives are all colloidal in nature. The list of such industrial goods is so long that it cannot be given fully.

Smoke Screens : Finely divided titanium dioxide particles dispersed in air are used in modern warfare as smoke screens for the purpose of camouflaging.

20.11 SUMMARY

In this unit, we have discussed the main features of colloidal systems:

- We have first defined the colloidal systems and then given their classification.

- We have described the characteristic properties of colloids.
- The origin of charge on the colloidal particles has been discussed.
- The characteristics of macromolecular solutions are discussed. The number average molar mass and the mass average molar mass are then defined.
- The methods for the determination of molar masses are described.
- A short discussion on the applications of colloids in industry as well as in our daily life has been given.

20.12 TERMINAL QUESTIONS

1) 1.00 m^3 of a sol has 10^{16} particles of radius 100 nm. Calculate the mass of a solid required to prepare 1.00 dm^3 of the sol. The density of the solid is 1.50×10^3 kg m^{-3}.

   (**Hints:** i) Consider the particles in the sol to be spherical and calculate the volume of each particle using the formula,

   $$\frac{4}{3}\pi r^3$$

   ii) Calculate the volume occupied by the particles in 1.00 m^3 of the sol; for this, multiply the answer for (i) by 10^{16}.

   iii) Calculate the mass of the substance dispersed in 1 m^3 of the sol.

   $$\left\{\begin{matrix}\text{Mass of the}\\ \text{substance in } 1\text{m}^3 \text{ of the sol}\end{matrix}\right\} = \left\{\begin{matrix}\text{Volume of the particles}\\ \text{in } 1\text{m}^3 \text{ of the sol}\end{matrix}\right\} \times \left\{\begin{matrix}\text{density of}\\ \text{the substance}\end{matrix}\right\}$$

   iv) Calculate the mass of the substance required to prepare 1 dm^3 of the sol ; multiply the answer for (iii) by 10^{-3} to get the answer for this step).

2) Give a few examples of colloids used by you in daily life.

3) What is the origin of charge on a colloidal particle? How are coions and counter ions distributed around the charged colloidal particles?

4) Calculate the volume of 0.1 M $BaCl_2$ solution (in cm^3 unit) required to coagulate 1 dm^3 of arsenious sulphide sol, if the flocculation value of $BaCl_2$ is 4.

5) What is Tyndall effect? Suggest an application for this effect.

6) Caculate the number average and mass average molar masses of a polymer sample with the following distribution of molar masses:

N_i	100	250	400	300	200	100
M_i /kg mol^{-1}	2.000	3.000	5.000	7.000	10.000	15.000

   Also calculate the polydispersity index.

7. What do you understand by protection of colloids? Explain the mechanism of protection of colloids.

8. Explain the term, 'electrophoresis'. State two of its applications.

20.13 ANSWERS

Self Assessment Questions

1) $$\left\{\begin{matrix}\text{Volume of each platinum}\\ \text{particle}\end{matrix}\right\} = \frac{4}{3} \times 3.14 \times (50 \times 10^{-9})^3 \text{ m}^3$$

$$= 5.23 \times 10^{-22} \text{ m}^3$$

$$\left\{\begin{array}{c}\text{Number of particles that}\\ \text{could be formed from}\\ 1.00\times10^{-6}\ \text{m}^3\ \text{platinum}\end{array}\right\} = \frac{1.00\times10^{-6}\ \text{m}^3}{5.23\times10^{-22}\ \text{m}^3}$$

$$= 1.91\times10^{15}$$

$$\left\{\begin{array}{c}\text{Surface area of each}\\ \text{platinum particle}\end{array}\right\} = 4\,\pi r^2$$

$$= 4\times3.14\times(50\times10^{-9})^2\ \text{m}^2$$

$$= 3.14\times10^{-14}\ \text{m}^2$$

$$\left\{\begin{array}{c}\text{Total surface area of all}\\ \text{the platinum particles}\end{array}\right\} = 1.91\times10^{15}\times3.14\times10^{-14}\ \text{m}^2$$

$$= 60.0\ \text{m}^2 = 6.00\times10^5\ \text{cm}^2$$

2) A dilute solution containing Cl^- ion or Ag^+ ion could function as peptizing agent in the preparation of silver chloride sol from solid silver chloride.

3) i) Charge on the micellar ion = [(–100)–(+80)] units

$$= -20\ \text{units}$$

ii) $$\left\{\begin{array}{c}\text{Number of ions present}\\ \text{after micelle formation}\end{array}\right\} = \left\{\begin{array}{l}1\ (\text{due to micelle})\ +\\ (20\ \text{due to free Na}^+\ \text{ions})\end{array}\right\}$$

$$= 21$$

iii) The number of ions before micelle formation = 200

The number of ions after micelle formation = 21

The decrease in the number of ions, which carry current, evidently results in the decrease of conductivity. Since osmotic pressure is a colligative property, its decrease due to the decrease in the number of species is understandable.

4) The polydispersity index will be equal to one, if the molar masses of all the polymers are same. You can get this result if you write M_i as M and take it out of $\sum$ sign in Eqs.20.1 and 20.9.

5) $$\overline{M}_n\,\overline{M}_w = \frac{\sum_i n_i M_i}{\sum_i n_i}\cdot\frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} = \frac{\sum_i n_i M_i^2}{\sum_i n_i} = M_{\text{rms}}\ \ (\text{as per Eq. 20.10}).$$

6) During electrophoresis, colloidal particles move towards an electrode whereas during electro-osmosis, dispersion medium moves.

7) The addition of sodium chloride solution to gold sol neutralises the charge on the colloidal particles and causes coagulation. Soluble starch particles get adsorbed on the surface of gold sol particles and increase their capability to interact with the dispersion medium thereby preventing coagulation.

