Chemical Kinetics and Reaction Dynamics

Santosh K. Upadhyay

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To
My Mother

Preface

Reaction dynamics is the part of chemical kinetics which is concerned with the microscopic-molecular dynamic behavior of reacting systems. Molecular reaction dynamics is coming of age and much more refined state-to-state information is becoming available on the fundamental reactions. The contribution of molecular beam experiments and laser techniques to chemical dynamics has become very useful in the study of isolated molecules and their mutual interactions not only in gas surface systems, but also in solute-solution systems.

This book presents the important facts and theories relating to the rates with which chemical reactions occur and covers main points in a manner so that the reader achieves a sound understanding of the principles of chemical kinetics. A detailed stereochemical discussion of the reaction steps in each mechanism and their relationship with kinetic observations has been considered.

I would like to take the opportunity to thank Professor R.C. Srivastava and Professor N. Sathyamurthy with whom I had the privilege of working and who inspired my interest in the subject and contributed in one way or another to help complete this book. I express my heavy debt of gratitude towards Professor M.C. Agrawal who was gracious enough for sparing time out of his busy schedule to go through the manuscript. His valuable comments and suggestions, of course, enhanced the value and importance of this book. I also express my gratitude to my colleagues, friends and research students, especially Dr. Neelu Kambo who took all the pains in helping me in preparing, typing and checking the manuscript.

Finally, I thank my wife Mrs. Manju Upadhyay, daughter Neha and son Ankur for their continuous inspiration during the preparation of the text.

SANTOSH K. UPADHYAY

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Chemical Kinetics and Reaction Dynamics

1

Elementary

Chemical kinetics deals with the rates of chemical reactions, factors which influence the rates and the explanation of the rates in terms of the reaction mechanisms of chemical processes.

In chemical equilibria, the energy relations between the reactants and the products are governed by thermodynamics without concerning the intermediate states or time. In chemical kinetics, the time variable is introduced and rate of change of concentration of reactants or products with respect to time is followed. The chemical kinetics is thus, concerned with the quantitative determination of rate of chemical reactions and of the factors upon which the rates depend. With the knowledge of effect of various factors, such as concentration, pressure, temperature, medium, effect of catalyst etc., on reaction rate, one can consider an interpretation of the empirical laws in terms of reaction mechanism. Let us first define the terms such as rate, rate constant, order, molecularity etc. before going into detail.

1.1 Rate of Reaction

The rate or velocity of a reaction may be expressed in terms of any one of the reactants or any one of the products of the reaction.

The rate of reaction is defined as change in number of molecules of reactant or product per unit time, i.e.

$$\text{Rate of reaction} = -\frac{dn_{\mathrm{R}}}{dt} = \frac{dn_{\mathrm{p}}}{dt} \tag{1.1}$$

where dn_{R} and dn_{p} are the changes in number of molecules of reactant and product, respectively, for a small time interval dt. The reactant is being consumed, i.e. number of molecules of reactant decreases with time. Hence, minus sign is attached so that rate will be positive numerically. For comparing the rates of various reactions, the volume of reaction system must be specified and rate of reaction is expressed per unit volume. If V_{t} is the volume of reaction mixture, then

$$\text{Rate of reaction} = -\frac{1}{V_{\mathrm{t}}}\frac{dn_{\mathrm{R}}}{dt} = \frac{1}{V_{\mathrm{t}}}\frac{dn_{\mathrm{p}}}{dt} \tag{1.2}$$

At constant V,

$$\text{Rate of reaction} = -\frac{d(n_R/V)}{dt} = \frac{d(n_p/V)}{dt} \tag{1.3}$$

Again n_R/V is the molar concentration of reactant and n_p/V the molar concentration of product. Therefore, in terms of molar concentrations

$$\text{Rate of reaction} = -\frac{d[\text{Reactant}]}{dt} = \frac{d[\text{Product}]}{dt} \tag{1.4}$$

where [Reactant] and [Product] are the molar concentrations of reactant and product, respectively. This conventional way of representing the rate of reaction is valid only at constant volume. However, if there is a change in the volume of the reactants, $-\frac{d(n_R/V_t)}{dt}$ would yield

$$-\frac{d(n_R/V_t)}{dt} = \frac{1}{V_t}\frac{dn_R}{dt} + \left(\frac{(n_R)}{(V_t)}\right)^2\frac{dV_t}{dt} \tag{1.5}$$

and, therefore, $-\frac{d[\text{Reactant}]}{dt}$ will not be equal to $-\frac{1}{V_t}\frac{dn_R}{d_t}$ and corrections need to be applied.

At constant volume, the rate of a general reaction, A + B → C + D in terms of molar concentration of reactant or product may be given as

$$\text{Rate of reaction} = -\frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = \frac{d[\text{C}]}{dt} = \frac{d[\text{D}]}{dt} \tag{1.6}$$

$$\text{Rate of reaction} = \begin{Bmatrix}\text{Decrease in molar}\\ \text{concentration of a}\\ \text{reactant per unit time}\end{Bmatrix} = \begin{Bmatrix}\text{Increase in molar}\\ \text{concentration of a}\\ \text{product per unit time}\end{Bmatrix}$$

However, if reaction is not of a simple stoichiometry but involves different number of moles of reactants or products, the rate should be divided by corresponding stoichiometric coefficient in the balanced chemical equation for normalizing it and making it comparable. For example, for a general reaction aA + bB → cC + dD

$$\text{Rate of reaction} = -\frac{1}{\text{a}}\frac{d[\text{A}]}{dt} = -\frac{1}{\text{b}}\frac{d[\text{B}]}{dt} = \frac{1}{\text{c}}\frac{d[\text{C}]}{dt} = \frac{1}{\text{d}}\frac{d[\text{D}]}{dt} \tag{1.7}$$

1.1.1 Experimental Determination of Rate

For the determination of rate of reaction at constant volume the concentration of a chosen reactant or product is determined at various time intervals. The change in concentration ΔC, for a given time interval $\Delta t(t_2 - t_1)$ is obtained. An average rate of reaction is then obtained by calculating $\Delta C/\Delta t$. The smaller the value of Δt, the closer the value of the rate will be to the real rate at time $(t_1 + t_2)/2$ because

$$\lim_{\Delta t \to 0} \frac{\Delta C}{\Delta t} \to \frac{dC}{dt} \tag{1.8}$$

The rate of reaction can also be obtained by plotting concentration of reactant or product against time and measuring the slope of the curve (*dc*/*dt*) at the required time. The rate of reaction obtained from such method is known as *instantaneous rate*. The concentration of the reactant or product varies exponentially or linearly with time as shown in Fig. 1.1.

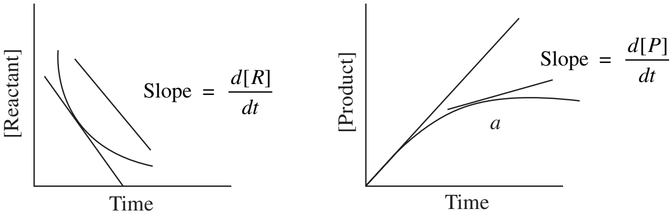


Fig. 1.1 Concentration variation of the reactant/product with time.

For determination of the instantaneous rate at any point *a*, the slope of the curve is determined. It may also be noted from Fig. 1.1 that if the concentration varies linearly with time, the slope of the curve or rate of the reaction will remain same throughout the course of reaction. However, if concentration of the reactant or product varies exponentially with time the slope of the curve or the rate of reaction will be different at different time intervals. Thus, it is not necessary that rate of reaction may always remain same throughout the course of reaction. The reaction may proceed with a different rate in the initial stage and may have different rate in the middle or near the end of the reaction.

In place of concentration of reactant or product any physical property, which is directly related with concentration, such as viscosity, surface tension, refractive index, absorbance etc. can be measured for the determination of the rate of reaction.

1.2 Rate Constant

For a general reaction

$$\mathrm{aA + bB \rightarrow cC + dD}$$

the rate is proportional to $[\mathrm{A}]^{\mathrm{a}} \times [\mathrm{B}]^{\mathrm{b}}$, i.e.

$$\text{Rate} = k\,[\mathrm{A}]^{\mathrm{a}}\,[\mathrm{B}]^{\mathrm{b}} \tag{1.9}$$

where proportionality constant *k*, relating rate with concentration terms, is known as *rate constant* or *velocity constant* at a given temperature.

When the reactants are present at their unit concentrations,

$$\text{Rate} = k$$

Thus, the rate constant is the rate of reaction when concentrations of the reactants are unity. The rate constant under these conditions is also known as the *specific rate* or the *rate coefficient*. The rate constant for any reaction can be determined

(i) either by measuring the rate of the reaction at unit concentrations of the reactants.
(ii) or by knowing the rate at any concentration of reactant using the relation

$$\text{Rate constant} = \text{Rate}/[\text{A}]^{a}\,[\text{B}]^{b} \tag{1.10}$$

The rate constant is measured in units of moles dm^{-3} sec^{-1}/(moles $dm^{-3})^n$, where $n = a + b$. Time may also be in minutes or hours. It should be noted that in case where the reaction is slow enough, the thermal equilibrium will be maintained due to constant collisions between the molecules and k remains constant at a given temperature. However, if the reaction is very fast the tail part of the Maxwell-Boltzmann distribution will be depleted so rapidly that thermal equilibrium will not be re-established. In such cases rate constant will not truly be constant and it should be called a rate coefficient.

1.3 Order and Molecularity

For reaction

$$\alpha\text{A} + \beta\text{B} + \ldots \rightarrow \text{Product}$$

rate of reaction is proportional to α^{th} power of concentration of A, to the β^{th} power of concentration of B etc., i.e.

$$\text{Rate} = k\,[\text{A}]^{\alpha}\,[\text{B}]^{\beta}\ldots \tag{1.11}$$

Then the reaction would be said to be α^{th} order with respect to A, β^{th} order with respect to B, . . . and the overall order of reaction would be $\alpha + \beta +$ . . . . Thus, order of reaction with respect to a reactant is the power to which the concentration of the reactant is raised into the rate law, and the overall order of reaction is the sum of the powers of the concentrations involved in the rate law.

The term '*molecularity*' is the sum of stoichiometric coefficients of reactants involved in the stoichiometric equation of the reaction. For example, a reaction whose stoichiometric equation is

$$2\text{A} + 3\text{B} = 3\text{C} + 2\text{D}$$

the stoichiometric coefficient of A and B are 2 and 3, respectively, and, therefore, the molecularity would be $2 + 3 = 5$.

There is not necessarily a simple relationship between molecularity and order of reaction. For differentiating between molecularity and order of a reaction, let us consider some examples.

For the reaction, $\text{A} + 2\text{B} \rightarrow \text{P}$, the molecularity is $1 + 2 = 3$. If the reaction occurs in a single step the order of reaction with respect to A would be one and order with respect to B would be two, giving overall order of reaction 3. Thus the molecularity and order would be same. However, if the reaction occurs in two different steps giving overall same reaction, e.g.

$$\begin{array}{ll} \text{(a)} & A + B = I \rightarrow \text{Slow} \\ \text{(b)} & \underline{I + B = P \rightarrow \text{fast}} \\ & \quad A + 2B \rightarrow P \end{array}$$

Now the rate of reaction will be governed by only slow step (a) and order of reaction would be one with respect to each reactant, A and B, giving overall order two. And, therefore, the order and molecularity will be different.

The inversion of cane sugar is

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

and the rate of inversion is given by

$$\text{Rate} = k\,[\text{Sucrose}]\,[H_2O] \tag{1.12}$$

This reaction seems to be second order, i.e. first order with respect to each sucrose and H_2O. The $[H_2O]$ is also constant as it is used as solvent and present in large amount. Therefore, the reaction is only first order with respect to sucrose.

The hydrolysis of ester in presence of acid is first order reaction (keeping catalyst constant)

$$CH_3COOC_2H_5 + H_2O \xrightarrow{[H^+]} CH_3COOH + C_2H_5OH$$

Since $[H_2O]$ remain constant as in case of inversion of cane sugar, it does not effect the rate of reaction and reaction is simply first order with respect to ester. However, the hydrolysis of ester in presence of alkali

$$CH_2COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

is second order being first order with respect to both ester and NaOH. While the molecularity of the reaction in each case, i.e. in hydrolysis of ester in presence of acid as well as in presence of alkali, is two.

The reactions, in which molecularity and order are different due to the presence of one of the reactant in excess, are known as *pseudo-order reactions*. The word (pseudo) is always followed by order. For example, inversion of cane sugar is pseudo-first order reaction.

The molecularity will always be a whole integer while order may be an integer, fraction or even a negative number. Molecularity is a theoretical concept, whereas order is empirical. Molecularity is, therefore, less significant as far as kinetic studies are concerned.

The order of reaction provides the basis for classifying reactions. Generally, the order of reaction can be anywhere between zero and three. Reactions having order three and above are very rare and can be easily counted.

The rate of a chemical reaction is proportional to the number of collisions taking place between the reacting molecules and the chances of simultaneous collision of reacting molecules will go on decreasing with an increase in number of molecules. The possibility of four or more molecules coming closer and colliding with one another at the same time is much less than in case of tri- or bi molecular reactions. Therefore, the reactions having order four or more are practically impossible. Further, many reactions which appear to be quite complex proceed in stepwise changes involving maximum two or three species. The stoichiometric representation has no relation either with the mechanism of reaction or with the observed order of reaction.

In older literature the terms unimolecular, bimolecular and termolecular have been used to indicate the number of molecules involved in a simple collision process and should not be confused with first, second and third order reactions.

1.4 Rate Equations

For a reaction

$$n\text{A} \xrightarrow{k} \text{Product}$$

The rate is related with concentration of A with the following differential form of equation

$$\text{Rate} = -\frac{d[\text{A}]}{dt} = k[\text{A}]^n \tag{1.13}$$

or

$$\log\left(-\frac{d[\text{A}]}{dt}\right) = \log k + n \log[\text{A}] \tag{1.14}$$

where k is the rate constant.

As discussed previously the rate is determined by drawing a graph between concentration and time and taking the slope corresponding to a concentration. If we have the values of the rates for various concentrations, we can find the order of reaction by plotting log (rate) against log [concentration]. The slope of the straight line obtained from the plot gives the order of reaction n while the intercept gives log k. Thus, order and rate constant can be determined.

However, the average rates calculated by concentration versus time plots are not accurate. Even the values obtained as instantaneous rates by drawing tangents are subject to much error. Therefore, this method is not suitable for the determination of order of a reaction as well as the value of the rate constant. It is best to find a method where concentration and time can be substituted directly to determine the reaction orders. This could be achieved by integrating the differential rate equation.

1.4.1 Integral Equations for n^{th} Order Reaction of a Single Reactant

Let us consider the following general reaction:

$$nA \xrightarrow{k} \text{Product}$$

If c_0 is the initial concentration of the reactant and c the concentration of reactant at any time t, the differential rate expression may be given as

$$-dc/dt = kc^n \tag{1.15}$$

Multiplying by dt and then dividing by c^n, we get

$$-dc/c^n = kdt \tag{1.16}$$

which may be integrated. The limits of integration are taken as $c = c_0$ and c at $t = 0$ and $t = t$, respectively, as

$$\int \frac{dc}{c^n} = k \int dt \tag{1.17}$$

For various values of n, the results may be obtained as follows:

$$n = 0; \quad k = \frac{C_0 - c}{t}$$

$$n = 1; \ln c = \ln (c_0) - kt \text{ or } c = c_0\, e^{-kt}$$

$$n = 2; k = 1/t\, [1/c - 1/c_0]$$

$$n = 3; k = 1/2t\, [1/c^2 - 1/c_0^2]$$

$$n = n; k = 1/(n-1)t\, [1/(c^{n-1}) - 1/(c_0^{n-1})]$$

1.4.2 Integral Equations for Reactions Involving More than One Reactants

When the concentrations of several reactants, and perhaps also products, appear in the rate expressions, it is more convenient to use as the dependent variable x, i.e. the decrease in concentration of reactant in time t. Then $c = a - x$, where a is commonly used to indicate the initial concentration in place of c_0 and rate equation (1.15) becomes

$$dx/dt = k\,(a - x)^n \tag{1.18}$$

or

$$\int dx/(a - x)^n = \int kdt$$

which can be integrated taking the conditions: at $t = 0$, x will also be zero, the value of rate constant can be obtained.