8) The detergent action of linear alkylbenzene sulphonates is similar to stearates. The main difference is that the sulphonate ion forms the polar part in the former whereas the carboxylate ion forms the polar part in the latter.

9) As per Eq. 20.15, $M = \dfrac{wRT}{V\Pi}$

$$= \frac{2.50\ \text{kg}\times8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\times298\ \text{K}}{1.00\ \text{m}^3\times250\ \text{Pa}}$$

$$= 24.8\ \text{kg mol}^{-1}$$

Terminal Questions

1) Volume of each particle $= \dfrac{4}{3}\pi r^3 = \dfrac{4}{3}\times3.14\times(100\times10^{-9}\ \text{m})^3$

$$= 4.19 \times 10^{-21} \text{ m}^3$$

There are 10^{16} particles in 1.00 m^3 of the sol.

$$\left\{\begin{array}{l}\text{Volume of the particles}\\ \text{in 1 m}^3 \text{ of the sol}\end{array}\right\} = 4.19 \times 10^{-21} \times 10^{16} \text{ m}^3$$

$$= 4.19 \times 10^{-5} \text{ m}^3$$

$$\left\{\begin{array}{l}\text{Mass of the substance}\\ \text{required to prepare}\\ \text{1 m}^3 \text{ of the sol}\end{array}\right\} = 4.19 \times 10^{-5} \text{ m}^3 \times 1.50 \times 10^3 \text{ kg m}^{-3}$$

$$= 6.29 \times 10^{-2} \text{ kg}$$

$$\left\{\begin{array}{l}\text{Mass of the substance}\\ \text{required to prepare}\\ \text{1 dm}^3 \text{ of the sol}\end{array}\right\} = 6.29 \times 10^{-2} \times 10^{-3} \text{ kg}$$

$$= 6.29 \times 10^{-5} \text{ kg}$$

2) Curd, cheese, butter, ice-cream, paints, ink, tooth paste and adhesives are some examples.

3) See Subsec. 20.6.4.

4) The flocculation value of barium chloride is 4. Hence, 4 millimoles of $BaCl_2$ are required to coagulate 1 dm^3 of arsenious sulphide sol. 1 dm^3 of 0.1 M $BaCl_2$ solution contains 0.1 mole of $BaCl_2$.

Hence, 1 cm^3 of 0.1 M $BaCl_2$ solution contains 0.1 millimole of $BaCl_2$

$$\left\{\begin{array}{l}\text{Volume of BaCl}_2 \text{ solution required}\\ \text{to have 4 millimoles}\end{array}\right\} = \frac{4}{0.1} \text{ cm}^3$$

$$= 40 \text{ cm}^3$$

5) See Subsec. 20.6.3.

6) $\overline{M}_n = 6.33$ kg

$\overline{M}_w = 8.17$ kg

The polydispersity index $= \dfrac{\overline{M}_w}{\overline{M}_n} = \dfrac{8.17}{6.33} = 1.29$

7) See Subsec. 20.6.5.

8) See Subsec. 20.6.4 for the explanation of the term, electrophoresis. For applications, see Sec. 20.10 under the captions, rubber, sewage disposal and smoke removal.

UNIT 21 SURFACE CHEMISTRY AND CATALYSIS

Structure

21.1 INTRODUCTION

In Unit 18, we discussed the dependence of the rates of reactions on the concentration of the reactants and temperature. In Unit 20, we explained the characteristics of the colloids which include surface activity also. In this unit, we shall discuss the effect of surface on chemical reactivity.

Surface, in the chemical sense, is a phase boundary. Geometrically a surface has an area but no thickness. Surface is an **interface region** where one phase ends and the other begins. Chemically it is a region in which the properties vary from one phase to another. The transition occurs over distance of molecular dimensions. Thus for a chemist, surface has a thickness which shrinks to zero in an ideal condition of a geometrical description. In this unit we shall discuss the properties of an interface which may be liquid/vapour, solid/liquid or solid/gas. We shall discuss adsorption of gases on solid surfaces. Such a discussion is important since many of the chemical reactions in industry or in the biological systems take place on the interface. We shall also explain the different types of catalysts, inhibition of catalysts and catalytic poisoning.

Objectives

After studying this unit, you should be able to :

- define an interface,
- state the relationship between the concentration of a surface active solute and the surface tension of a solution,
- discuss different isotherms for adsorption on solid surfaces,
- state the role of photoelectron spectroscopy in surface chemical analysis,
- describe the functioning of different types of catalysts, and
- explain the inhibition of chemical reactions and poisoning of catalysts.

21.2 SURFACE TENSION OF SOLUTIONS

Liquids assume a shape with minimum surface area. The molecules in the bulk have less energy than the molecules in the surface, since a molecule in the bulk interacts with larger number of molecules as compared to a molecule on the surface. You are aware that any system tries to assume a state in which it has minimum energy. Hence, a liquid tries to take a shape which has the least surface area. The shape assumed is spherical, as a sphere has the smallest surface to volume ratio. The force that opposes the increase in area of a liquid is referred to as surface tension. In Unit 4 of this course, we have defined surface tension as a force per unit length acting on the surface opposing the expansion of surface area. An alternative definition was also suggested that surface tension is the surface energy per unit area of the surface. Normally the surface tension values reported are for the liquid-vapour interface in presence of air.

When we dissolve a solute in a solvent, the surface tension of the solution changes. A relationship could be derived to establish the fact that the concentration of the solute that lowers the surface tension would tend to be more on the surface of a solvent as compared to that in the bulk. This is the basis of **Gibbs adsorption isotherm**, about which we do not intend giving a detailed discussion. Substances which produce a remarkable lowering of interfacial tension are called 'surface active agents or surfactants'. We have seen one of the applications of the surfactants in Sec. 20.7 of Unit 20 where we dealt with the cleansing action of soaps and detergents. Another application of surfactants is in the formation of surface films. Some insoluble substances such as long-chain fatty acids and alcohols could spread on water surface to form a thin film. The formation of such surface films using long-chain alcohols has been helpful in retarding the evaporation of water from reservoirs.