For various values of n the results obtained are as follows:

$n = 0 \quad dx/dt = k;\ k = x/t$

$n = 1 \quad dx/dt = k(a - x);\ k = 2.303/t \log a/a - x$

$n = 2 \quad dx/dt = k(a - x)^2;\ k = 1/t\, [1/a - x - 1/a]$

$n = 3 \quad dx/dt = k(a - x)^3;\ k = 1/2t\ [1/(a - x)^2 - 1/a^2]$

$n = n \quad dx/dt = k(a - x)^3;\ k = 1/(n - 1)t\ [1/(a - x)^{n-1} - 1/a^{n-1}];\ n \geq 2$

1.5 Half-life of a Reaction

The reaction rates can also be expressed in terms of half-life or half-life period. The half-life period is defined as the time required for the concentration of a reactant to decrease to half of its initial value.

Hence, half-life is the time required for one-half of the reaction to be completed. It is represented by $t_{1/2}$ and can be calculated by taking $t = t_{1/2}$ when $x = a/2$ in the integrated rate equation of its order.

Problem 1.1 Write the differential rate equations of the following reactions:

(a) $A + 2B \xrightarrow{k} P$
(b) $3A + 2B \xrightarrow{k'} 3C + D + 2E$

Solution The differential rates of above reactions can be written assuming them to be elementary steps

(a) $$-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{d[P]}{dt} = k[A]^2[B]$$

(b) $$-\frac{1}{3}\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = \frac{d[D]}{dt} = \frac{1}{2}\frac{d[E]}{dt} = k'[A]^3[B]^2$$

Problem 1.2 Write the differential rate equations of the following reactions:

(a) $A + 3B \rightarrow 4C$
(b) $A + 2B \rightarrow C + 3D$
(c) $3A + B + 2C \rightarrow D + 3E$

Solution Assuming these reactions as elementary steps, the differential rate can be written as:

(a) $$-\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{4}\frac{d[C]}{dt} = k[A][B]^3$$

(b) $$-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{1}{3}\frac{d[D]}{dt} = k[A][B]^2$$

(c) $$-\frac{1}{3}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = -\frac{1}{2}\frac{d[C]}{dt} = \frac{d[D]}{dt} = \frac{1}{3}\frac{d[E]}{dt} = k[A]^3[B][C]^2$$

Problem 1.3 Express the rate constant k in unit of $dm^3\ mol^{-1}s^{-1}$, if

(i) $k = 2.50 \times 10^{-9}\ cm^3 molecule^{-1} s^{-1}$
(ii) $k = 2 \times 10^{-6}\ s^{-1}\ atm^{-1}$

Solution

(i) $$1\ \text{dm}^3 = 1000\ \text{cm}^3\text{, i.e. } 1\ \text{cm}^3 = 10^{-3}\ \text{dm}^3$$

$$1\ \text{mol} = 6.02 \times 10^{23}\ \text{molecule}$$

$$\text{molecule}^{-1} = 6.02 \times 10^{23}\ \text{mol}^{-1}$$

$$k = 2.50 \times 10^{-9}\ \text{cm}^3\ \text{molecule}^{-1}\text{s}^{-1}$$

$$= 2.50 \times 10^{-9}\ (10^{-3}\ \text{dm}^3)(6.02 \times 10^{23}\ \text{mol}^{-1})\text{s}^{-1}$$

$$= 2.50 \times 6.02 \times 10^{-9-3+23}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

$$= 15.05 \times 10^{11}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

(ii) We know $$\underset{(1\ \text{atm})}{P} = \frac{n}{v}RT = CRT$$

or $$C = \frac{P}{RT} = \frac{1\ \text{atm}}{0.0821\ \text{atm dm}^3\ \text{mol}^{-1}\text{K}^{-1} \times 273\ \text{K}}$$

$$= 0.0446\ \text{mol dm}^{-3}$$

Therefore, $$1\ \text{atm} = 0.0446\ \text{mol dm}^{-3}$$

or $$1\ \text{atm}^{-1} = \frac{1}{0.0446}\ \text{mol}^{-1}\ \text{dm}^3$$

$$k = 2.0 \times 10^{-6}\ \text{s}^{-1}\ \text{atm}^{-1}$$

$$= 2.0 \times 10^{-6}\ \text{s}^{-1}.\left(\frac{1}{0.0446}\right)\text{mol}^{-1}\text{dm}^3$$

$$= 44.8 \times 10^{-6}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

Problem 1.4 For a certain reaction, the value of rate constant is 5.0×10^{-3} $\text{dm}^3\ \text{mol}^{-1}\text{sec}^{-1}$. Find the value of rate constant in (i) $\text{dm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1}$ (ii) $\text{cm}^3\ \text{mol}^{-1}\ \text{sec}^{-1}$ and (iii) $\text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1}$.

Solution

(i) in $\text{dm}^3\ \text{mol}^{-1}\text{sec}^{-1}$

$$\text{Rate constant} = 5.0 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}\text{sec}^{-1}$$

$$1\ \text{mol} = 6.02 \times 10^{23}\ \text{molecules}$$

$$\text{Rate constant} = 5.0 \times 10^{-3}\ \text{dm}^3\ (6.02 \times 10^{23}\ \text{mol})^{-1}\ \text{sec}^{-1}$$

$$= 0.83 \times 10^{-26}\ \text{dm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1}$$

(ii) in $\text{cm}^3\ \text{mol}^{-1}\text{sec}^{-1}$

$$1\ \text{dm}^3 = 1000\ \text{cm}^3$$

$$\text{Rate constant} = 5.0 \times 10^{-1}\ \text{dm}^3\ \text{mol}^{-1}\text{sec}^{-1}$$

$$= 5.0 \times 10^{-3}(1000)\ \text{cm}^3\ \text{mol}^{-1}\text{sec}^{-1}$$

$$= 5.0\ \text{cm}^3\ \text{mol}^{-1}\ \text{sec}^{-1}$$

(iii) in cm^3 $\text{molecules}^{-1}\text{sec}^{-1}$

$$\text{Rate constant} = 5.0\ \text{cm}^3\ (6.02 \times 10^{23})^{-1}\ \text{molecules}^{-1}\text{sec}^{-1}$$

$$= 0.83 \times 10^{-23}\ \text{cm}^3\ \text{molecules}^{-1}\text{sec}^{-1}$$

1.6 Zero Order Reactions

When no concentration term affects the rate of reaction, or the rate of reaction remains same throughout the reaction, the reaction is known as zero-order reaction.

Let us consider a reaction

$$\text{A} \rightarrow \text{Product}$$

Since the rate of reaction remains same

$$\frac{dx}{dt} = k$$

On integrating the expression as

$$\int dx = k \int dt$$

we get

$$x = kt + z$$

The value of integration constant z may be obtained by taking the conditions $x = 0$, when $t = 0$, the value of z is zero and, therefore, rate equation becomes

$$x = kt \quad \text{or} \quad k = \frac{x}{t} \tag{1.19}$$

which gives the unit of rate constant as mol dm^{-3} sec^{-1} or conc. $(\text{time})^{-1}$ in general.

- The half-life period $t_{1/2}$ of a zero order reaction can be calculated with the help of equation (1.19), taking $t = t_{1/2}$ and $x = a/2$ as

$$t_{1/2} = \frac{a}{2k} \tag{1.20}$$

Thus, the half-life period of zero order reaction is directly proportional to the initial concentration of the reactant. For example, on increasing the initial concentration by two fold, the half-life period of the reaction would also be double.

- According to equation (1.19) the slope of a plot of x or $(a - x)$ (i.e. the concentration of product or concentration of reactant) versus time will give the value of rate constant k (Fig. 1.2).

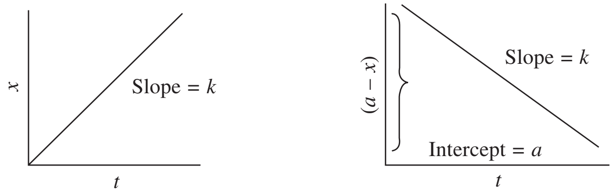


Fig. 1.2 Concentration versus time plot for zero order reaction.

The combination of H_2 and Cl_2 to form HCl in presence of sunlight is a zero order reaction

$$H_2 + Cl_2 \rightarrow 2HCl$$

The rate of formation of HCl is not affected by a change in concentration of either the reactant or product. However, it is influenced by the intensity of sun light.

Problem 1.5 A zero order reaction is 50% complete in 20 min. How much time will it take to complete 90%?

Solution Let $a = 100$ mol dm^{-3}. For a zero-order reaction

$$k = \frac{x}{t} = \frac{50\ (\text{mol dm}^{-3})}{20 \times 60\ (\text{sec})}$$

When reaction is 90% completed, $x = 90$. Therefore,

Thus, $$\frac{50}{1200} = \frac{90}{t}$$

or $$t = \frac{90 \times 1200}{50} = 2160 \text{ sec} = 36 \text{ min}$$

Problem 1.6 A reaction is 50% complete in 20 min. How much time will be taken to complete 75% reaction?

Solution For a zero order reaction

$$k = x/t$$

$$x = a/2 \text{ for } 50\%$$

$$k = \frac{a}{2t} = \frac{a}{2 \times 20}$$

$$x = \frac{3a}{4} \text{ for } 75\% \text{ reaction}$$

Therefore,
$$k = \frac{3a}{4t}$$

or
$$\frac{a}{2 \times 20} = \frac{3a}{4t}$$

$$t = \frac{40 \times 3}{4} = 30 \text{ min}$$

75% reaction will complete in 30 min.

1.7 First Order Reactions

Let us consider a first-order reaction

$$\begin{array}{lll} & \text{A} \longrightarrow & \text{Products} \\ \text{Initially,} & a & 0 \\ \text{At time } t, & a - x & x \end{array}$$

We know that in case of a first-order reaction, the rate of reaction, dx/dt is directly proportional to the concentration of the reactant. Therefore,

$$\frac{dx}{dt} = k(a - x) \quad \text{or} \quad \frac{dx}{(a-x)} = k\,dt$$

Integrating, we get ln $(a - x) = kt + z$.

The integration constant z is determined by putting $t = 0$ and $x = 0$. Thus

$$z = \ln a$$

and, therefore, the rate constant for a first order reaction is obtained as

$$k = \frac{1}{t} \ln \frac{a}{a - x}$$

or
$$k = \frac{2.303}{t} \log \frac{a}{a - x} \tag{1.21}$$

- The units of rate constant for a first order reaction from equation (1.21) is measured as $(\text{time})^{-1}$ and can be represented as $\sec^{-1}$, $\min^{-1}$ or hour^{-1}.
- The half-life period for a first-order reaction may be obtained from equation (b) by substituting $t = t_{1/2}$ when $x = a/2$, i.e.

$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - a/2}$$

or
$$t_{1/2} = \frac{2.303 \log 2}{k} \tag{1.22}$$

Thus, the half-life period of a first-order reaction is independent of initial concentration of reactant. Irrespective of how many times the initial concentration of reactant changes, the half-life period will remain same.

- Further, equation (1.21) can be rearranged as

$$\log (a - x) = -\frac{k}{2.303} t + \log a \tag{1.23}$$

which suggests that a plot of log $(a - x)$ versus time will give a straight line with a negative slope (k/2.303) and an intercept log a (Fig. 1.3).

Thus, in case of a first-order reaction a plot between log [conc.] and time will always be linear and with the help of slope, the value of rate constant can be obtained.

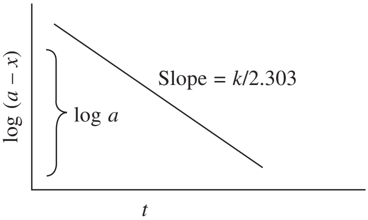


Fig. 1.3 The log [conc.] versus time plot for first-order reaction.

Examples

1. Inversion of cane sugar (sucrose)

$$C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\text{D-glucose}}{C_6H_{12}O_6} + \underset{\text{D-fructose}}{C_6H_{12}O_6}$$

The reaction is pseudo-first order and rate is proportional to [Sucrose]. The progress of the reaction can be studied by measuring the change in specific rotation of a plane of polarised light by sucrose. Let r_0, r_t and r_∞ are the rotation at initially (when $t = 0$), at any time t and final rotation, respectively. The initial concentration a is proportional to $(r_0 - r_\infty)$ and concentration at any time t, $(a - x)$ is proportional to $(r_0 - r_t)$. Thus, the rate constant may be obtained as

$$k = \frac{2.303}{t} \log \frac{(r_0 - r_\infty)}{(r_t - r_\infty)} \tag{1.24}$$

2. The hydrolysis of ester in presence of acid

$$\underset{(a-x)}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} \underset{(x)}{CH_3COOH} + C_2H_5OH$$

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

Since one of the product is acetic acid, the progress of reaction may be studied by titrating a known volume of reaction mixture against a standard alkali solution using phenolphthalein as indicator. Let V_0, V_t and V_∞ be the volumes of alkali required for titrating 10 ml of reaction mixture at zero time, at any time t and at the completion of the reaction, respectively.

V_0 = Amount of H^+ (catalyst) present in 10 ml of reaction mix.

V_t = Amount of H^+ (catalyst) in 10 ml of reactions mix + Amount of CH_3COOH formed at any time t.

V_∞ = Amount of H^+ (catalyst) present in 10 ml of reaction mix + Amount of CH_3COOH formed at the end of reaction (or amount of ester present initially because 1 mol of ester gives 1 mol of CH_3COOOH).

Thus, we can take $V_\infty - V_0 = a$

$$V_t - V_0 = x$$

or $(V_\infty - V_0) - (V_t - V_0) = V_\infty - V_t = a - x$

Therefore, the rate constant for the reaction may be obtained as

$$k = \frac{2.303}{t} \log \frac{(V_\infty - V_0)}{(V_\infty - V_t)} \tag{1.25}$$

3. Decomposition of N_2O_5

$$N_2O_5 \rightarrow 2\ NO_2 + {}^1\!/_2\ O_2$$

Nitrogen pentaoxide in carbon tetrachloride solution decomposes to give O_2.

The progress of reaction is monitored by measuring the volume of O_2 at different time intervals and using the relation

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t} \tag{1.26}$$

where V_∞ is the final value of O_2 when reaction is complete and corresponds to initial concentration of N_2O_5, V_t is the value of O_2 at any time t and $(V_\infty - V_t)$ corresponds to $(a - x)$.

4. Decomposition of H_2O_2 in aqueous solution

$$H_2O_2 \xrightarrow{Pt} H_2O + O$$

The concentration of H_2O_2 at different time intervals is determined by titrating the equal volume of reaction mixture against standard $KMnO_4$.

Problem 1.7 The specific rotation of sucrose in presence of hydrochloric acid at 35°C was measured and is given as follows:

Time (min)	0	20	40	80	180	500	∞
Rotation (°C)	32.4	28.8	25.5	19.6	10.3	6.1	–14.1

Calculate the rate constant at various time intervals and show that the reaction is first order.

Solution

$$k = \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

$$k_{20} = \frac{2.303}{20} \log \frac{32.4 - (-14.1)}{28.8 - (-14.1)} = -\ .00403\ \text{min}^{-1}$$

$$k_{40} = \frac{2.303}{40} \log \frac{32.4 - (-14.1)}{25.5 - (-14.1)} = -\ .00406\ \text{min}^{-1}$$

$$k_{80} = \frac{2.303}{80} \log \frac{32.4 - (-14.1)}{19.6 - (-14.1)} = -.004025 \text{ min}^{-1}$$

$$k_{200} = \frac{2.303}{200} \log \frac{32.4 - (-14.1)}{6.1 - (-14.1)} = -.004002 \text{ min}^{-1}$$

Average = 0.0040295 min^{-1}

Since the first order rate constant remains same, the reaction is of first order.

Problem 1.8 A first order reaction is 25% complete in 50 min. What would be concentration at the end of another 50 min if the initial concentration of the reactant is 5.0×10^3 mol dm^{-3}?

Solution Reaction is 25% consumed in 50 min. After 50 min the concentration c will be

$$a - x = 5.0 \times 10^3 - \frac{5.0 \times 10^3 \times 25}{100} = 3.75 \times 10^3$$

Now $$k = \frac{2.303}{t} \log \frac{C_0}{C} = \frac{2.303}{50} \log \frac{(5.0 \times 10^3)}{3.75 \times 10^3} = 5.375 \times 10^3 \text{ min}^{-1}$$

Again, concentration after another 50 min, i.e. (50 + 50 = 100 min)

$$c = c_0\, e^{-kt} = 5.0 \times 10^3\, e^{-(5.35 \times 10^{-3}/100)} = 2.81 \times 10^3 \text{ mol dm}^{-3}$$

Problem 1.9 Following observations were made for decomposition of a reactant at 35°C:

[A] mol dm^{-3}	Rate of decomposition $[-d[\text{A}]/dt]$ (mol dm^{-3} sec^{-1})
0.15	0.05
0.30	0.10
0.60	0.20

Find the order of reaction. Calculate rate constant and the rate of decomposition of A, when [A] = 0.45 mol dm^{-3}.