SAQ 1

What is the essential characteristic of a surface active agent ?

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21.3 ADSORPTION ON SOLIDS

In Sec. 21.2, we studied that the molecules on the surface of a liquid experiences an inward pull. The liquid surface is thus in a state of unsaturation. The surface of a solid also behaves in a similar manner. In a solid, the ions or the molecules at the surface of a crystal do not have all their valencies satisfied by union with other particles. Such forces also arise due to the fact that when a new solid surface is created by breaking a solid, some interatomic bonds are broken and some of the valencies of surface atoms are left unsatisfied. As a result of these residual forces, the surface of the solid has a tendency to attract and retain available molecules and other particles towards itself; such a condition is helpful in decreasing the surface energy of a solid. The molecules so attracted are retained on the surface of the solid and do not go deeper into the bulk. Their concentration is more on the surface than in the bulk of the solid. This phenomenon of higher concentration of a substance on the surface of a solid is called **adsorption**. The substance attracted to the surface is called **adsorbate** while the substance to which it is attached is called **adsorbent**. For example, charcoal adsorbs acetic acid when kept in contact with it; here, acetic acid is adsorbate and charcoal is adsorbent.

Porous substance; A substance having tiny openings through which fluids or air could pass.

The extent of adsorption by charcoal can be increased by subjecting charcoal to a process of activation. It involves heating of wood charcoal between 625 K and 1275 K in vacuum, air, steam, chlorine or carbon dioxide. During activation, hydrocarbons and other impurities are removed from charcoal leading thereby to a large surface area for adsorption. The resulting substance is called activated charcoal.

Adsorption should be clearly distinguished from absorption. In absorption, the substance is not only retained on the surface but passes through the surface and is distributed throughout the bulk of the solid. Thus, anhydrous calcium chloride absorbs water to form a hydrate while acetic acid is adsorbed from its solution by charcoal. Sometimes the word 'sorption' is used when there is a doubt whether a process is true adsorption or absorption.

Adsorption of Gases by Solids

The studies of the adsorption of gases by solids are similar to those of the adsorption of liquids by solids. In this unit, we shall mainly study the adsorption of gases by solids.

Although all solids adsorb gases, the effects are not evident unless the adsorbent is porous and has a very large area for a given mass. That is why silica gel and charcoal, which have porous structure, are very effective as adsorbing agents.

The amount of a gas adsorbed by a solid depends upon

- the nature of the gas and the adsorbent,
- the surface area of the adsorbent, and
- temperature and pressure of the adsorbent - adsorbate system.

Table 21.1 gives the volume of various gases adsorbed by 1.00 kg of charcoal at 288 K. The volume of gases have all been reduced to 273 K and 1.013×10^5 Pa pressure. It can be seen from Table 21.1 that gases which can be liquefied easily are more readily adsorbed.

Table 21.1 : Adsorption of Gases on Charcoal

Gas	Volume adsorbed m^3	Critical temperature K
H_2	4.7×10^{-3}	33
N_2	8.0×10^{-3}	126
CO	9.3×10^{-3}	134
CO_2	4.8×10^{-2}	304
HCl	7.2×10^{-2}	324
H_2S	9.9×10^{-2}	373
NH_3	1.8×10^{-1}	406

The total amount of the gas adsorbed increases with the surface area of the adsorbent. During adsorption an equilibrium is established between the gas in contact with the solid and the gas on the surface. An increase in temperature decreases the amount of the gas adsorbed.

In the next section, we shall discuss quantitative relationships regarding adsorption.

21.4 ADSORPTION ISOTHERMS

The amount of a substance adsorbed by an adsorbent at constant temperature depends upon the concentration or pressure of an adsorbate. For the adsorption of a substance (adsorbate) present in a solution by a solid adsorbent, Freundlich gave an empirical equation. This equation gives the relationship between the mass of the adsorbate (x) adsorbed by a particular mass (m) of the adsorbent and the equilibrium concentration of the adsorbate (c) in the solution at a particular temperature as given below:

$$\frac{x}{m} = Kc^{1/n} \qquad \dots (21.1)$$

where K and n are constants. Eq. 21.1 is a form of Freundlich adsorption isotherm. By plotting log x/m against log c (Fig. 21.1), we can evaluate K and n. The values of K and n depend on

- nature of the adsorbate,
- nature and particle size of the adsorbent, and
- temperature.

It is worth mentioning that as the particle size becomes smaller, the surface area increases enormously. This increases the adsorbing capacity of an adsorbent.

Eq. 21.1 could be slightly modified to express the adsorption of a gas by a solid as given below:

$$\frac{x}{m} = Kp^{1/n} \qquad \dots (21.2)$$

In this equation, p stands for the pressure of the gas adsorbate; other terms have the same significance as given in Eq. 21.1.

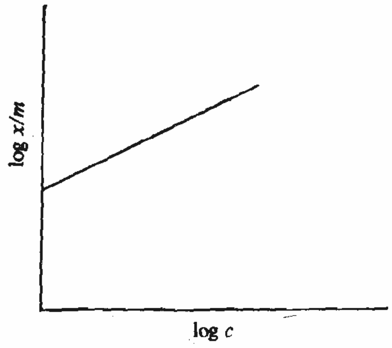

Fig. 21.1: Graphical representation of Freundlich adsorption isotherm.

Freundlich isotherm (Eq. 21.1 or 21.2) is applicable only if the concentration or pressure of the adsorbate is low.