Solution It can be observed from the data that the rate of decomposition in directly proportional to [A], i.e.

$$-\frac{d[\text{A}]}{dt} \propto [\text{A}]$$

or $$-\frac{d[\text{A}]}{dt}\, k\, [\text{A}]$$

where k is the rate constant. Hence, the reaction is first order.

$$k = \frac{-d[\mathrm{A}]/dt}{[\mathrm{A}]} = \frac{0.05}{0.15} = 0.33; \quad \frac{0.10}{0.30} = 0.33 \quad \text{and} \quad \frac{0.20}{0.60} = 0.33 \text{ sec}^{-1}$$

k (average) = 0.33 sec^{-1}

Again, rate of decomposition when [A] = 0.45 mol dm^{-3} is

$$-\frac{d[\mathrm{A}]}{dt} = k\,[\mathrm{A}] = 0.33\ (\text{sec}^{-1}) \times 0.45 \text{ mol dm}^{-3}$$

$$= 0.1485 \text{ mol dm}^{-3}\text{ sec}^{-1} = 0.15 \text{ mol dm}^{-3}\text{ sec}^{-1}$$

Problem 1.10 The kinetics of a reaction was followed by measuring the absorbance due to a reactant at its $\lambda_{\max}$ at 25°C. The log (absorbance) versus time (min) plot was a straight line with a negative slope (0.30×10^{-2}) and a positive intercept. Find the half-life period of reaction.

Solution When log $(a - x)$ versus time plot is straight line, the reaction is first order and slope gives the value of $k/2.303$ while intercept gives the value of log a.

$$\frac{\text{Rate constant } k}{2.303} = \text{Slope} = 0.30 \times 10^{-2}$$

Therefore, $k = 0.6909 \times 10^{-2} \text{ min}^{-1}$

$$\text{Half-life period } t_{1/2} = \frac{2.303 \log 2}{k(\text{min}^{-1})} = \frac{0.6939}{0.6939 \times 10^{-2}} = 100 \text{ min}$$

Problem 1.11 In a first order reaction the log (concentration of reactant) versus time plot was a straight line with a negative slope $\approx 0.50 \times 10^{4}$ sec^{-1}. Find the rate constant and half-life period of reaction.

Solution The equation of first order rate constant may be written as

$$\log(a - x) = -\frac{k}{2.303}\,t + \log a$$

Thus, plot of log $(a - x)$ versus time will be a straight line with a negative slope equal to $\frac{k}{2.303}$.

Therefore, $$\frac{k}{2.303} = \text{Slope} = 0.50 \times 10^{4} \text{ sec}^{-1}$$

or $$k = 2.303 \times 0.5 \times 10^{4} = 1.1515 \times 10^{4} \text{ sec}^{-1}$$

Again half-life period $t_{1/2} = \dfrac{2.303 \log 2}{k} = \dfrac{0.693}{1.1515 \times 10^4}$

$$= 0.60 \times 10^{-4} \text{ sec}^{-1} = 60 \ \mu\text{sec}$$

1.8 Radioactive Decay as a First Order Phenomenon

When a radioactive substance is separated from its parent and its activity is measured from time to time, the rate of decay follows the law as

$$-\frac{dI}{dt} = \lambda I \tag{1.27}$$

where I is activity at any time t and λ a constant called the *radioactive disintegration constant* which is characteristic of the radioactive element irrespective of its physical condition or state of chemical combination. This equation, on integration, gives

$$I = I_0 \, e^{-\lambda t} \tag{1.28}$$

where I_0 in the initial activity, i.e. when $t = 0$.

Since the activity I is proportional to number of atoms that have not yet disintegrated, we can use relation

$$n = n_0 \, e^{-\lambda t} \tag{1.29}$$

or
$$\lambda = \frac{2.303}{t} \log \left(\frac{n_0}{n} \right)$$

where n_0 and n are the number of atoms of radioactive substance at time $t = 0$ and at any time t, respectively.

Equation (1.29) suggests that there is a definite probability of any particular atom disintegrating at a given moment and this is proportional to the number of atoms present at that moment.

Half-life period gives the time T which must elapse for the radioactivity to decay to half its value at any instant and may be obtained by pulling $n = \frac{1}{2} n_0$ in equation (1.29).

Thus

$$\frac{1}{2} n_0 = n_0 \, e^{-\lambda T}$$

or
$$T = \frac{\log 2}{\lambda} = \frac{0.693}{\lambda} \tag{1.30}$$

In time T the activity is reduced to one-half of its initial value and, therefore, in nT time, the activity is decreased to $\left(1 - \frac{1}{2}\right)^n$. Theoretically, therefore the activity never falls to zero.

Average-life period ι of any radioactive atom is the length of time, which can exist before the atom disintegrates and can be calculated as follows.

Since the activity is proportional to number of atoms, which have not disintegrated, equation (1.27) may be written as

$$-dn/dt = \lambda n$$

or $$-dn = \lambda n_0 \, e^{-\lambda t} dt; \; n = n_0 \, e^{-\lambda t} \text{ (from eq. (1.29)} \tag{1.31}$$

The number of atoms disintegrating in the interval between t and $t + dt$ is equal to dn. Since dt is very small, dn may be taken as number of atom disintegrating at time t. The period of average life ι is obtained by multiplying every possible life period t from zero to infinity, by the number of atoms dn and then dividing the product by the total number of atoms n_0 present at the beginning of the time. Thus,

$$\iota = \int_0^\infty \frac{t\,dn}{n_0} \tag{1.32}$$

Substituting the value of dn from equation (1.31) and ignoring the sign of dn, we have

$$\iota = \int_0^\infty t\,\lambda\, e^{-\lambda t} dt \tag{1.33}$$

or $$\iota = 1/\lambda \tag{1.34}$$

The average-life ι of a radioactive atom is thus equal to the reciprocal of its radioactive constant λ and is a measure of mean expectation of future life of the atoms present at any instant.

Radioactive Equilibrium

The rate of decay of a given radioactive substance must also represent the rate at which its disintegration product is being formed. The product will also disintegrate at a rate depending on its amount present. This will be small initially, but will increase with time. Thus, in any given series a state of equilibrium will eventually be reached, when the rate of formation of any element from its parent is equal to the rate at which it itself disintegrated. Mathematically, it can be represented as

$$\frac{dn_1}{dt} = \frac{dn_2}{dt} = \frac{dn_3}{dt} \ldots \tag{1.35}$$

where n_1, n_2, n_3 . . . represent the number of atoms of different radioactive elements in the series present at equilibrium.

Again, since $-dn/dt = \lambda n$, we may have

$$\lambda_1 n_1 = \lambda_2 n_2 = \lambda_3 n_3 \ldots$$

or
$$\frac{\lambda_1}{\lambda_2} = \frac{n_2}{n_1} \ldots \tag{1.36}$$

Therefore, at radioactive equilibrium, the amount of different radio elements present will be inversely proportional to their decay constant, or directly proportional to their half- or average-life periods.

The time taken for the complete equilibrium to be established depends on the life periods of elements involved. The longer the average life of any element, more slowly an equilibrium with its product is reached.

Problem 1.12 The half-life of a radioactive substance ^{91}X is 20 years. Calculate the decay constant. In how many years three quarters of the given amount of substance will disappear?

Solution

$$1 \text{ year} = 365 \times 24 \times 60 \times 60 = 3.15 \times 10^7 \text{ sec}$$

$$t_{1/2} = \frac{0.693}{\lambda\,(\text{decay constant})}$$

$$\lambda = \frac{0.693}{20 \times 3.15 \times 10^7}$$

Since decay follows first-order kinetics, $t_{1/2}$ is independent of a i.e. initial concentrations. 50% of substance decays in 20 years, next 50% of remaining, i.e. 25% will decay in 20 years. Therefore, 75% will decay in 40 years.

Problem 1.13 A radioactive element gives 2000 counts per min at a given time. After one hour, counts were found to be 750 per min. What is half-life of the element?

Solution The decay constant

$$\lambda = \frac{0.303}{t} \log\left(\frac{N_0}{N}\right) = \frac{0.693}{t_{1/2}}$$

$$N_0 \propto 2000 \quad \text{and} \quad N \propto 750$$

$$t = 1 \text{ hour} = 60 \text{ min}$$

$$\frac{0.303}{60} \log \frac{2000}{750} = \frac{0.693}{t_{1/2}}$$

or
$$t_{1/2} = 42.5 \text{ min}$$

Problem 1.14 Half-life of radioactive element is 2800 years. How many atoms of the element are required to produce an average of 10 beta emissions per hour?

Solution

$$t_{1/2} = 2800 \times 365 \times 24 = 2.45 \times 10^7 \text{ hours}$$

$$\lambda = \frac{0.693}{2.45 \times 10^7} = 0.28 \times 10^{-7} \text{ hour}^{-1}$$

$$-\frac{dN}{dt} = \lambda n$$

or $$n = \frac{-dN/dt}{\lambda} \quad \text{and} \quad -dN/dt = 10 \text{ (given)}$$

$$n = \frac{10 \text{ (atoms/hour)}}{0.28 \times 10^{-7} \text{ hours}^{-1}} = 35.7 \times 10^7 = 3.57 \times 10^8 \text{ atoms}$$

1.9 Second Order Reactions

Let us take a second order reaction

$$\text{A} + \text{B} \xrightarrow{k} \text{Products}$$

in which initial concentration of each reactant A and B is same, say, a mol dm^{-3}. If after time t, x moles of each reactant is reacted, the concentration of each will be $(a - x)$ and rate of reaction would be

$$\frac{dx}{dt} = k\,(a - x)(a - x) = k\,(a - x)^2$$

Rearranging the equations, we have

$$\frac{dx}{(a - x)^2} = kdt$$

On integrating, it gives

$$\frac{1}{(a - x)} = kt + Z$$

The integration constant Z can be obtained by putting $x = 0$ when $t = 0$

$$Z = \frac{1}{a}$$

On substituting the value of Z, the rate equation becomes

$$\frac{1}{(a - x)} = kt + \frac{1}{a} \tag{1.37}$$

or $$k = \frac{1}{t} = \frac{x}{a(a - x)} \tag{1.38}$$

- The unit of rate constant is (conc.)$^{-1}$ (time)$^{-1}$ or mol^{-1} dm^3 sec^{-1}
- The half-life period $t_{1/2}$ is obtained by putting $t = t_{1/2}$ and $x = a/2$ in equation (1.38) as

$$k = \frac{1}{t_{1/2}} \cdot \frac{a/2}{a(a - a/2)}$$

or
$$t_{1/2} = \frac{1}{ka} \tag{1.39}$$

Thus the half-life period of a second order reaction is inversely proportional to the initial concentration of the reactant.

- According to equation (1.37), it is observed that a plot of $1/(a - x)$ versus time should be linear with slope k and a positive intercept $1/a$ (Fig. 1.4).

Thus, in case of a second-order reaction, a plot of 1/(conc. of reactant) versus time would always be linear with a positive intercept.

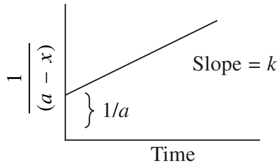


Fig. 1.4 Second order plot.

Second Order Reaction with Reactants having Different Initial Concentrations

Let the reaction

$$\begin{array}{lcccc} & \mathrm{A} & + \quad \mathrm{B} & \xrightarrow{k} & \text{Products} \\ \text{Initially} & a & b & & 0 \\ \text{At time } t, & (a-x) & (b-x) & & x \end{array}$$

The rate of reaction is represented as

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

or
$$\frac{dx}{(a - x)(b - x)} = kdt \tag{1.40}$$

Now we use the method of partial fractions to write the left side as sum of two simple terms. Let

$$\frac{1}{(a - x)(b - x)} = \frac{p}{(a - x)} + \frac{q}{(b - x)}$$

where p and q are evaluated by using a common denominator and equating coefficients of like powers of x in numerator. The values of p and q may be determined as $p = 1/(b - a)$ and $q = -1/(b - a)$. Equation (1.40) then becomes

$$\frac{dx}{(b - a)(a - x)} - \frac{dx}{(b - a)(b - x)} = kdt \tag{1.41}$$

Now the integration of each term is simple and the result is

$$1/(b-a)\ \ln a/(a-x) - 1/(b-a)\ \ln b/(b-a)\ \ln b/(b-x) = kt$$

which reduces to

$$k = \frac{1}{(b-a)t} \ln \left\{ \frac{(b-x)a}{b(a-x)} \right\} \quad \text{or} \quad k = \frac{1}{(a-b)t} \ln \left\{ \frac{b(a-x)}{a(b-x)} \right\}$$

or
$$k = \frac{2.303}{(b-a)t} \log \left\{ \frac{(b-x)\,a}{b\,(a-x)} \right\} \tag{1.42}$$

Thus, equation (1.42) is used to obtain the rate constant for a second-order reaction in which both the reactants have different initial concentration. Whether the experimental data satisfy this expression can be checked by plotting log $\{a(b-x)/b(a-x)\}$ against time, which should be a straight line passing through the origin. The slope of straight line gives the value of $2.303/k(b-a)$ from which the value of rate constant k can be evaluated.

The half-life period in this case can only be determined if the reactants are taken in stoichiometric amounts.

Let a and b be the initial concentrations of A and B, respectively, for the reaction

$$l\text{A} \quad + \quad m\,\text{B} \rightarrow \text{Products}$$

$$\text{A} \quad + \quad \frac{m}{l}\,\text{B} \rightarrow \text{Products}$$

Initially	a	b	0
At time t	$a-x$	$\left(\frac{m}{l}x\right)$	x

The rate,

$$\frac{dx}{dt} = k\,(a-x)\left(b - \frac{m}{l}x\right)$$

If a and b are in stoichiometric amounts, i.e. $b = (m/l)a$, the above equation reduces to

$$\frac{dx}{dt} = k(m/l)(a-x)^2$$

Rearranging and integrating, the rate constant and half-life period may be obtained as

$$k = \frac{1}{t(m/l)}\left(\frac{1}{(a-x)} - \frac{1}{a}\right) \tag{1.43}$$

and
$$t_{1/2} = l/mka \tag{1.44}$$

Problem 1.15 Hydrolysis of ester, in presence of NaOH, was followed keeping their concentration same at 0.02 mol dm^{-3}. The specific rate constant at 35°C was found to be 5.55 mol^{-1}dm^{3}min^{-1}. What proportion of ester will be hydrolysed in 30 min? Also calculate the time for 30% decomposition of ester.

Solution The rate constant for a second-order reaction when the initial concentrations of both reactants are same is given as

$$k = \frac{1}{t}\frac{x}{(a-x)}; \qquad \begin{aligned} a &= 0.02 \text{ mol dm}^{-3} \\ k &= 5.55 \text{ mol}^{-1}\text{ dm}^{3}\text{min}^{-1} \end{aligned}$$

(i) Let f fraction decompose in 30 min. Then

$$x = af$$

$$k = \frac{1}{30}\left(\frac{af}{a(a-af)}\right) = \frac{1}{30a}\frac{f}{(1-f)}$$

or

$$5.55 = \frac{1}{30 \times 0.02} \times \frac{f}{(1-f)}$$

$$\frac{f}{1-f} = 5.55 \times 30 \times 0.02 = 3.33$$

$$f = 0.76 \quad \text{or} \quad 76\%$$

This is the integrated rate equation for a second-order reaction.

Problem 1.16 For the reaction

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

the following data were obtained:

Time (sec)	0	178	275	530	860	1500
[A] × 10^3 (mol dm^{-3})	9.8	8.9	8.6	8.0	7.3	6.5
[B] × 10^3 (mol dm^{-3})	4.8	4.0	3.7	3.0	2.3	1.5

Calculate the rate constant and confirm that reaction is of second order. How the rate constant can be obtained graphically?

Solution

$$k = \frac{2.303}{t(a-b)} \log\left(\frac{b(a-x)}{a(b-x)}\right)$$

$$a = 9.8 \times 10^{-3} \text{ mol dm}^{-3}$$

$$b = 4.8 \times 10^{-3} \text{ mol dm}^{-3}$$

Time(sec)	log($a-x$)	log($b-x$)	$b(a-x)/a(b-x)$	k
0	$\bar{3}.9912$	$\bar{3}.6812$	–	–
178	$\bar{3}.9420$	$\bar{3}.6020$	1.078	0.844×10^{-4}
275	$\bar{3}.9340$	$\bar{3}.5682$	1.138	0.939×10^{-4}
530	$\bar{3}.9030$	$\bar{3}.4770$	1.306	1.007×10^{-4}
860	$\bar{3}.8633$	$\bar{3}.3617$	1.554	1.025×10^{-4}
1500	$\bar{3}.8125$	$\bar{3}.1760$	2.122	1.003×10^{-4}
				Average = 0.9636×10^{-4}

k almost remains constant. Therefore, the reaction is of second order.

Problem 1.17 A reactant reacts 30% in 30 min. If the reaction follows a second order kinetics, find rate constant and remaining concentration of reactant after 60 min.

Solution For a second order reaction

$$k = \frac{1}{t}\left[\frac{1}{a-x} - \frac{1}{a}\right]$$

Let $a = 100$, $x = 30$ and $a - x = 70$. Putting the values in above, we get

$$k = \frac{1}{30}\left[\frac{1}{70} - \frac{1}{100}\right] = \frac{1}{7000} = 1.42 \times 10^{-4}\ \text{mol}^{-1}\text{dm}^{3}\text{sec}^{-1}$$

Further,
$$k = \frac{1}{60}\left[\frac{1}{a-x} - \frac{1}{100}\right]$$

$$1.42 \times 10^{-4} = \frac{1}{60}\left[\frac{100-(a-x)}{(a-x)100}\right]$$

$$1.42 \times 10^{-4} \times 60 \times 100\ (\text{a} - x) = 100 - (a - x)$$

$$85.20\ (a - x) + (a - x) = 100$$

$$86.20\ (a - x) = 100$$

$(a - x) = \dfrac{100}{86.20} = 1.16$, i.e. 1.16% concentration of reactant will remain after 60 min.

Reduction of Order

Let us consider a second order reaction which is first order with respect to each reactant and the reactants have different initial concentrations.

$$\underset{a}{\text{A}} + \underset{b}{\text{B}} \xrightarrow{k} \text{Products}$$

The rate constant for this reaction is given by

$$k = \frac{2.303}{t(b-a)} \log \left\{ \frac{a(b-x)}{b(a-x)} \right\}$$

If one of the reactants, say B, has a very high concentration in comparison to that of A, i.e. $b \gg a$ then, the following conditions would be valid:

$$b - a \approx b \quad \text{and} \quad b - x \approx b$$

(because x depends on both A and B and is small as a is small). Therefore, the equation of rate constant reduces to

$$k = \frac{1}{b}\,\frac{2.303}{t} \log \frac{a}{(a-x)} \tag{1.45}$$

This rate expression is similar to the integrated expression for a first order reaction, only the magnitude of rate constant is changed by ($1/b$) times. Therefore, the reaction is said to be pseudo-first order. The reaction is first order with respect to reactant A, which is present at low concentration. The order with respect to B is arranged to be zero by virtue of its high concentration.

Thus, it may be concluded that if any reactant is present at a very high concentration, it does not affect the rate of reaction. The rate will depend only on those reactants, which are present at low concentrations. This is because, if reactant B is taken in very large concentration compared to other reactant A, then even if all of the reactant A is used up in the reaction, there will be very little decrease in the concentration of B. Therefore, the reaction is taking place under the conditions, where the concentration of B is practically constant. For this reason, the rate of the reaction is a function of the concentration of only the reactant, which is present at low concentration. Usually, to maintain the concentration of one reactant constant during the reaction, its concentration should be taken in at least ten-fold excess of the other reagent.

Second Order Reaction When Concentrations of Reactants Differ Only Slightly

If the concentration of two reactants differ only slightly, i.e. by a small amount, $(a - x)/(b - x)$ will almost be unity and, therefore, equation

$$k = \frac{1}{t\,(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

cannot be used. In this case, an equation is obtained by expansion of the logarithm.

Let $a = d + S$ and $b = d - S$, where d is the mean initial concentration, i.e. $d = (a + b)/2$ and $2S$ is excess of concentration of a over that of b.

This can be written in terms of *S* and *d* as

$$2kSt = \ln\left(1 + \frac{S}{d-x}\right) - \ln\left(1 - \frac{S}{d-x}\right) + \ln\left(1 - \frac{S}{d}\right) - \ln\left(1 + \frac{S}{d}\right)$$

On expanding the logarithm terms, the equation may be obtained as

$$\begin{aligned}2kSt = &\left(\frac{S}{(d-x)} - \frac{S^2}{2(d-x)^2} - \frac{S^3}{3(d-x)^3} + \ldots\right)\\ &- \left(-\frac{S}{(d-x)} - \frac{S^3}{2(d-x)^2} - \frac{S^3}{3(d-x)^3} + \ldots\right)\\ &+ \left(-\frac{S}{d} - \frac{S^2}{2d^2} - \frac{S^3}{3d^3} + \ldots\right) - \left(\frac{S}{d} - \frac{S^2}{2d^2} - \frac{S^3}{3d^3} + \ldots\right) \quad (1.46)\end{aligned}$$

On collecting the terms and arranging, the equation becomes

$$kt = \frac{1}{(d-x)} - \frac{1}{d} + \frac{S^2}{3}\left(\frac{1}{(a-x)^3} - \frac{1}{d^3}\right) + \ldots \quad (1.47)$$

When *S* is zero, the equation reduces to

$$kt = \frac{1}{(d-x)} - \frac{1}{d} \quad (1.48)$$

This is equivalent to equation used when both the reactants have same initial concentrations, i.e.

$$kt = \left(\frac{1}{C} - \frac{1}{C_0}\right) \quad \text{or} \quad \left(\frac{1}{(a-x)} - \frac{1}{a}\right)$$

Equation (1.48) may be used to determine the value of rate constant when the concentrations of two reactants differ only slightly ($S << d$). Here, *a* plot of $1/(d - x)$ against time will be linear with a slope equal to *k*.

Second Order Autocatalytic Reaction

When a product, formed in a second order reaction, acts as a catalyst or effects the rate of reaction, the reaction is known as *autocatalytic reaction*. For example, the acid catalysed hydrolysis of various esters and similar compounds and various biochemical processes.

Let us take the example of hydrolysis of an ester in presence of HCl

$$\begin{array}{lccccccc} \text{Initially at time } t & \text{Ester} & + & H_2O & \xrightarrow{HCl} & \text{Acid} & + & \text{Alcohol} \\ & a & & b & c & 0 & & 0 \\ & (a-x) & & (b-x) & & x & & x \end{array}$$

Since, water being in excess, its concentration may be taken constant. Again concentration of acid (HCl) is *c*, the rate will depend on $(c + x)$, i.e.

acid present initially + acid formed at any time t. Thus, the rate of reaction is given by

$$\frac{dx}{dt} = k(a - x)(c + x)$$

On rearranging and integrating, we get

$$k = \frac{2.303}{t(a + c)} - \log \frac{a(c + x)}{c(a - x)} \tag{1.49}$$

Equation (1.49) can be used for calculating the rate constant for a second-order autocatalytic reaction.

When the concentration $(c + x)$ is plotted against time t, a S-shaped curve is obtained. (Fig. 1.5). This curve is characteristic of autocatalytic reactions and many growth processes. It can be seen from equation (1.49) that rate will be maximum when

$$(a - x) = (c + x) \text{ or } x = (a - c)/2$$

Thus, if c is small in comparison to a, the maximum rate will be obtained when the concentration a has decreased by 50%. Again the rate constant at the point, where the rate is maximum, can be obtained by substituting $c = (a - 2x)$ in equation (1.49). Thus, the rate will be given as

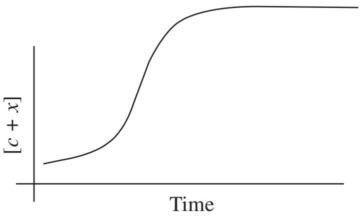


Fig. 1.5 Plot of $(c + x)$ versus time.

$$k = \frac{2.303}{2t(a - x)} \log \frac{a}{(a - 2x)} \tag{1.50}$$

Problem 1.18 A second order reaction with initial concentration of each reactant as 0.5 mol dm^{-3} was carried out in presence of acid as catalyst. At pH 4.0 the half-life of reaction was found to be 60 min. Calculate the observed and true rate constant for the reaction.

Solution

$$\text{Rate} = k_{\text{true}}\,[\text{H}^+][\text{A}][\text{B}] = k_{\text{obs}}\,[\text{A}][\text{B}], \quad \text{when} \quad k_{\text{obs}} = k_{\text{true}}\,[\text{H}^+]$$

$$[\text{A}]_0 = [\text{B}]_0 = 0.5 \text{ mol dm}^{-3}$$

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-4} \text{ mol dm}^{-3}$$

For a second order reaction

$$t_{1/2} = \frac{1}{k_{\text{obs}} \times [\text{initial conc.}]}$$

$$k_{\text{obs}} = \frac{1}{60 \times 0.5}\ \text{mol}^{-1}\text{dm}^3\ \text{min}^{-1} = 0.0333$$

$$= 3.33 \times 10^{-2}\ \text{mol}^{-1}\text{dm}^3\text{min}^{-1}$$

$$k_{\text{true}} = \frac{k_{\text{obs}}}{[\text{H}^+]} = \frac{3.33 \times 10^{-2}}{10^{-4}\ \text{mol dm}^{-3}}\ \text{mol}^{-1}\text{dm}^3\ \text{min}^{-1}$$

$$= 3.33 \times 10^{2}\ \text{mol}^{-2}\text{dm}^6\text{min}^{-1}$$

1.10 Third Order Reactions

A third order reaction can be the result of the reaction of a single reactant, two reactants or three reactants. If the two or three reactants are involved in the reaction they may have same or different initial concentrations. Depending upon the conditions the differential rate equation may be formulated and integrated to give the rate equation. In some cases, the rate expressions have been given as follows.

(a) Where three reactants are involved with same initial concentrations

Consider the reaction:

$$\begin{array}{lccccccc} & \text{A} & + & \text{B} & + & \text{C} & \xrightarrow{k} & \text{Products} \\ \text{Initially at time } t & a & & a & & a & & 0 \\ & (a-x) & & (a-x) & & (a-x) & & x \end{array}$$

Then

$$\text{Rate} = \frac{dx}{dt} = k(a-x)^3$$

On rearranging and integrating the equation, We get

$$k = \frac{1}{2t}\left(\frac{1}{(a-x)^2} - \frac{1}{a^2}\right) \qquad (1.51)$$

which can be used for calculating the rate constant of a third-order reaction, when all the reactants have same initial concentrations.

- Units of rate constant is (conc.)$^{-2}$ (time)$^{-1}$ or generally mol^{-2} lit^{2}sec^{-1} or mol^{-2} dm^6 sec^{-1}.
- Half-life period may be obtained from equation (1.51) by substituting $t = t_{1/2}$ when $x = a/2$. Thus,

$$t_{1/2} = \frac{3}{2ka^2} \qquad (1.52)$$

Therefore, in case of third order reactions the half-life period is inversely proportional to the square of initial concentration.

- Equation (1.51) can be rearranged as

$$\frac{1}{(a-x)^2} = 2kt + \frac{1}{a^2} \tag{1.53}$$

Therefore, a plot of $1/(a-x)^2$ versus time will give a straight line with a positive intercept $(1/a^2)$ and a slope $(2k)$. Thus, the value of rate constant may by obtained from the slope of the straight line.

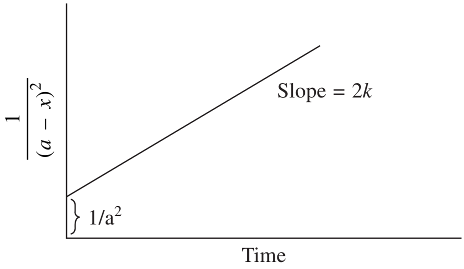


Fig. 1.6 Third order plot.

(b) Where three reactants are involved with different initial concentrations

Let us consider the reaction

$$\begin{array}{lccccccc} \text{Initially at time } t & \text{A} & + & \text{B} & + & \text{C} & \rightarrow & \text{Products} \\ & a & & b & & c & & 0 \\ & (a-x) & & (b-x) & & (c-x) & & x \end{array}$$

The rate expression is given by

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x)$$

This equation can be integrated with help of partial fractions. The integrated rate equation is obtained as

$$k = \frac{2.303}{t(a-b)(b-c)(c-a)}$$
$$\left((b-c)\log\frac{a}{(a-x)} + (c-a)\log\frac{b}{(b-x)} + (a-b)\log\frac{c}{(c-x)}\right) \tag{1.54}$$

(c) Where two reactants are involved and stoichiometry is 2:1

$$\begin{array}{lcccccc} \text{Initially at time } t & 2\text{A} & + & \text{B} & + \rightarrow & \text{Products} \\ & a & & b & & 0 \\ & (a-2x) & & (b-x) & & x \end{array}$$

The differential rate equation is given by

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

After rearranging and integrating, the integrated form of equation is obtained as

$$kt = \frac{1}{(2b-a)} - \left(\frac{1}{(a-2x)} - \frac{1}{a}\right) + \frac{2.303}{(2b-a)^2}\left(\log\frac{b(a-2x)}{a(b-x)}\right) \quad (1.55)$$

(d) Where two reactants have same initial concentrations and third has different concentration

$$\begin{array}{lccccccl} & A & + & B & + & C & \rightarrow & \text{Products} \\ \text{Initially at time } t & a & & a & & c & & \\ & (a-x) & & (a-x) & & (c-x) & & x \end{array}$$

The differential rate equation is given by

$$\frac{dx}{dt} = k(a-x)^2(c-x)$$

and integral form of equation for the rate constant may be obtained as

$$kt = \frac{1}{t(b-a)}\left(\frac{1}{(a-x)} - \frac{1}{a}\right) + \frac{2.303}{(a-b)^2}\left(\log\frac{b(a-x)}{a(b-x)}\right) \quad (1.56)$$

The differential rate equations, corresponding integral rate equations and rate constants for various reactions (having order zero to three) under different sets of conditions are summarized in Table 1.1.

1.11 Determination of Order of Reaction

The kinetic investigation of a reaction is carried out to establish the rate law and to measure the rate coefficients. The first step is to identify or examine the role of each component, i.e. to determine the order of reaction with respect to each reactant or product. There are various methods, which can be used to determine the order of reaction with respect to a reactant. However, every method requires essentially the measurement of concentration of the reactant or product at various time intervals.

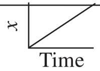
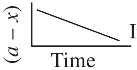
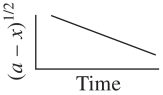
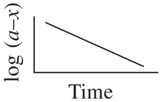
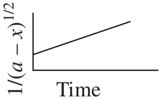
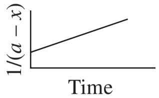
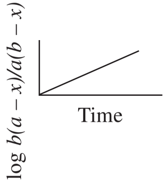
1.11.1 Integration Method

In this method, the different rate equations in their integrated forms (given in Table 1) are used. The amount of reactant $a-x$ or product x at different time intervals t is first experimentally determined. Then the values of x, $a-x$ and time are introduced into the different rate equations and the value of rate constant k is calculated at different time intervals. The equation which gives the constant value of rate constant indicates the order of reaction. For example, the values of rate constants at different time intervals are same in equation

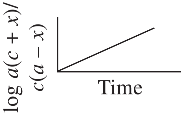
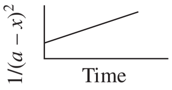
$$k = \frac{1}{2t}\left\{\frac{1}{a-x} - \frac{1}{a}\right\}$$

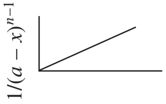
the order of reaction will be 2. Thus, this is the method of trial and can be used for simple homogenous reactions.

Table 1.1 Differential rate equations, corresponding integral rate equations and rate constants for various reactions

Reaction	Order	Differential equation	Integral equation	$t_{1/2}$	Units of k	Nature of plot		
$\underset{(a)}{A} \xrightarrow{k}$ Product	0	$\frac{dx}{dt} = k$	$k = \frac{x}{t}$	$\frac{a}{2k}$	mol $dm^{-3}s^{-1}$		Slope = k or 	Intercept = a
$\underset{(a)}{A} \xrightarrow{k}$ Product	1/2	$\frac{dx}{dt} =$ $k(a - x)^{1/2}$	$k = \frac{2}{t}$ $[a^{1/2} - (a - x^{1/2}]$	$\frac{0.586}{k} a^{1/2}$	$mol^{1/2}dm^{-3/2}s^{-1}$		Slope = $k/2$	Intercept = $a/2$
$\underset{(a)}{A} \xrightarrow{k}$ Product	1	$\frac{dx}{dt} =$ $k(a - x)$	$k = \frac{2.303}{t}$ $\log \frac{a}{(a - x)}$	$\frac{0.693}{k}$	s^{-1}		Slope = $k/2.303$,	Intercept = $\log a$
$\underset{(a)}{A} \xrightarrow{k}$ Product	3/2	$\frac{dx}{dt} =$ $k(a - x)^{3/2}$	$k = \frac{2}{t}$ $\left(\frac{1}{(a - x)^{1/2}} - \frac{1}{a^{1/2}}\right)$	$\frac{0.828}{ka^{1/2}}$	$mol^{-1/2}dm^{3/2}s^{-1}$		Slope = $k/2$,	Intercept = $\frac{1}{a^{1/2}}$
$\underset{(a)}{A} + \underset{(a)}{B} \xrightarrow{k}$ Product	2	$\frac{dx}{dt} =$ $k(a - x)^2$	$k = \frac{1}{t}$ $\left(\frac{1}{(a - x)} - \frac{1}{a}\right)$	$\frac{1}{ka}$	$mol^{-1/2}dm^{3}s^{-1}$		Slope = k	Intercept = $\frac{1}{a}$
$\underset{(a)}{A} + \underset{(b)}{B} \xrightarrow{k}$ Product	2	$\frac{dx}{dt} =$ $k(a - x)(b + x)$	$k = \frac{2.303}{t(a - b)}$ $\log \frac{b(a - x)}{a(b - x)}$	–	$mol^{-1}dm^{3}s^{-1}$		Passing through the origin,	Slope = $\frac{k(a - b)}{2.303}$

(Contd.)