Langmuir Adsorption Isotherm

Langmuir obtained a relationship for the adsorption of a gas by a solid. Langmuir started with the assumptions stated below:

Desorption is the process of release of the adsorbed molecules. Desorption may also be called the evaporation of the adsorbed molecules.

- The adsorbed gas behaves ideally in the vapour phase; there are no attractive or repulsive forces among the gas molecules.
- The surface of a solid is homogeneous and there are a fixed number of adsorption sites. Each site has the same attraction for the gas molecules.
- Each adsorption site can adsorb only one molecule. A solid surface cannot form a layer more than a single molecule in depth. In other words, the adsorption of a gas could lead only to the formation of unimolecular layer on the solid.
- There is an equilibrium between the condensation of gas molecules on the adsorbent and their desorption from it. The initial rate of condensation of gas molecules on the solid surface is high and it decreaseas as the surface available for adsorption decreases. The desorption can occur by thermal agitation and the rate of desorption will depend upon the amount of solid surface covered by gas molecules. It will increase as the surface becomes more and more saturated. At a certain stage, the rates of condensation and desorption become equal and an equilibrium is established.
- Using the above assumptions, Langmuir equation for adsorption can be derived as follows:

  Let the fraction of the total surface covered by gas molecules be θ; then the surface available for adsorption is $1-\theta$. According to kinetic theory of gases, the rate at which the molecules strike the unit area of surface is proportional to the pressure of the gas. If p is the equilibrium gas pressure, then,

  rate of condensation $\alpha\ (1-\theta)p$

  or rate of condensation $= k_1(1-\theta)p$ ... (21.3)

  where k_1 is a constant of proportionality.

  Rate of evaporation from the surface will be proportional only to the fraction of the surface which has adsorbed gas molecules on it. Thus,

  rate of evaporation $= k_2\theta$ ...(21.4)

  k_2 is also a proportionality constant.

  At equilibrium, the rates of condensation and evaporation are equal. Hence,

  $k_1(1-\theta)p = k_2\theta$ ... (21.5)

Rearranging Eq. 21.5, we can get,

$$\theta = \frac{k_1 p}{k_2 + k_1 p} = \frac{(k_1/k_2)p}{1 + (k_1/k_2)p} \quad \text{(dividing the numerator and denominator by } k_2\text{)}$$

$$\theta = \frac{Kp}{1 + Kp} \quad \text{(where } k_1/k_2 = K\text{, another constant)} \qquad \ldots (21.6)$$

Eq. 21.6 could be modified to find a relationship between the amount of gas adsorbed and the gas pressure. The amount of gas adsorbed (y) at a pressure p is proportional to the fraction of the total surface covered (θ) by the gas molecules.

i.e., $y \propto \theta$

Hence, $$y = y_m\theta \text{ or } y/y_m = \theta \qquad \ldots (21.7)$$

Where y_m is the proportionality constant and is equal to the amount of the gas molecules required to form a unimolecular layer; i.e., $y = y_m$ when $\theta = 1$.

Using Eqs. 21.6 and 21.7,

$$\frac{y}{y_m} = \frac{Kp}{1 + Kp}$$

$$y = \frac{y_m Kp}{1 + Kp}$$

$$\text{or } \frac{p}{y} = \frac{1 + Kp}{y_m K} = \frac{1}{y_m K} + \frac{p}{y_m} \qquad \ldots (21.8)$$

Eq. 21.8 is known as Langmuir adsorption isotherm.

- When the gas pressure is low, p / y_m is small when compared to $\frac{1}{y_m K}$. Hence $\frac{p}{y} = \frac{1}{y_m K}$

or $p/y =$ constant, since y_m and K are constants.

or $p \propto y$

This means that at low pressures, the amount of gas adsorbed is proportional to gas pressure.

- When the gas pressure is high, $\frac{p}{y_m}$ is much larger than $1 / y_m K$. Hence Eq. 21.8 could be written as,

$$\frac{p}{y} = \frac{p}{y_m}$$

or $y = y_m$ which means that at high pressures, the amount of gas adsorbed is sufficient to form a unimolecular layer. A way to verify Langmuir adsorption isotherm (Eq. 21.8) is to plot p / y against p. A straight line must be obtained. (Fig. 21.2)

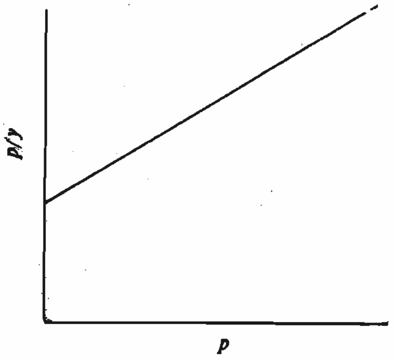

Fig. 21.2 Graphical representation of Langmuir adsorption isotherm.

It is observed that straight line plots are obtained when the surfaces are smooth and nonporous and when the pressures are not too high. Under these conditions, Eq. 21.8 is obeyed. Deviations from Langmuir adsorption isotherm are seen if

- surface is porous (i.e., a good adsorbent) and
- pressure is very high.

Under these conditions, gas molecules give rise to multilayer adsorption on the solid surface which accounts for deviations from Eq. 21.8. For explaining multilayer adsorption, **Brunauer, Emmet and Teller** have proposed a model which is known as **BET** isotherm which we are not going to discuss in detail.

SAQ 2

Starting from Eq. 21.6, derive the following equation:

$$p = \frac{\theta}{K(1-\theta)}$$

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21.5 PHYSISORPTION AND CHEMISORPTION

Both physisorption and chemisorption are generally exothermic processes. That is why we talk about enthalpy decrease while comparing energies of physisorption and chemisorption.

Depending on the type of interaction between the adsorbate and the adsorbent, adsorption is of two types–physisorption (physical adsorption) and chemisorption (chemical adsorption).