Reaction	Order	Differential equation	Integral equation	$t_{1/2}$	Units of k	Nature of plot		
$A + B \xrightarrow{k}$ Autocatalytic Product	2	$\frac{dx}{dt} = k(a-x)(c+x)$	$k = \frac{2.303}{t(a+c)} \log \frac{a(c+x)}{c(a-x)}$	–	$mol^{-1}dm^3s^{-1}$		Passing through the origin,	Slope = $\frac{k(a+c)}{2.303}$
$\underset{(a)}{A} + \underset{(a)}{B} + \underset{(a)}{C} \xrightarrow{k}$ Product	3	$\frac{dx}{dt} = k(a-x)^3$	$k = \frac{1}{2t}\left(\frac{1}{(a-x)^2} - \frac{1}{a^2}\right)$	$\frac{3}{2ka^2}$	$mol^{-2}dm^6s^{-1}$		Slope = $2k$,	Intercept = $\frac{1}{a^2}$
$\underset{(a)}{A} + \underset{(b)}{B} + \underset{(c)}{C} \xrightarrow{k}$ Product	3	$\frac{dx}{dt} = k(a-x)(b-x)(c-x)$	$k = \frac{2.303}{t(a-b)(b-c)(c-a)} \left(b-c)\log\frac{a}{(a-x)} + (c-a)\log\frac{b}{(b-x)} + (a-b)\log\frac{c}{(c-x)}\right)$	–	$mol^{-2}dm^6s^{-1}$			

$2\underset{(a)}{A}+\underset{(b)}{B}\xrightarrow{k}$ Product	3	$\frac{dx}{dt}=k(a-2x)^2(b-x)$	$\frac{1}{t}\left(\frac{1}{2b-a)}\times\left\{\frac{1}{(a-2x)}-\frac{1}{a}\right\}+\frac{2-303}{(2b-a)^2}\times\log\frac{b(a-2x)}{a(b-x)}\right)$	–	$mol^{1/2}dm^{-6}s^{-1}$		
$\underset{(a)}{A}+\underset{(a)}{B}+\underset{(a)}{C}+\ldots\xrightarrow{k}$ Product	$n \geq 2$	$\frac{dx}{dt}=k(a-2x)^2$	$\frac{1}{t(n-1)}\times\left(\frac{1}{(a-x)^{n-1}}-\frac{1}{a^{n-1}}\right)$	$\frac{2^{(n-1)}-1}{(n-1)Ka^{(n-1)}}$	$mol^{-(n-1)}$ $dm^{3(n-1)}s^{-1}$		Slope = $(n-1)k$, Intercept = $\frac{1}{a^{n-1}}$

1.11.2 Half-life Period Method

Table 1 shows that the half-life depends on the initial concentration in a characteristic manner for reactions of different order and thus its measurement serves as a guide to the order. In general it may be concluded that

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

If a_1 and a_2 are the initial concentrations of the reactant in two experiments of same reactions and $(t_{1/2})_1$ and $(t_{1/2})_2$ are the corresponding half-life periods, respectively, then

$$(t_{1/2})_1 \propto \frac{1}{(a_1)^{n-1}} \quad \text{and} \quad (t_{1/2})_2 \propto \frac{1}{(a_2)^{n-1}}$$

or

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

Taking logarithms on both sides, the equation becomes

$$\log\left(\frac{(t_{1/2})_1}{(t_{1/2})_2}\right) = (n-1)\log\left(\frac{a_2}{a_1}\right) \tag{1.57}$$

The order n may be calculated with the help of above equation. Again a plot of logarithms of ratio of half-life periods versus ratio of initial concentrations will be linear passing through the origin with a slope equal to $(n - 1)$ and thus the order can be determined from its slope.

1.11.3 Graphical Method

The integrated forms of equations (Table 1) can be rearranged in the form of a straight line equation $y = mx + c$. For example

Order	Equation
0	$x = kt$
1	$\log(a-x) = -\frac{k}{2.303}t + \log a$
2	$\frac{1}{(a-x)} = kt + \frac{1}{a}$
3	$\frac{1}{(a-x)^2} = 2kt + \frac{1}{a^2}$
. . .	. . .
n	$\frac{1}{(a-x)^{n-1}} = (n-1)kt + \frac{1}{a^{n-1}}$

In order to confirm the order of a reaction, the left hand side of the expression, when plotted against time, should give a straight line. Thus, if a plot of $(1/a - x)$ versus time is a straight line, reaction would be of second order. This is a simple and accurate method and is applied generally for determination of the order of the reaction. The method is also advantageous, as the rate constant for the reaction can be evaluated with slope of the straight line and if initial concentration of the reactant is not known, can be determined with the help of intercept.

1.11.4 Differential Method

This method, used by Van't Hoff, is called *Van't Hoff's differential method.* Consider a reaction

$$n\text{A} \rightarrow \text{Product}$$

The rate of reaction at two different concentrations c_1 and c_2 can be given as

$$\text{Rate}_1 = -\frac{dc_1}{dt} = kc_1^n \tag{I}$$

$$\text{Rate}_2 = -\frac{dc_2}{dt} = kc_2^n \tag{II}$$

Dividing equation (I) by (II), we get

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{(-dc_1/dt)}{(-dc_2/dt)} = \left(\frac{c_1}{c_2}\right)^n$$

or
$$n = \frac{\log(\text{Rate}_1) - \log(\text{Rate}_2)}{\log c_1 - \log c_2} \tag{1.58}$$

The reaction is carried out with different initial concentrations of the reactant. The concentration versus time plots for both the experiments are obtained. The slope (*–dc/dt*) at a given time interval is measured in both the cases and using these values, *n* is determined with the help of above equation.

The differential rate equation can also be used alternatively as

$$-\frac{dc}{dt} = kc^n$$

or
$$-\log\left(\frac{dc}{dt}\right) = \log k + n \log c \tag{1.59}$$

Thus, a plot of log (rate) versus log [concentration] will be a straight line with an intercept log *k* and slope *n*. This is one of the procedures that gives the order directly. However, if log (rate) versus log [concentration] plot is not linear, the reaction is of complex nature.

1.11.5 Ostwald Isolation Method

When more than one reactant is involved in the reaction, it is necessary to isolate one of the reactants and its influence on the rate of reaction. The technique of isolating one reactant from rest of the reactants, developed by

Ostwald (1902), is based on the fact that 'if any reactant is taken in large excess, its concentration virtually remains constant, and thus it will not affect the rate of reaction'.

Let us consider a reaction in which three reactants, viz. A, B and C are involved, and α, β and γ are the order with respect to A, B and C, respectively. Now if reaction is carried out under the conditions of large excess of B and C, the reaction rate will be given by

$$-\frac{d\,[\mathrm{A}]}{dt} = k\mathrm{C}_{\mathrm{A}}^{\alpha}$$

Then apparent order α with respect to A may be determined by any method described earlier. The value of β can similarly be determined by using a large excess of A and C. For determination of γ, the experiment can be repeated by taking large excess of A and B. Thus, order with respect to each reactant can be determined.

The methods discussed above are suitable for simple and direct reactions where rates are simple power function of concentrations. These methods would not be helpful when the reactions are of complex nature and are occurring in multiple steps. The methods are also not applicable for the study of fast reactions where some special technique are required to be employed.

Problem 1.19 In a reaction when initial concentration doubles, the half-life is reduced to half. What is the order of reaction?

Solution

$$t_{1/2} \propto \left(\frac{1}{a^{n-1}}\right) \tag{a}$$

When $$a = 2a, \text{ and } t_{1/2} = \frac{t_{1/2}}{2}$$

Therefore, $$\frac{t_{1/2}}{2} \propto \frac{1}{(2a)^{n-1}} \tag{b}$$

From equations (a) and (b), we get

$$2 = (2)^{n-1}$$

$$\log 2 = (n-1)\log 2$$

$$n - 1 = 1$$

$$n = 2$$

The reaction is, therefore, of second order.

Problem 1.20 The rate of decomposition of a substance was 14.5 when it reacted 5% while the rate of decomposition in same unit was 10.25 when it reacted 20%. Find the order of reaction.

Solution

$$-\frac{dc}{dt} = kc^n \text{ (assume initiation concentration } c_0 = 100 \text{ unit)}$$

$$14.5 = k(100 - 5)^n = k(95)^n$$

$$10.25 = k(100 - 20)^n = k(80)^n$$

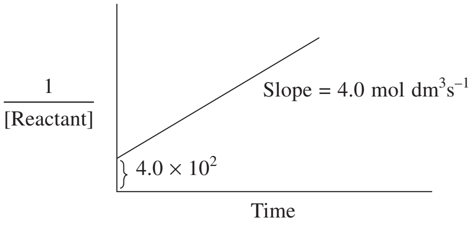
$$\left(\frac{95}{80}\right)^n = \frac{14.5}{10.25} = 1.414$$

$$(1.5)^n = 1.414$$

$$n = 2$$

Hence, reaction is of second order.

Problem 1.21 The data of a chemical reaction is plotted as 1/[reactant] vs time and the plot is a straight line with intercept 4.0×10^2 mol^{-1} dm^3 and slope 4.0 mol dm^3 s^{-1} as shown in the figure. Calculate the half-life of the reaction.



Solution Given that 1/[reactant] vs time plot is a straight line, the reaction is of second order and intercept gives the initial concentration (intercept = 1/*a*) and slope = *k*.

Therefore, $$a = \frac{1}{4.0 \times 10^2} = 0.25 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3$$

$$k = 4.0 \text{ mol dm}^{-3}\text{s}^{-1}$$

Now half-life period for second order reaction is given as

$$t_{1/2} = \frac{1}{ka} = \frac{1}{4 \text{ mol dm}^{-3}\text{s}^{-1} \times 0.25 \times 10^{-2} \text{ mol}^{-1} \text{dm}^3} = 100 \text{ sec}$$

Problem 1.22 In an experiment consisting of two reactants A and B, the half-life of reaction was measured. The half-life remained same when concentration of B doubled keeping [A] constant. On the other hand, when concentration of B is kept constant and [A] was doubled, the half-life reduced to half of its original value. Find the order of reaction with respect to each A and B. Suggest the rate law and also suggest which of the following mechanism agrees with rate law:

(i) $2A + B \rightarrow E$ (slow)

$E + B \xrightarrow{k_2} C + D$ (fast)

(ii) $2A \xrightarrow{k_1} A_2$ (fast)

$A_2 + B \xrightarrow{k_2} C + D$ (slow)

Solution When concentration of B was doubled, half-life remained same, half-life is independent to initial concentration in case of first order reaction. Therefore, reaction is first order with respect to B.

When concentration of A was doubled, half-life reduces to its half value, i.e.

$$t_{1/2} \propto \frac{1}{[A]}$$

Therefore, the reaction is second order with respect to [A].

The rate law may be given as

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

(i) According to this mechanism

$$\text{Rate} = \frac{d[C]}{dt} \quad \text{or} \quad \frac{d[C]}{dt} = k_2 [E][B]$$

By applying the steady state with respect to [E], we get

$$k_1[A]^2[B] = k_2[E][B]$$

or

$$[E] = \frac{k_1}{k_2} [A]^2$$

Therefore, rate law becomes

$$\text{Rate} = \text{k}_2 \, [E][B] = k_2 \frac{k_1}{k_2} [A]^2 [B] = k_1 [A]^2 [B]$$

which is matching with experimental results.
(ii) The rate of reaction is given as

$$\text{Rate} = \frac{d[C]}{dt} = \frac{d[C]}{dt} = k_2 [A_2][E]$$

Applying the steady state conditions with respect to $[A_2]$, we get

$$k_1[A]^2 = k_2[A_2][B] \quad \text{or} \quad [A_2] = \frac{k_1[A]^2}{k_2[B]}$$

Thus, rate law becomes

$$\text{Rate} = k_2[A_2][B] = k_1k_2\frac{[A]^2[B]}{[B]} = k_1k_2[A]^2 = k[A]^2$$

This rate law does not match with the experimental results. Thus, mechanism (i) agrees with the rate law.

1.12 Experimental Methods of Chemical Kinetics

A kinetic study requires the determination of the concentration (in mol dm^{-3}) of at least one of the reactant or product as a function of time. In case of gaseous phase, in place of concentration, the partial pressure is determined. The method of analysis employed must be faster than the rate of reaction. The conventional methods of analysis can be applied to the reactions which have a half-life of at least a few minutes. The measurement of some physical property which is proportional to the concentration/partial pressure can also be taken for determination of the rate. In many cases of reactions in solution, it is necessary to take out aliquots from the reaction mixture at suitable intervals of time, arrest the reaction in aliquots by means of suitable means and then analyse the sample. Some conventional physical methods used to study the kinetics of slow reactions are described as follows.

1.12.1 Conductometric Method

If the reaction system has a ionic species and if there is a change in number and/or nature of the ionic species during the reaction, the electrical conductance of the solution can be measured as a function of time. Let us consider the hydrolysis of an ester in presence of NaOH

$$RCOOR' + Na^+ + OH^- \rightarrow RCOO^- + Na^+ + R'OH$$

The conductivity at time $t = 0$ will be due to only Na^+ and OH^- while the conductivity at time $t = \infty$ (when reaction is complete) will be due to contribution of $RCOO^-$ and Na^+. At any time t, the conductivity will be the result of Na^+, OH^- and $RCOO^-$. Let y be the number of equivalents of ester that has reacted at any time t, and c the concentration in equivalent per liter. Then specific conductance at $t = 0$, i.e.

$$k_0 = (\lambda_{Na^+} + \lambda_{OH^-})\frac{C}{1000}$$

$t = \infty$, i.e.

$$k_\infty = (\lambda_{RCOO^-} + \lambda_{Na^+})\frac{C}{1000}$$

$t = t$, i.e.

$$k_t = (\lambda_{\mathrm{Na}^+} + \lambda_{\mathrm{OH}^-})\frac{(C - y)}{1000} + (\lambda_{\mathrm{RCOO}^-} + \lambda_{\mathrm{Na}^+})\frac{y}{1000}$$

and

$$\begin{aligned} k_t &= k_0 + [\lambda_{\mathrm{RCOO}^-} - \lambda_{\mathrm{OH}^-}]\, y/1000 \\ &= k_0 + (k_\infty - k_0) \times 1000/c \times y/1000 \\ &= k_0 + (k_\infty - \mathrm{k}_0)y/c \end{aligned} \qquad (1.60)$$

Thus, y at any time t can be determined with the relation

$$y = \left(\frac{k_t - k_0}{k_\infty - k_0}\right)c$$

The kinetics of various ligand exchange reactions have been studied by the conductometric methods.

1.12.2 Polarographic Technique

Polarography is electrolysing a solution of an electroactive substance between a dropping mercury electrode (DME, microelectrode) and some reference electrode (usually a pool of mercury), which acts as anode. The area of anode is large so that it may be regarded as incapable of becoming polarised and potential of such an electrode remains fairly constant. On applying the potential between these two electrodes, the current-voltage relationship is observed as shown in Fig. 1.7. The curve is known as *polarogram*.

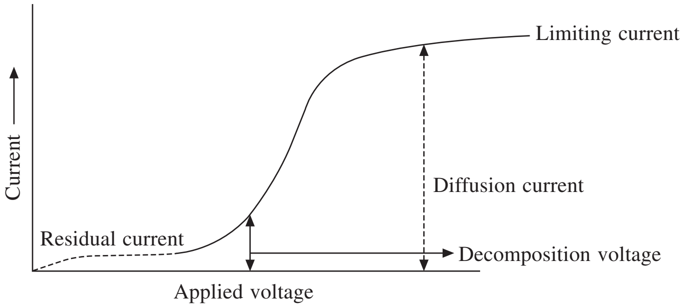


Fig. 1.7 A typical polarogram.

Initially, a small current, called *residual current*, flows and continues till the decomposition potential of reducible ionic species is reached. A further increase in applied potential increases the current linearly and reaches to a maximum value called *limiting current*. Three factors effect the current that during the electrolysis are: (i) migration or an electrical effect which depends upon the charge and transference number of the electroactive species, (ii) diffusion of all charged and uncharged species in solution between the two electrodes and (iii) convection, i.e. the motion of small particles under the influence of temperature, stirring and mechanical agitation. The migration effect is usually eliminated by electrolysis in presence of excess of a supporting electrolyte. The convection effects are also eliminated by electrolysis under controlled conditions. Thus, the only process by which the mass transfer occurs is diffusion and under appropriate conditions, the limiting current is almost solely a diffusion current. The diffusion current is given by the following equation:

$$i_d = 607\, n\, D^{1/2}\, c\, m^{2/3}\, t^{\,1/6} \tag{1.61}$$

where n is the number of electrons consumed in reduction of one molecule of the electroactive species (e.g. $\mathrm{Mn}^{n+} + ne \rightleftharpoons \mathrm{M};\ n = 2$), D is diffusion coefficient of the reducible or oxidisable substance in $\mathrm{cm^2 sec^{-1}}$, c is concentration of depolarizer in millimoles per liter, m is rate of flow of mercury from dropping electrode in mg sec^{-1} and t is drop time in sec. Thus, the diffusion current is related to the concentration of the species getting reduced at the electrode. The diffusion current can be measured at various time intervals and corresponding concentration can be estimated. A calibration curve relating diffusion current and concentration must be prepared in order to estimate the correct concentration and to obtain rate constant. The method has been used to measure the rate of relatively fast redox reactions, e.g.

$$\mathrm{Fe^{2+} + V^{5+} \rightarrow Fe^{3+} + V^{4+}}$$

$$\mathrm{Cd(CN)_3^{-} + CN^{-} \rightarrow Cd(CN)_4^{--}}$$

1.12.3 Potentiometric Method

The half-cell potential of metal electrode ($\mathrm{M} \rightarrow \mathrm{M}^{n+} + ne$) in a solution of its own ion is given by

$$E = E^0 + 2.303\, RT/(nF)\, \log Q_\mathrm{M} \tag{1.62}$$

where E^0 is the standard potential of the electrode, n its valency and Q_M is the activity of metal-ion. The above equation in terms of pH can be written as

$$E = E^0 + 2.303\, R\mathrm{T}/(nF)\ \mathrm{pH} \tag{1.63}$$

The half-cell potential is thus related with the concentration of the active ion and, therefore, the measurement of half-cell potential can be used to study the progress of reaction. For example, the formation of complex between $\mathrm{Fe^{3+}}$ and $\mathrm{F^-}$ can be studied by measuring the potential of half-cell $\mathrm{Fe^{2+}/Fe^{3+}}$ at various time intervals. Since the complex formation changes the concentration of $\mathrm{Fe^{3+}}$, the potential of half-cell $\mathrm{Fe^{2+}/Fe^{3+}}$ will also change.

If there is a change in pH of the medium due to reaction and this change corresponds to the change in concentration of the reactant species (e.g. $\mathrm{H^+}$), the measurement of pH as a function of time can also be used to follow the progress of the reaction.

1.12.4 Optical Methods

The specific rotation of an optically active substance $[\alpha]_D^T$ at a given temperature is given by

$$[\alpha]_D^T = \theta/(1 \times c \times M \times 1000) \qquad (1.64)$$

where θ is the angle through which polarised light is rotated, *l* (in decimeters) is the path length of beam of polarised light through the solution, *c* (mol dm^{-3}) is the concentration and *M* the molecular weight of the substance. Therefore,

$$c = \theta/([\alpha]_D^T \times l \times M \times 1000)$$

or

$$c \propto \theta \qquad (1.65)$$

Thus, if optically active substance is involved in the reaction, the change in optical rotation can be used directly to follow the progress of reaction. The inversion of sucrose in presence of HCl giving rise to fructose and glucose can, thus, be monitored polarimetrically.

1.12.5 Refractometry

Whenever a beam of light enters from a rarer (air) medium into a denser medium (glass or liquid) it bends towards the normal. Conversely, the beam of light is deflected away from the normal when it leaves a denser medium to enter a rarer medium (Fig. 1.8). According to Snell's Law

$$\sin i/\sin r = \text{Constant} = \eta$$

where *i* and *r* angles of incidence and refraction, respectively. The constant η is called refractive index and can be defined as

$$\eta = (\text{Velocity of light in vacuum})/(\text{Velocity of light in a given medium}) = c/c_n$$

The refractive index is a characteristic of a chemical species and depends upon temperature, wavelength of light and pressure.

The change in refractive index of the reaction mixture can be used to follow the progress of reaction provided all the constituents present in the

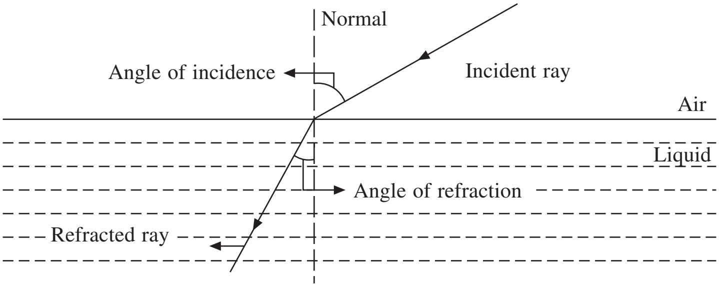


Fig. 1.8 Deflection of beam of light from normal.

system are known. This is necessary because one has first to prepare a calibration curve relating composition and refractive index for the mixtures of known composition. Once the calibration curve is obtained, the refractive index of the sample at various time intervals can be determined and the corresponding composition can be read on the calibration curve, e.g. A → B.

A calibration curve is prepared for mixtures of A and B. For studying the progress of a reaction, aliquots of the reaction mixture are taken at different intervals of time, and the refractive index is determined. The corresponding composition of A and B, can then be read on the calibration curve.

1.12.6 Spectrophotometry

The absorption spectroscopy has been widely used for monitoring the rate of chemical reactions. During the reaction, if there is either appearance of colour in a colourless solution or disappearance of colour in a coloured solution or a species which absorbed at a specific wavelength is formed, the spectroscopic technique can be used. Instruments like colorimeters and spectrophotometers are available to cover the visible, near infrared and ultra violet region of the spectrum (200-1000 nm). The absorption spectroscopy is governed by well-known Beer-Lambert's Law according to which:

$$\text{Absorbance or optical density} = I_0/I_t = Ecl$$

where I_0 and I_t are the intensity of incident and transmitted light, respectively, c is concentration of solution, l is the path length of beam of light within the solution and E is molar extinction coefficient which is characteristic of the absorbing substance. The instruments give the optical density directly. If l remains constant

$$\text{Optical density} = \text{Constant} \times c$$

or

$$\text{Absorbance} \propto c$$

First the Beer-Lambert Law is tested with the solutions of known composition at λ_{max} of solution by plotting (absorbance) versus concentration as shown in Fig. 1.9. The concentration range for which the plot is a straight line is determined and method is applied within this concentration range.

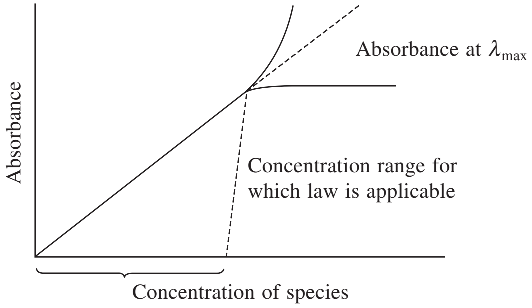


Fig. 1.9 Testing of Beer's Law.

The optical density of samples are measured at different times using same cell (to keep l constant) and concentration can be calculated using relation $c = A/El$. To verify the order of reaction, optical density data can be used directly.

EXERCISES

1. Differentiate between the following:
   (a) Order and molecularity.
   (b) Rate constant and equilibrium constant.
   (c) Rate constant and specific rate constant.
   (d) First order and pseudo-first order reaction.
2. What is meant by rate of reaction? How it can be determined experimentally? Explain why the rate cannot be determined by dividing total amount of a reactant reacted by total time taken?
3. What is meant by half-life period ($t_{1/2}$) of a reaction. Show that $t_{1/2} \propto \frac{1}{a^{n-1}}$ for n^{th} order of reaction, where a is initial concentration of the reactant.
4. Show that a second-order reaction behave like a first order, if concentration of one reactant is at least ten times greater than that of other reactant.
5. Explain why the H_2O in following reactions does not effect the rate of reaction and reaction is simple first order with respect to the substrate:

   $$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

   $$CH_3COOC_2H_5 + H_2O \xrightarrow{[H^+]} CH_3COOH + C_2H_5OH$$
6. Explain, why hydrolysis of an ester follows first-order kinetics in presence of an acid and it follows a second-order kinetics in presence of dilute alkali.
7. What is meant by an autocatalytic reaction? Derive an expression for rate constant of a simple autocatalytic reaction.
8. How the graphical method is most useful in determining the order of a reaction?
9. The reaction A $\xrightarrow{k}$ P follows the rate law $-\frac{d(c)}{dt} = k[c]^{3/2}$, where c is the concentration of A at time t. If C_0 is initial concentration of A, calculate the half-life period of reaction. Also find units of k.
10. Discuss the various techniques that can be used in determination of the rate of a reaction.
11. In an experiment, the following data have been measured for the reaction A + B → C:

$[A] \times 10^3$ (mol liter^{-1})	10.0	2.0	30	10.0	10.0
$[B] \times 10^3$ (mol liter^{-1})	10.0	10.0	10.0	20.0	30.0
(Rate) $\times 10^2$ (mol liter^{-1} min^{-1})	2.5	5.0	7.5	2.45	2.5

    Determine the order with respect to A and B. Also find the total order of reaction and suggest rate law.
12. For a gaseous reaction between A and B, the half-life period ($t_{1/2}$) were measured and data reported are

P_A (mm)	400	200	200
P_B (mm)	20	40	20
$t_{1/2}$ (min)	40	40	20

Find the order with respect to A and B. Suggest rate law and evaluate the rate constant.

13. A second-order reaction in which both the reactants were at same initial concentration was 50% completed in 500 sec. How long will it take to complete 75% of the reaction? Determine the rate constant also.
14. A first-order reaction has the rate constant = 1.0×10^{-4} sec^{-1}at 298 K. Calculate the half-life period of the reaction.
15. Derive an expression for the rate constant of a reaction having order n. Also calculate the half-life period.

2

Temperature Effect on Reaction Rate

It has been observed that in homogeneous thermal reactions, for every ten degree rise in temperature, the rate constant is doubled or tripled. The ratio of rate constants at two temperatures separated by 10°C is called the *temperature coefficient*. Mathematically

$$\text{Temperature coefficient} = \frac{k_t + 10}{k_t} \approx 2 \text{ to } 3 \tag{2.1}$$

For majority of reactions the temperature coefficient lies between 2 and 3. However, it has also been found to be less than 2 or greater than 3 in some specific reactions.

The first mathematical relation between the rate constant k and absolute temperature T was given by Hood (1878) as

$$\ln k = A - B/T \tag{2.2}$$

where A and B are constants for the reaction system. The values of A and B may be obtained from the intercept and slope of the linear plot between $\ln k$ and $1/T$.

The Hood's equation was based on the experimental results. Some theoretical significance to this equation was given by Vant Hoff (1884) on the basis of the effect of temperature on equilibrium constants. This idea was extended by Arrhenius in his attempt to obtain the relation between rate constant and temperature. The relation obtained was successfully applied by him to the effect of temperature data for a number of reactions and the equation is usually called the *Arrhenius equation*.

2.1 Derivation of Arrhenius Equation

Let us consider a general reaction

$$\underset{E_\mathrm{A}}{\mathrm{A}} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \underset{E_\mathrm{B}}{\mathrm{B}}$$

where k_1 is forward rate constant and k_1' backward rate constant are related with equilibrium constant, K_c for the reaction as

$$K_c = k_1/k_1' \tag{2.3}$$

Again, let $\Delta E = E_A - E_B$, i.e. the energy change.

The variation of equilibrium constant K_c with absolute temperature can be given by Vant Hoff's relation,

$$\frac{d(\ln K_c)}{dT} = \Delta E/RT^2 \tag{2.4}$$

Substituting the values of K_c and ΔE, the above equation becomes

$$\frac{d(\ln k_1/k_1')}{dT} = \frac{E_A - E_B}{RT^2} \tag{2.5}$$

Equation (2.5) can be split into two equations, viz.

$$\frac{d(\ln k_1)}{dT} = \frac{E_A}{RT^2} + Z \tag{2.6}$$

$$\frac{d(\ln k_1')}{dT} = \frac{E_B}{RT^2} + Z \tag{2.7}$$

where Z is a constant and can be set equal to zero. From equations (2.6) and (2.7) it can be considered that the rate constant is always related with energy of the reaction. And, therefore, for a general reaction $\underset{E}{A} \xrightarrow{k} P$, the following relation may be given

$$\frac{d(\ln k)}{dT} = \frac{E}{RT^2} \tag{2.8}$$

Integrating above equation and assuming E as independent of temperature, we get

$$\ln k = -E/RT + Z' \tag{2.9}$$

where Z' is an integration constant.

Equation (2.9) is similar as Hood's equation and can also be written as

$$k = Ae^{-E/RT} \tag{2.10}$$

where A is constant and is usually known as *frequency factor* or *Arrhenius factor* for the reaction and E is known as *energy of activation*. When the reaction occurs, there exists an equilibrium between the reactants on the one hand and a particular collision complex on the other. This complex represents a special type of collision complex, which is generally called *activated complex*.

The energy required to pass the reactant to activated complex is known as *energy of activation* or the *activation energy* as shown in Fig. 2.1.

$$\underset{\text{Reactant}}{A + B} \rightarrow \underset{\substack{\text{Activated}\\\text{complex}}}{X^{\neq}} \rightarrow \underset{\text{Product}}{C + D}$$

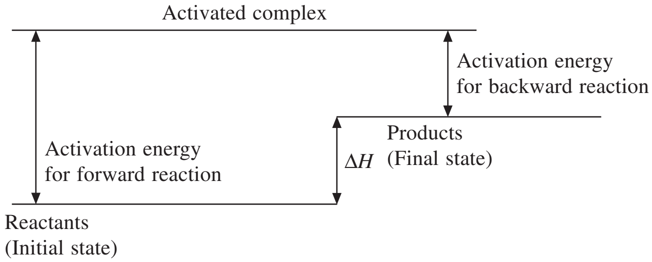


Fig. 2.1 Energy representation and $E_{act.}$

2.2 Experimental Determination of Energy of Activation and Arrhenius Factor

Equation (2.10) can be written in the form

$$\log k = \log A - E_{act}/2.303RT \tag{2.11}$$

According to equation (2.11) a plot of log k versus $1/T$ will be linear with a negative slope (Fig. 2.2) equal to $E_{act}/2.303R$ and an intercept equal to log A. Thus, the values of E_{act} and Arrhenius factor may be determined with the help of slope and intercept, respectively.

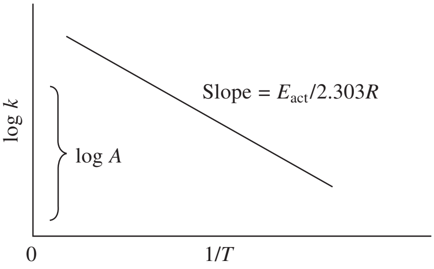


Fig. 2.2 Arrhenius plot.

This law has been applied and found to be obeyed with high accuracy for all types of chemical reactions. The energy of activation may also be calculated by another form of the Arrhenius equation as follows:

$$\log (k_1/ k_2) = E_{act}/2.303R\ [1/T_2 - 1/T_1] \tag{2.12}$$

where k_1 and k_2 are rate constants at two different absolute temperatures T_1 and T_2, respectively.

According to equation (2.10), a plot of k versus T is shown in Fig. 2.3.