Physisorption

If the adsorbate molecules are weakly bound to the adsorbent, it is classified as physisorption. It is also known as van der Waals adsorption since the forces involved are of van der Waals type and are of the same magnitude as are involved in the liquefaction of gases. The enthalpy decrease ($-\Delta H$) associated with physisorption is much low (less than 40 kJ mol^{-1}) and is of the same order as the enthalpy of condensation of the adsorbate. Increase of temperature is not favourable to physisorption. Adsorption of gases by charcoal is an example of physisorption. Physisorption is generally independent of the chemical nature of the adsorbate. All gases exhibit van der Waals adsorption.

The unsatisfied valencies of the surface atoms may cause breakage of the bonds in the chemisorbed molecules. The fragments that result in the process are responsible for the increased chemical activity.

Chemisorption

If the adsorbed molecules react chemically with the surface, we call it chemisorption. The enthalpy decrease associated with chemisorption is much high (between 40 kJ mol^{-1} and 400 kJ mol^{-1}) and is of the order of bond enthalpies. We shall see in Sec. 21.8 as to how the type of bonding caused by chemisorption between the adsorbent and the adsorbate determines the reactivity pattern. Many chemisorption processes involve activation energy as in a chemical reaction. In such cases, the rates of chemisorption and desorption increase with temperature in contrast with the rate of physisorption.

High bond enthalpy of nitrogen (945 kJ mol^{-1}) is mainly responsible for its low reactivity.

Let us see how the type of adsorption of nitrogen on iron surface varies with temperature. The studies on the adsorption of nitrogen on iron surface indicate that at about 770 K (the temperature chosen for Haber process), nitrogen is chemisorbed on the iron surface. Chemisorption results in large release of energy. The optimum temperature chosen for the reaction and the energy released during chemisorption are helpful in overcoming the large bond enthalpy of nitrogen. Hence, when nitrogen is chemisorbed at 770 K it is present as nitrogen atoms but not as molecules.

One of the methods followed in scientific reasoning is to arrive at the same conclusion through more than one method. Take for instance manufacture of ammonia. Based on Le Chatelier principle, we stated in Unit 14 that high pressure (200–300 atm) and optimum temperature (670–870 K) are needed for a good yield of ammonia. These conclusions could be reached from surface studies also. In this section, we have explained that around 770 K, nitrogen is chemisorbed on iron to a large extent and, this facilitates formation of ammonia. As an explanation for the need of high pressure for this reaction, answer SAQ 3.

At temperatures less than 770 K, there is not much of chemisorption of nitrogen on iron surface. At room temperature, iron does not adsorb nitrogen at all. But as temperature is lowered and brought near 80 K, the boiling point of liquid nitrogen, iron adsorbs nitrogen gas physically as N_2 molecules! In short, near 770 K, nitrogen is chemisorbed by iron as nitrogen atoms and near 80 K, it is physisorbed as nitrogen molecules.

The dissociation of nitrogen molecule on iron surface at 770 K could facilitate its further reaction such as the formation of ammonia through Haber process. Although the mechanism of iron catalysis in Haber process is not completely understood, the chemisorption of nitorgen on iron certainly plays a role in it.

SAQ 3

Assuming that chemisorption of nitrogen on iron at 770 K follows Langmuir isotherm, could you justify the use of high pressure in Haber process for the manufacture of ammonia?

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21.6 MODERN METHODS OF SURFACE STUDIES

The composition of the adsorbent surface, the nature of binding between the adsorbent and the adsorbate and the extent of surface coverage could be studied by using methods such as X-ray or UV photoelectron spectroscopy, Auger spectroscopy and low energy electron diffraction (LEED). Of these methods, we shall explain the principle of X-ray and UV photoelectron spectroscopy only.

Auger effect is the emission of a second electron after high energy radiation has expelled an electron. Auger effect is the basis of Auger Spectroscopy and is much used in microelectronics industry.

Low energy electron diffraction is the diffraction caused by atoms on the surface by using low energy electrons. The LEED pattern depicts the two dimensional structure of a surface. Low energy electrons are used to ensure diffraction by atoms on the surface only, but not by atoms in the bulk.

In Unit 1 of Atoms and Molecules course, we have explained the photoelectric effect, according to which photoelectrons could be ejected by irradiating a metal surface with UV rays. The minimum energy that UV rays must possess for photoelectron emission corresponds to the ionisation energy of the valence electrons. If we are interested in the emission of inner electrons, we must use X-rays. The studies on electron emission which is caused by X-ray or UV irradiation are called X-ray or UV photoelectron spectroscopy (X.p.e.s or UV p.e.s). Since such photoelectron spectroscopy studies are useful in obtaining the finger print of the materials present in a surface of a material, these methods are known as **electron spectroscopy for chemical analysis (ESCA)**. It is possible to identify the elements present in a given surface using X.p.e.s since each element has characteristic inner shell ionisation energies. The surface study using ESCA is made possible by the fact that the ejected electrons cannot escape except from within a few nanometers from the surface. The nature of chemisorption between a catalyst surface and the reactant molecules could be established by ESCA studies.

SAQ 4

What is the basic principle for ESCA studies of the surfaces?

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21.7 TYPES OF CATALYSTS

We have seen in Unit 18, that the rate of a chemical reaction can be increased by raising the temperature. This increases the fraction of molecules having energies in excess of some threshold energy (nearly equal to activation energy). Another way to increase the rate of chemical reaction is to find an alternate path for the reaction that has a lower activation enery. A catalyst produces this alternate path for a chemical reaction. The sole function of the catalyst is to lower the activation energy of a reaction. Thus a small amount of manganese dioxide increases the rate of decomposition of $KClO_3$; the decomposition of nitrous oxide is accelerated by iodine; in presence of Ni , unsaturated hydrocarbons can be hydrogenated to saturated hydrocarbons. The amount of a catalyst remains unchanged at the end of a reacion and, may be used again and again. **A substance which can influence the rate of a chemical reaction but itself remains unchanged chemically is called a catalyst.**

A catalyst cannot start a chemical reaction that could not take place in its absence. A catalyst does not alter the position of equilibrium; in other words, it cannot change the relative amounts of the reactants and products at the equilibrium. Consequently a catalyst must accelerate equally both the forward and the reverse reactions. A catalyst is highly specific in its action, e.g., MnO_2 can catalyse the decomposition of $KClO_3$ but not that of KNO_3. In certain reactions, one of the products could catalyse the reaction. For instance, in the oxidation of oxalic acid by acidified $KMnO_4$, Mn^{2+} ions formed during the reaction, increase the rate of reaction. This type of phenomenon is called **auto-catalysis**.

Catalysis may be of homogeneous or heterogeneous type. In homogeneous catalysis, the catalyst forms a single phase with the reactants and products, whereas in heterogeneous catalysis, it constitutes a seperate phase.

There is another type of catalysis, known as enzyme catalysis. Enzymes have high relative molecular masses and are protein molecules. The enzymes catalyse a variety of chemical reactions in living organisms. The enzyme reaction medium is colloidal in nature and strictly speaking, enzyme catalysis does not fall under homogeneous or heterogeneous catalysis. The enzymes are specific in catalysing only a particular set of reactions. Enzyme activity depends on pH of the medium.

Examples for all the three types of catalysis are provided in Table 21.2.

Table 21.2 : Three Types of Catalysis

Type		Illustrative reaction	Catalyst
Homogeneous catalysis	1)	$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	NO (*g*)
	2)	$CH_3COOC_2H_5(l) + H_2O(l) \rightarrow CH_3COOH(l) + C_2H_5OH(l)$	$H_3O^+(aq)$
Hetero-geneous catalysis	1)	$HCOOH(g) \rightarrow H_2O(g) + CO(g)$	$Al_2O_3(s)$
	2)	$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	Pt (*s*)
Enzyme* catalysis	1)	$NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2$	Urease
	2)	$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$	Zymase

* Note that in enzyme catalysis, we have not specified the states of the substances.

In the next section, we shall discuss the theories of catalysis.

21.8 MECHANISMS OF CATALYTIC REACTIONS

A mechanism offered to explain the specificity of enzymes suggests that the shapes of the reacting molecule and the enzyme must fit together as lock and key. The reactant and the active site of the enzyme get attached through hydrogen bonding, ionic bonding or metal ion-ligand bonding or a combination of these.

In homogeneous or enzyme catalysis, a reaction intermediate is formed between the reactant and the catalyst or the enzyme. The intermediate compound then decomposes to give the product. The reaction sequence can be represented as follows:

Step (i)Formation of the intermediate compound $S + C \rightleftharpoons SC$

Step (ii) Decomposition of the intermediate compound $SC \longrightarrow P + C$

Where S and P are the reactant and the product and C is the catalyst or the enzyme; SC is the intermediate compound. The role of the catalyst or the enzyme is to lower the activation energies of the forward and reverse reactions. In Fig. 21.3, E_c is the activation energy for the conversion of a reactant to a product in the presence of a catalyst and E_{uc} is the activation energy for the same reaction in the absence of catalyst. You can see that $E_c < E_{uc}$. The same is true of the reverse reaction also.

It is interesting to note that many of the biological reactions are catalysed by enzymes. This is facilitated by the fact that the enzyme catalysed reactions have much lower activation energies than systems containing chemical catalysts. Look at Table 21.3 which indicates the activation energies for the decomposition of hydrogen peroxide under different conditions and make your own judgement!

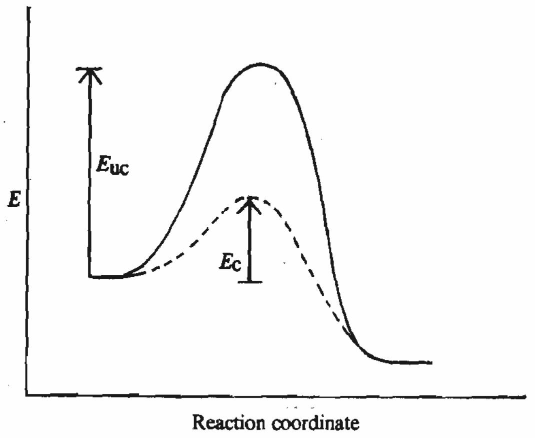

Fig.21.3. Relative activation energies for catalysed and uncatalysed reactions.

Table 21.3 : Activation Energies for the Decomposition of Hydrogen Peroxide Solution

Catalyst	Activation energy/kJ mol^{-1}	Relative rate of reaction
None	75.3	1
I^- (*aq*) (homogeneous)	56.5	2.0×10^3
Pt (*s*) (heterogeneous)	49.0	4.1×10^4
Catalase (enzyme)	8	6.3×10^{11}

In heterogeneous catalysis also, the role of the catalyst surface is to bring down the activation energies of the reactions. This happens due to chemisorption which is similar to intermediate compound formation in homogeneous catalysis. The ability of a surface to have chemisorption of the reactant molecules depends on the chemical nature of surface. ESCA studies (Sec. 21.6) are helpful in deciding the nature of chemisorption between the surface and the reactant molecules. The difference in the nature of chemisorption could lead to different products even from the same reactant. For example, ethyl alcohol is dehydrogenated on Ni, Pd or Pt catalysts to give acetaldehyde.