The value of k reaches the constant value z asymptotically. For most of the reactions, k remains in lower (rising) part of curve in the accessible temperature range. However, in reactions involving free radicals or atoms with very low activation energy k reaches a value of z asymptotically and in these conditions

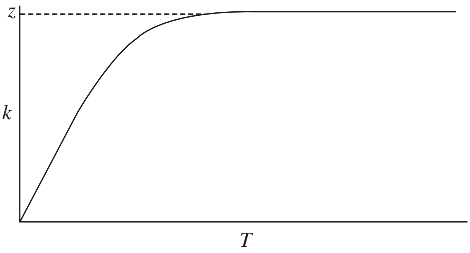


Fig. 2.3

the value of z is also a function of temperature. Therefore, a more accurate equation must be used as follows:

$$k = AT^n e^{-E_{act}/RT} \tag{2.13}$$

or

$$\ln k = -E_{act}/RT + n \ln T + \ln A \tag{2.14}$$

where exponent n has a particular value depending on nature of reaction.

In treating the experimental data by equations (2.10) and (2.13), the activation energy will differ and the difference of the two activation energies will be of hundreds or a few thousands of calories per mole. According to equation (2.14), a plot of log k versus $1/T$ will show a slight curvature (Fig. 2.4).

Sometimes the curve may be resolved into two parts, each of which approaches linearity. This may be observed in the case where two competing reactions with different activation energies take place or same reaction may occur—both homogenously (higher activation energy) and heterogeneously (lower activation energy).

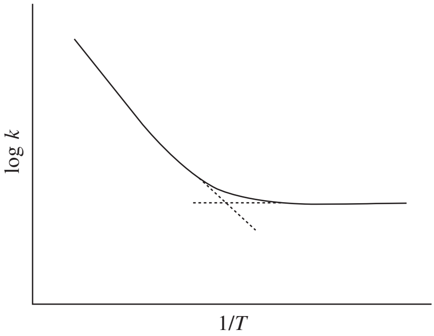


Fig. 2.4 Plot of log k versus $1/T$.

Problem 2.1 The values of rate constants for reaction

$$2HI \rightleftharpoons H_2 + I_2$$

were observed as 3.0×10^{-5} mol^{-1} dm^{3}s^{-1} and 2.5×10^{-3} mol^{-1}dm^{3}s^{-1} at 357°C and 447°C, respectively. Calculate the E_{act} for forward and backward reaction of $\Delta H = 15.5$ kJ mol^{-1}.

Solution For E_{act} (forward)

$$\frac{(E_{act})_{for}}{8.314}\left(\frac{1}{630} - \frac{1}{720}\right) = \ln\left\{\frac{2.50 \times 10^{-3}}{3.0 \times 10^{-5}}\right\}$$

Hence, $(E_{\text{act}})_{\text{forward}} = 185.08 \text{ kJ mol}^{-1}$

We have $\Delta H = (E_{\text{act}})_{\text{forward}} - (E_{\text{act}})_{\text{backward}}$

or $(E_{\text{act}})_{\text{backward}} = (E_{\text{act}})_{\text{forward}} - \Delta H = 185.08 - 15.5 = 169.58 \text{ kJ mol}^{-1}$.

2.3 Potential Energy Surface

Potential energy surface (PES) can be understood by making a plot of energy as a function of various interatomic distances in the complex that is formed during the reaction. For simplicity, let us consider a simplet chemical reaction between an atom A and a diatomic molecule BC to yield another atom C and a diatomic molecule AB as

$$\underset{\text{Reactants}}{A + BC} \rightarrow \underset{\text{Activated complex}}{A - B - C} \rightarrow \underset{\text{Products}}{AB + C}$$

The activated complex must be described in terms of three internuclear distances, i.e. R_{AB}, R_{BC} and R_{AC} or in terms of two internuclear distances and angle between the bonds. Thus, in order to plot energy against three parameters, a four dimensional diagram would be necessary. However, if only a linear activated complex (A–B–C) is considered, only two distances are involved (because $R_{AC} = R_{AB} + R_{BC}$) and a three dimensional diagram is adequate to describe the energy variation with internuclear distances as shown in Fig. 2.5.

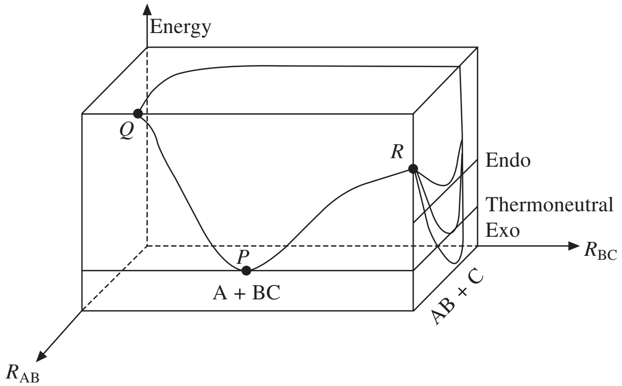


Fig. 2.5 Schematic diagram of a potential energy surface for a collinear reaction A + BC → AB + C.

The course of reaction may be considered to be transition on potential energy surface from point *P* to *Q*. Point *R* represents the activated complex A–B–C.

To trace the course of such reaction it is necessary to make the quantum mechanical calculations corresponding to a number of points in the interior of the diagram, i.e. at different number of values of R_{AB} and R_{BC}. Eyring and Polanyi made such calculations which were based on theoretical treatment of London. These calculations have shown that starting from points P and Q (Fig. 2.5), there are two valleys, which meet in the interior of the diagram at a point which is known as *col* or *saddle point*. The results are indicated by contour lines shown in Fig. 2.6.

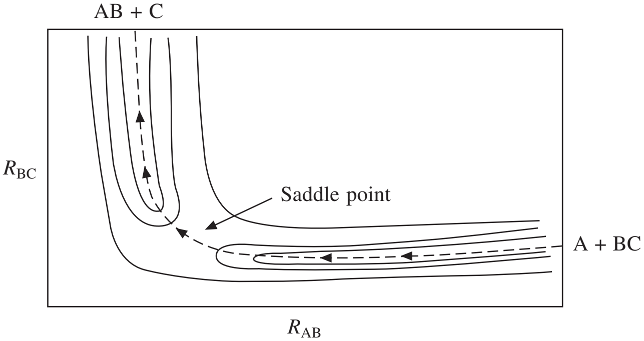


Fig. 2.6 Potential energy contour diagram for a thermoneutral reaction. Dashed line is the minimum energy path and the arrows indicate the direction of reaction.

The reaction path is represented by the dashed line. In order to pass the system from point P to Q, using the minimum amount of energy, it will travel along the first valley over the saddle point and down into the second valley. The energy corresponding to saddle point is minimum energy from one point of view and maximum energy from another view point. It is minimum energy since the system cannot pass from P to Q by using less energy than this energy while it is maximum energy because the system travels along its path, the saddle point represents the highest point in the path. The height of saddle point represents the activation energy of the system. The saddle point generally lies in the entrance channel in exothermic reactions and lies in exit channel in case of endothermic reactions.

2.4 Significance of Energy of Activation

The activation energy of a chemical reaction may conveniently be considered using method of potential energy surface.

As the reactants approach each other, there is some repulsion leading to a maximum barrier when the reactants are close to each other and subsequently there is a drop in the energy leading to the separation of products. This means that before the chemical reaction can occur, the reactants involved must be raised to a higher energy level, i.e. they must be in an energy rich or activated state before they can react. The variation of energy of a reacting system ($A + B \rightarrow C + D$) in relation to the reaction coordinate (all internuclear distances and structural variation) can be represented as shown in Fig. 2.7.

There is minimum energy level for the reaction denoted by E_x to which the reactant molecules must be raised in order to enable them to convert

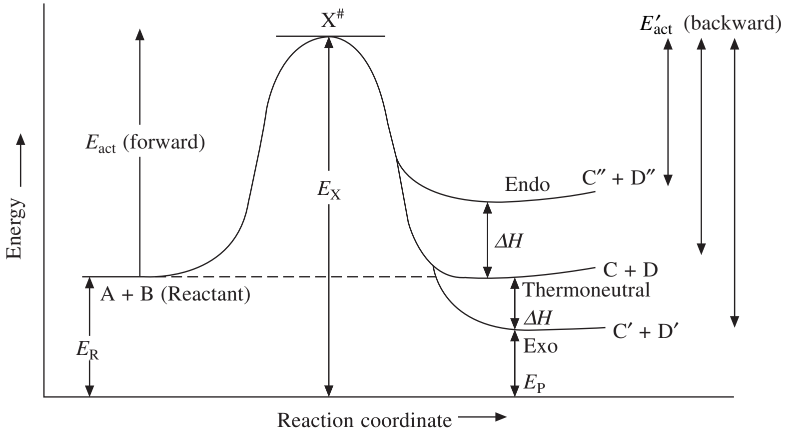


Fig. 2.7 Energy-reaction coordinate diagram for reaction (E_R: energy of reactant; E_P: energy of products; E_X: energy corresponding to activated complex (also known as threshold energy); ΔH: heat of reaction).

into products. Since reactants already having the energy E_R, the additional energy

$$A + B \rightarrow X^{\neq} \rightarrow C + D$$

i.e. $E_X - E_R$ must be acquired by the reactants to undergo transformation. This additional amount of energy, which should be supplied to reactants in order to form the activated complex is known as *energy of activation*. This additional energy may be supplied in any form, i.e. mechanical, chemical or thermal. This concept that molecules must possess the activation energy before they can undergo the chemical change has now been universally accepted for all reactions.

For the reverse reaction.

$$C + D \rightarrow X^{\neq} \rightarrow A + B$$

Again the C and D (which are now reactants) must reach the level of E_X by acquiring energy E'_{act} and thus be activated to be transformed into A and B. It is also clear from Fig. 2.7 that energies of activation for forward and backward reactions may be same or different depending on the nature of reaction. For a thermoneutral reaction, $\Delta H = 0$, energy of activation for both direction is same. For endothermic reaction, $E_{act} > E'_{act}$ while for exothermic reaction $E'_{act} > E_{act}$. However, knowing E_{act} and E'_{act}, ΔH can be evaluated. It is also understood that higher the value of energy of activation, the reaction will be slower.

Problem 2.2 Prove that for n^{th} order reaction, the plot of ln $t_{1/2}$ versus $1/T$ is a straight line and slope of the line is equal to E_{act}.

Solution We know that

$$\ln k = \ln A - \frac{E_{\text{act}}}{RT} \tag{i}$$

and the half-life period for n^{th} order is

$$t_{1/2} = \frac{2^{n-1} - 1}{k(n - 1)a^{n-1}} \tag{ii}$$

Taking natural log of equation (ii), we get

$$\ln(t_{1/2}) = \ln\left\{\frac{2^{n-1} - 1}{(n - 1)a}\right\} - \ln k \tag{iii}$$

Substituting the value of ln k from equation (i), we get

$$\ln(t_{1/2}) = \ln(X) - \ln A + \frac{E_{\text{act}}}{RT}$$

where $X = \dfrac{2^{n-1} - 1}{(n - 1)}$ is a constant.

Therefore,

$$\ln(t_{1/2}) = \ln(X') + \frac{E_{\text{act}}}{RT}$$

where $X' = X/A$ is again a constant.

Thus, a plot of ln ($t_{1/2}$) versus $1/T$ will give a straight line with slope equal to E_{act}.

EXERCISES

1. Define the following terms and give their significance:
   (a) Temperature coefficient
   (b) Energy of activation
   (c) Arrhenius factor
   (d) Activated complex
2. Draw energy-reaction coordinate diagram and discuss the physical significance of energy of activation. Also differentiate between energy of activation and heat of reaction.
3. In a reversible reaction, show how the E_{act} for forward and backward reactions are related with the following:
   (a) in an exothermic reaction
   (b) in an endothermic reaction
   (c) in a thermoneutral reaction
4. Derive a relation between absolute temperature and half-life period for a n^{th} order reaction.
5. A first-order reaction at 25°C and 45°C has rate constants equal to 2.5×10^{-4} and 17.0×10^{-4} sec^{-1}, respectively. Calculate Arrhenius factor and E_{act} for the reaction.

6. The rate constant of a reaction becomes double on increasing the temperature from 20°C to 30°C. Calculate E_{act}.
7. Calculate the ratio of rate constants of two reactions which have some value of Arrhenius factor and a difference of 5 k mol^{-1} in E_{act} at 25°C.
8. A reaction has an activation energy of 50 kJ mol^{-1}. Calculate the ratio of rate constant at 117°C and 127°C.
9. The following data was obtained for a reaction:

t°C	$k \times 10^4 (sec^{-1})$
35	3.81
40	5.11
45	7.67
50	12.70

   Plot log k versus $1/T$ and determine E_{act} from slope of the straight line. Check the answer using method of least squares.
10. Derive Arrhenius equation and explain how the parameters involved in equation can be determined experimentally?

3

Complex Reactions

3.1 Reversible Reactions

In a reversible process, if the rate of backward reaction is much less as compared to the rate of forward reaction, the equilibrium will be far away from the starting end and the reaction may be found to follow a simple and straightforward path as discussed earlier. However, when the reaction rates are appreciable for both the forward and backward directions, the kinetics must be taken into consideration for both the direction.

Let us consider a simple reaction

	$n\mathrm{A} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}}$	$m\mathrm{B}$
Concentration at initiation	a	0
Concentration at time t	$(a - x)$	x

where k_1 and k_1' are rate constants for forward and backward directions, respectively.

Rate of forward reaction = $k_1\ (a - x)^n$
Rate of backward reaction = $k_1'(x)^m$

The net rate of formation of products will be the difference between the two, i.e.

$$\text{Net rate of reaction} = \frac{dx}{dt} = k_1(a - x)^n - k_1'(x)^m \qquad (3.1)$$

At equilibrium, the rate of forward reaction is equal to backward reaction and, therefore, net rate of reaction will be zero. Thus, at equilibrium when $x = x_\mathrm{e}$ (concentration of B, measured separately)

$$k_1(a - x_e)^n - k_1'(x_e)^m = 0$$

or

$$k_1' = \frac{k_1(a - x_e)^n}{(x_\mathrm{e})^m} \qquad (3.2)$$

Substituting the value of k_1' from equation (3.2), in (3.1), we get

$$\frac{dx}{dt} = k_1(a-x)^n - \frac{k_1(a-x_e)^n x^m}{x_e^m}$$

or
$$\frac{dx}{dt} = \frac{k_1}{x_e^m}[(a-x)^n x_e^m - (a-x_e)^n x^m] \tag{3.3}$$

If reaction is simple first order in both directions, i.e.

$$\mathrm{A} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

equation (3.3) reduces to

$$\frac{dx}{dt} = \frac{k_1 a}{x_e}(x_e - x)$$

which on integration gives

$$k_1 = \frac{x_e}{at}\ln\left(\frac{x_e}{x_e - x}\right) \tag{3.4}$$

The measurement of x at different times would give the value of k_1. The value of k_1' can be obtained with the help of equation (3.2), which reduces to

$$k_1' = \frac{k_1(a-x_e)}{(x_e)} \tag{3.5}$$

An alternate expression may also be used if equilibrium concentration x_e is not known. Equation (3.1) for above simple reaction can be reduced to

$$\frac{dx}{dt} = k_1(a-x) - k_1'(x) = k_1 a - (k_1 + k_1')x$$

On integration, we get

$$t = -\frac{1}{(k_1 + k_1')}\ln\{k_1 a - (k_1 + k_1')x\} + z$$

The value of integration constant z is obtained as follows:

When $t = 0$, $x = 0$; $\quad z = \frac{1}{(k_1 + k_1')}\ln(k_1 a)$

Substituting the value of z and rearranging, gives

$$(k_1 + k_1') = \frac{1}{t}\ln\left(\frac{k_1 a}{k_1 a - (k_1 + k_1')x}\right) \tag{3.6}$$

Again, equilibrium constant $K = k_1/k_1'$ and, therefore, equation (3.6) can be written in terms of K as

$$k_1 = \frac{1}{t(K+1)} \ln\left(\frac{Ka}{Ka-(K+1)x}\right) \tag{3.7}$$

Thus, with the help of equations (3.6) and (3.7), the values of k_1 and k_1' can be obtained.

For a given reaction at constant temperature, the equilibrium concentrations, i.e. $(a - x_e)$ and x_e attain the definite values depending on the value of a and therefore, a/x_e can be considered to be a constant under these conditions. The differential equation can be written as

$$\frac{dx}{dt} = k_1''(x_e - x) \tag{3.8}$$

where $k_1'' = k_1 a/x_e$.