You can have an idea about the importance of enzyme reactions from the fact that ammonia produced from nitrogen by nitrogenase enzyme is ten times more than that produced by Haber process. Further the enzyme gives good yields of ammonia at room temperature and pressure. Compare this with the experimental conditions needed for Haber process (200-300 atm pressure and 670-870 K temparature).

$$CH_3CH_2OH \xrightarrow{\text{Ni, Pd or Pt}} CH_3CHO + H_2$$

On the other hand, ethyl alcohol undergoes dehydration reaction on alumina.

$$CH_3CH_2OH \xrightarrow{\text{Alumina}} CH_2 = CH_2 + H_2O$$

On Ni, Pd or Pt surfaces, the linkage of ethyl alcohol is through two hydrogen atoms (Fig. 21.4). The strong affinity between Ni and hydrogen accounts for the removal of two hydrogen atoms from ethyl alcohol.

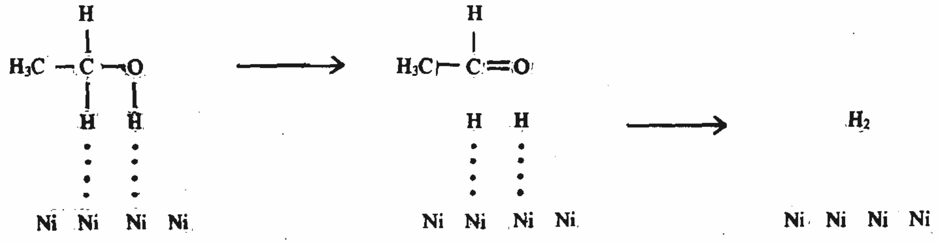

Fig. 21.4 : Dehydrogenation process on Ni

On the other hand, alumina acts differently due to its different structure. Alumina has both oxide groups and hydroxyl groups. The linkage of ethyl alcohol to alumina is through hydrogen and oxygen atoms as shown in Fig. 21.5. The removal of hydrogen and hydroxyl groups from adjacent carbon atoms leads to the dehydration reaction.

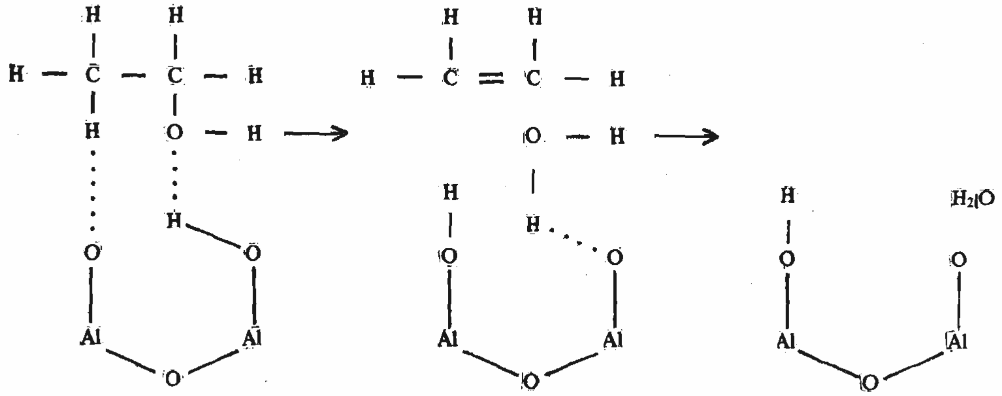

Fig. 21.5: Dehydration process on alumina.

Certain substances improve the activity of a catalyst. Such substances are called **promoters**. These substances may not themselves be effective catalysts. A promoter may increase the number of active sites on a catalyst surface. In the light of this discussion, let us examine the catalysis in Haber process of manufacture of ammonia. A mixture of iron oxide, potassium oxide and aluminium oxide facilitates this reaction. The hydrogen atmosphere reduces iron oxide into porous iron which has large surface area that acts as the catalyst. The mixture of potassium oxide and aluminium oxide acts as promoters.

Let us now see a few applications of catalysts in chemical industries.

- In the preparation of edible fats from vegetable and animal fats, controlled partial hydrogenation with a catalyst such as nickel helps in removing some of the double bonds. In the absence of hydrogenation, these double bonds could be oxidised by air which impart the oil a rancid odour on storage.
- Careful studies of the catalytic surfaces have been helpful in preferential formation of a product starting from a reactant. Thus it is possible to prepare various oxidation products of ethylene such as ethanol, acetaldehyde, vinyl chloride or vinyl acetate by proper choice of catalysts and reaction conditions.
- You may be aware that 'cracking' is the process of producing small organic molecules by the breaking of long-chain hydrocarbon molecules. Usually, silica-alumina catalysts are used for this purpose. Cracking is required to produce branched chain isomeric hydrocarbons which have more fuel efficiency in automobile engines.

SAQ 5

At 310 K (blood temperature), sucrose could be hydrolysed using an enzyme, saccharase or a mineral acid. The reaction rate for one reaction is 10^{12} times higher than the other. Identify the faster reaction.

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SAQ 6

In Unit 18, it has been explained that the rate ~~of a~~ reaction is proportional to $e^{-E/RT}$. The activation energy of the reaction $H_2(g) + I_2(g) \quad 2HI(g)$ is reduced from 184 kJ mol^{-1} to 59 kJ mol^{-1} in the presence of platinum catalyst. By what factor will the reaction rate be increased by platinum at 600 K? Assume that the frequency factor remains unchanged.

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21.9 INHIBITION AND POISONING

We studied that the reactants are to be adsorbed on the surface for the chemical reaction to be influenced by the surface. For the enhancement of the reaction rate, the reactants must be adsorbed more or less to same extent. If one of the reactants is more strongly adsorbed than the other or if a product is adsorbed to a greater extent than the reactants, then the active centres on the catalyst surface would not be available completely for the reaction and the reaction rate decreases. Such a condition is called inhibition of the catalyst. One of the reactants or the products which gets strongly adsorbed and thereby decreases the reaction rate is called the inhibitor. For example, in the decomposition of ammonia on platinum surface, hydrogen (a product) is strongly adsorbed and inhibits the reaction.

It is possible that the reaction could be inhibited by a foreign molecule that does not take part in a reaction. This type of inhibition is called catalytic poisoning. It is observed that even a small amount of the catalytic poison could be effective in stopping a reaction. This phenomenon could be explained by the fact that the active centres constitute only a small fraction of the total surface sites on a catalyst and, the meagre amount of poison could occupy these positions. This prevents the occupation by reactant molecules. For example, in the contact process of sulphuric acid manufacture, even a small amount of arsenic impurity poisons the platinised asbestos catalyst and the reaction almost stops.

SAQ 7

State the conditions under which a catalyst loses its influence over a reaction.

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21.10 SUMMARY

In this unit, we discussed the role of surface in chemical reactions. Here we have

- defined a surface active agent,
- discussed the significance of adsorption isotherms,
- explained physisorption and chemisorption,
- outlined the modern methods of surface studies,
- described the types of catalysts and indicated the mechanisms of their activity, and
- discussed the inhibition and poisoning of catalysts.

21.11 TERMINAL QUESTIONS

1) The activation energies required for the uncatalysed decomposition of ammonia and for its decomposition in presence of tungsten are 350 and 162 kJ mol^{-1} respectively. Explain the reason for this difference in activation energy.

2) The adsorption of a gas follows Langmuir isotherm with $K = 8.50 \times 10^{-4}$ Pa^{-1} at 298 K. Find the pressure at which surface coverage is (a) 15.0% (b) 95%. Comment on your results.

3) The heterogeneous catalyst is often taken in the form of a finely divided powder rather than as a smooth surface. Explain the reason.

4) Based on adsorption studies, justify the temperature choice for Haber process.

5) Copper catalyses the formation of steam from hydrogen and oxygen through the formation of CuO as an intermediate. Suggest a reaction sequence for this condition.

6) Define the terms; (i) adsorption (ii) adsorbate (iii) adsorbent.

7) A particular mass of charcoal adsorbs a larger volume of ammonia than of hydrogen at a given temperature. Explain.

8) Based on energy released during adsorption, how can you distinguish between physisorption and chemisorption?

21.12 ANSWERS

Self-assessment Questions

1) The surface tension of a solution must decrease when a surface active agent is added so that its concentration is more in the surface than in the bulk.

2) According to Eq. 21.6, $\theta = \dfrac{Kp}{1+Kp}$

$$\theta(1+Kp) = Kp$$

$$Kp(\theta-1) = -\theta$$

$$Kp(1-\theta) = \theta$$

Hence, $$p = \frac{\theta}{K(1-\theta)}$$

3) As per Eq. 21.6, at sufficiently high pressure $\theta = 1$. Thus at high pressure, we can expect large coverage of iron surface by nitrogen which could lead to its dissociation and also to its reaction with hydrogen to form ammonia on a large scale.

4) Even though X-rays may penetrate into the bulk sample, the ejected electrons cannot escape except from within a few nanometers from the surface. Hence this technique is mainly limited to the study of surface layers.

5) Enzyme catalysed reaction needs lower activation energy than the mineral acid catalysed reaction. Hence, enzyme catalysed reaction must be faster than the other.

6) Let r_1 and r_2 be the reaction rates in the absence of platinum and in the presence of platinum, respectively. Let E_1 and E_2 be the corresponding activation energies. Assuming frequency factors to be equal,

$$\frac{r_1}{r_2} = e^{-E_1/RT}/e^{-E_2/RT} = e^{(E_2-E_1)/RT}$$

Taking natural logarithms, $\ln \dfrac{r_1}{r_2} = \dfrac{E_2-E_1}{RT}$

or $$\ln \frac{r_2}{r_1} = \frac{E_1-E_2}{RT}$$

$$2.303 \log \frac{r_2}{r_1} = \frac{E_1-E_2}{RT}$$

$$\log \frac{r_2}{r_1} = \frac{E_1-E_2}{2.303\,RT}$$

$$\frac{r_2}{r_1} = \left(\text{Antilog of } \frac{E_1-E_2}{2.303\,RT}\right)$$

$$= \text{Antilog of} \left(\frac{125 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \times 600 \text{ J mol}^{-1}}\right)$$

$$\frac{r_2}{r_1} = 7.6 \times 10^{10}$$

Hence the reaction rate is increased by 7.6×10^{10} times by platinum.

7) When a catalyst surface is strongly adsorbed by reactant or product or foreign gas molecules, the catalyst cannot influence the reaction rate.

Terminal Questions

1) In presence of tungsten catalyst, there is chemisorption of ammonia which is an exothermic process. This helps in bringing down the activation energy of the reaction.

2) a) 208 Pa;

   b) 2.24×10^4 Pa.

   It is seen that if adsorption of a gas follows Langmuir isotherm, then high pressure is required for larger coverage of the surface.

3) For a heterogeneous catalyst to be effective, a large surface area is required. Since a finely divided powder has large surface area, a heterogeneous catalyst is employed in this form.

4) See Sec. 21.5.

5) $$Cu(s) + \frac{1}{2}O_2(g) \rightarrow CuO(s)$$

   $$CuO(s) + H_2(g) \rightarrow H_2O(g) + Cu(s)$$

6) See Sec. 21.3.

7) The interaction between charcoal and gases such as ammonia and hydrogen is of van der Waals type. It is a weak interaction. Ammonia which could be liquefied easily is more readily adsorbed than hydrogen since the forces responsible for physical adsorption and liquefaction of gases are the same.

8) Energy released during chemisorption is much larger than that during physisorption.