Equation (3.8) on integration and rearrangement becomes

$$k_1'' = \frac{1}{t} \ln\left(\frac{x_e}{x_e - x}\right) \tag{3.9}$$

Also $$k_1(a - x_e) = k_1' x_e$$

or $$\frac{k_1}{k_1'} = \frac{a - x_e}{x_e}$$

or $$\frac{k_1 + k_1'}{k_1} = \frac{a}{x_e}$$ (adding 1 on both sides in equation)

Therefore, $$k_1 + k_1' = \frac{k_1 a}{x_e} = k_1''$$

Thus, equation (3.9) becomes

$$k_1 + k_1' = \frac{1}{t} \ln\left(\frac{x_e}{x_e - x}\right) \tag{3.10}$$

Therefore, the reaction will behave like a first order with $(k_1 + k_1')$ as the rate constant and x_e as the initial concentration in place of a.

3.1.1 Reversible Reaction When Both the Opposing Processes are Second Order

Let us consider a general reaction

$$\mathrm{A + B} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \mathrm{C + D}$$

Concentration at starting	a	b	c	d
Concentration at time	$t\ (a-x)$	$(b-x)$	$(c+x)$	$(d+x)$

The net rate of reaction can be written as

$$\frac{dx}{dt} = k_1(a-x)(b-x) - k_1'(c+x)(d+x) \tag{3.11}$$

$$\text{or } \frac{1}{k_1'}\frac{dx}{dt} = K(a-x)(b-x) - (c+x)(d+x); \quad \text{where} \quad K = \frac{k_1}{k_1'}$$

$$= K\,[ab - (a+b)x + x^2] - [cd + (c+d)x + x^2]$$

$$= (K-1)x^2 - K\{(a+b) + (c+d)\}x + K(ab-cd)$$

$$\text{or } \frac{1}{k_1'(K-1)}\frac{dx}{dt} = x^2 - \frac{K\{(a+b)+(c+d)\}}{K-1}x + \frac{K(ab-cd)}{K-1}$$

$$= x^2 - Lx + M \tag{3.12}$$

where $L = \dfrac{K\{(a+b)+(c+d)\}}{K-1}$ and $M = \dfrac{K(ab-cd)}{K-1}$.

Again, equation (3.12) can be written as

$$\frac{1}{k_1 - k_1'}\frac{dx}{dt} = \left(x - \frac{L - \sqrt{L^2 - 4M}}{2}\right)\left(x - \frac{L + \sqrt{L^2 - 4M}}{2}\right)$$

$$= (x-A)\,(x-B)$$

where $A = \frac{1}{2}(L - \sqrt{L^2 - 4M})$ and $B = \frac{1}{2}(L + \sqrt{L^2 - 4M})$.

The above equation can also be written as

$$\frac{dx}{(x-A)(x-B)} = (k_1 - k_1')\,dt$$

$$\text{or} \qquad \frac{1}{(A-B)}\left(\frac{1}{(x-A)} - \frac{1}{(x-B)}\right)dx = (k_1 - k_1')\,dt$$

Which, on integrating and rearranging, gives

$$k_1 - k_1' = \frac{1}{t(A-B)}\ln\left(\frac{B(x-A)}{A(x-B)}\right) \tag{3.13}$$

Since $K = k_1/k'$, knowing the value of equilibrium constant, k_1 and k_1' can be determined.

Problem 3.1

Find the values of k_f and k_b for reaction

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

if $[A]_0 = 0.30 \text{ mol dm}^{-3}$ $\quad$ $[A]_e = 0.172 \text{ mol dm}^{-3}$

$[A]_{10} = 0.285$ and $\quad$ $[A]_{100} = 0.21$ M

Solution

$$\frac{k_f}{k_b} = \frac{a - x_e}{x_e} = \frac{0.30 - 0.172}{0.172} = 0.744$$

Again $$\frac{a}{a - x_e} k_f t = \ln \left\{ \frac{a - x_e}{x_t - x_e} \right\}$$

$$\frac{0.30}{0.30 - 0.172} k_f \ 10 = \ln \left\{ \frac{0.30 - 0.172}{0.285 - 0.172} \right\}$$

$$k_f = 5.31 \times 10^{-3} \text{ sec}^{-1}$$

$$\frac{0.30}{0.30 - 0.172} k_f \ 100 = \ln \left\{ \frac{0.30 - 0.172}{0.21 - 0.172} \right\}$$

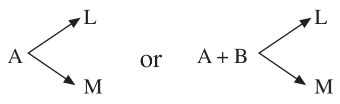
$$k_f = 5.18 \times 10^{-3} \text{ sec}^{-1}$$

$$k_{f_{\text{average}}} = 5.25 \times 10^{-3} \text{ sec}^{-1}$$

$$k_b = \frac{5.25 \times 10^{-3}}{0.744} = 7.05 \times 10^{-3} \text{ sec}^{-1}$$

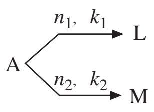
3.2 Parallel Reactions

When a reactant in the reaction undergoes in more than one pathway giving rise to different products, the reactions are termed as parallel or side reactions, e.g.



3.2.1 Determination of Rate Constants

Consider a parallel reaction as follows:



Let *a* be the initial concentration of A and *x* the amount of A disappeared in time *t*, partly as L and partly as M. Let n_1 and n_2 be the orders of reaction with respect to A and k_1 and k_2 the rate constants for paths 1 and 2, respectively. Then,

$$\frac{dx}{dt} = \text{Rate of formation of L + Rate of formation of M}$$

$$= \frac{d[\mathrm{L}]}{dt} + \frac{d[\mathrm{M}]}{dt}$$

Again
$$\frac{d[\mathrm{L}]}{dt} = k_1(a - x)^{n_1} \qquad \text{(a)}$$

$$\frac{d[\mathrm{M}]}{dt} = k_2(a - x)^{n_2} \qquad \text{(b)}$$

Therefore,
$$\frac{dx}{dt} = k_1(a - x)^{n_1} + k_2(a - x)^{n_2} \qquad (3.14)$$

If the reaction is first order with respect to reactant in both the paths, i.e. $n_1 = n_2 = 1$, equation (3.14) reduces to

$$\frac{dx}{dt} = (k_1 + k_2)(a - x)$$

or
$$\frac{dx}{(a - x)} = (k_1 + k_2)\,dt$$

On integration, we get

$$(k_1 + k_2) = \frac{1}{t} \ln \frac{a}{(a - x)} \qquad (3.15)$$

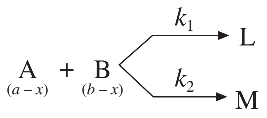
Thus, the value of the sum of two rate constants can be found by following the concentration changes in reactant with time.

Further, for the determination of individual values of k_1 and k_2, following relation between k_1 and k_2 is needed

$$\frac{\text{Rate of formation of L}}{\text{Rate of formation of M}} = \frac{k_1(a - x)}{\mathrm{k}_2(a - x)} = \frac{k_1}{k_2} = z \text{ (say)} \qquad (3.16)$$

The estimation of L and M at any state will give the value of ratio of k_1/k_2. Using equations (3.15) and (3.16), the individual rate constants k_1 and k_2 can be evaluated.

For a simple second order reaction, which is first order with respect to each reactant, i.e.



The differential rate law may be given as

$$\frac{dx}{dt} = k_1(a - x)(b - x) + k_2(a - x)(b - x)$$

$$= (k_1 + k_2)(a - x)\,(b - x)$$

The above equation, on integration will give

$$(k_1 + k_2) = \frac{1}{t(a - b)} \ln\left(\frac{b(a - x)}{a(b - x)}\right) \tag{3.17}$$

Again, using equations (3.16) and (3.17) the individual rate constants k_1 and k_2 can be evaluated.

Equation (3.16) is valid only when the orders of two parallel reactions are same (Wegschider test). However, if order of two side reactions is not same, an alternate method may be applied as follows:

From equations (a) and (3.14), we get

$$\frac{d[\mathrm{L}]}{dx} = \frac{k_1(a - x)^{n_1}}{k_1(a - x)^{n_1} + k_2(a - x)^{n_2}} = \frac{1}{1 + (k_2/k_1)(a - x)^{n_2 - n_1}} \tag{3.18}$$

According to equation (3.18), a plot between [L] (i.e., concentration of one of the product) and x will give a curve, and tangent of the curve at $x = 0$ will be equal to $\{1 + (k_2/k_1)\,a^{(n_2 - n_1)}$. Thus for $(n_2 - n_1) = 1$, the ratio (k_2/k_1) may be determined. However, when $(n_2 - n_1) > 1$, the determination of $(n_2 - n_1)$ is also involved.

Problem 3.2 For a reversible reaction

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{P}$$

k_1 is 4.0×10^{-2} s^{-1} and k_2 is half of k_1. Initial concentration of A is 2.0 mol dm^{-3}. At what time the concentration of P will be 1.0 mol dm^{-3}.

Solution

$$\frac{k_1}{k_2} = \frac{x_e}{a - x_e}$$

$$\frac{4.0 \times 10^{-2}}{2.0 \times 10^{-2}} = \frac{x_e}{2.0 - x_e}$$

Thus $\quad x_e = 1.33$ mol dm^{-3}

Again $\quad k_1 = \dfrac{x_e}{at} \ln\left(\dfrac{x_e}{x_e - x}\right)$

or $$t = \frac{2.303x_e}{a}\log\left(\frac{x_e}{x_e - x}\right) = \frac{2.303 \times 1.33}{2.0}\log\left(\frac{1.33}{1.33 - 1.00}\right)$$

$$= \sim 56 \text{ sec approximately}$$

Problem 3.3

For a side reaction

$$\mathrm{A} \xrightarrow{k_1} P_1$$

$$\xrightarrow{k_2} P_1$$

Prove that $[P_1] : [P_2] = k_1 : k_2$.

Solution

Let A_0 is initial concentration of A

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}] + k_2[\mathrm{A}]$$

$$-\frac{d[\mathrm{A}]}{dt} = (k_1 + k_2)[\mathrm{A}]$$

$$-\frac{d[\mathrm{A}]}{[\mathrm{A}]} = (k_1 + k_2)\,dt$$

Integrating with the condition that when $t = 0$, $[\mathrm{A}] = A_0$, we get

$$[\mathrm{A}] = A_0 e^{-(k_1+k_2)t}$$

or $$[\mathrm{A}] = \mathrm{A}_0 e^{-kt}, \quad \text{where } k = k_1 + k_2$$

Now $$\frac{d[P_1]}{dt} = k_1[\mathrm{A}] \quad \text{and} \quad \frac{d[P_2]}{dt} = k_2[\mathrm{A}]$$

Taking $\frac{d[P_1]}{dt} = k_1[\mathrm{A}] = k_1 A_0 e^{-kt}$ and integrating, we get

$$P_1 = -\frac{k_1}{k}A_0 e^{-kt} + z \text{ (integration constant)}$$

When $t = 0$, $P_1 = 0$ and therefore, $z = \frac{k_1}{k}A_0$.

Substituting the value of z, we get

$$P_1 = \frac{k_1}{k}A_0(1 - e^{-kt})$$

Similarly $$P_2 = \frac{k_2}{k}A_0(1 - e^{-kt})$$

Therefore, $$\frac{P_1}{P_2} = \frac{k_1}{k_2}$$

3.3 Consecutive Reactions

The reactions in which the reactants are converted to products through one or more intermediate stages are called *consecutive reactions.* The overall reaction is a result of several consecutive steps. Every stage has its own reactant and rate constant.

Let us consider a simple reaction

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

The concentration of the reactant A decreases regularly with time while that of intermediate B increases, passes through a maximum and then finally decreases to zero. The value of maximum concentration will depend on the rate of its formation and rate of its disappearance. The formation of final product C will start after formation of a certain amount of intermediate. Therefore, the final product will be formed with a certain induction period.

Let c_0 be the initial concentration and c_1, c_2 and c_3 be the concentrations of A, B and C, respectively, at any time t, then

$$c_0 = c_1 + c_2 + c_3 \tag{3.19}$$

The concentration of various species at different time is obtained by solving the corresponding differential equations.

The rate of disappearance of A is given as

$$-\frac{d[\mathrm{A}]}{dt} \quad \text{or} \quad -\frac{dc_1}{dt} = k_1 c_1$$

Integrating, we get

$$c_1 = c_0 e^{-k_1 t} \tag{3.20}$$

Equation (3.20) gives the concentration of reactant A at any time t.

Again,

Rate of formation of B, $dc_2/dt = k_1 c_1$

Rate of disappearance of B, $-dc_2/dt = k_2 c_2$

Therefore, rate of accumulation of B in the system, i.e.

$$dc_2/dt = k_1 c_1 - k_2 c_2$$

or $$dc_2/dt + k_2 c_2 = k_1\, c_0\, e^{-kt}\ (c_1 = c_0\, e^{-k_1 t}) \tag{3.21}$$

This is a differential equation in terms of c_2 and can be integrated by multiplying $e^{k_2 t}$ on both sides of equation

$$e^{k_2t}\frac{dc_2}{dt}+k_2c_2e^{k_2t}=k_1c_0e^{-k_1t}e^{k_2t}\ =k_1c_0e^{(k_2-k_1)t}$$

Integrating, we get

$$c_2e^{k_2t}=\frac{k_1c_0}{k_2-k_1}e(k_2-k_1)t+z\ \text{(constant)}$$

when $t = 0$, $c_2 = 0$ and, therefore, $z = -\,k_1\,c_0\,/\,(k_2 - k_1)$.

Substituting the value of z, the above equation becomes

$$c_2e^{k_2t}=\frac{k_1c_0}{k_2-k_1}(e^{(k_2-k_1)t}-1)$$

or
$$c_2=\frac{k_1c_0}{k_2-k_1}(e^{-k_1t}-e^{-k_2t})\tag{3.22}$$

The value of c_3 may be obtained by substituting the values of c_1 and c_2 from equations (3.20) and (3.22), respectively, in equation (3.19). Thus, we get

$$c_3=c_0\left(1-\frac{k_2}{k_2-k_1}e^{-k_1t}-\frac{k_1}{k_1-k_2}e^{-k_2t}\right)\tag{3.23}$$

which reduces to

$c_3=c_0(1-e^{-k_1/t)})$ when $k_2 >> k_1$ and $c_3=c_0(1-e^{-k_2t})$ when $k_1 >> k_2$

Thus, with the knowledge of initial concentration c_0 and experimental determination of c_1, c_2 and c_3 at any time t, the value of k_1 and k_2 may be evaluated.

3.3.1 Concentration-Time Relation

It is clear from equation (3.20) that c_1 decreases exponentially while the amount of product c_3 will rise until it approaches that of A.

Equation (3.22) shows that c_2, i.e. concentration of the intermediate will first increase and then decrease. The concentration-time plots for various species are given in Fig. 3.1.

The concentration of intermediate c_2 will be maximum when $dc_2/dt = 0$,

i.e.
$$\frac{dc_2}{dt}=\frac{k_1c_0}{k_2-k_1}(-k_1e^{-k_1t}+k_2e^{-k_2t})^2\ =0\tag{3.24}$$

or
$$k_1e^{-k_1t}=k_2e^{-k_2t}$$

or
$$k_1/k_2=e^{(k_1-k_2)t}$$

or
$$t=\frac{\ln k_1-\ln k_2}{k_1-k_2}\tag{3.25}$$

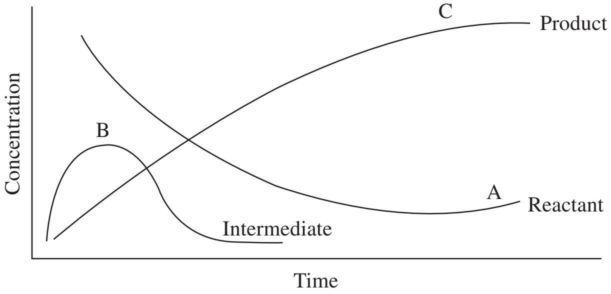


Fig. 3.1 Variation of concentration with time.

Thus, time at which the concentration of intermediate is maximum, will depends on the rate constants k_1 and k_2.

Problem 3.4 For a first order parallel reaction, the Arrhenius factor for formation of two products are 10^{10} and 10^8 $\sec^{-1}$ and their energy of activation are 150 and 75 kJ mol^{-1}, respectively. At what temperature the two products will be formed at the same rate?

Solution

$$A \begin{array}{l} \nearrow \text{B} \quad A_1 = 10^{10};\ E_{\text{act}} = 150 \text{ kJ mol}^{-1} \\ \searrow \text{C} \quad A_2 = 10^{8};\ E_{\text{act}'} = 75 \text{ kJ mol}^{-1} \end{array}$$

$$k_1 = A_1 e - E_{\text{act}}/RT = 10^{10}\, e^{-\frac{150\times10^3}{8.314\times T}}$$

$$k_2 = A_2 e - E_{\text{act}'}/RT = 10^{8}\, e^{-\frac{75\times10^3}{8.314\times T}}$$

$$k_1 = k_2$$

$$10^{10}\, e^{-\frac{150\times10^3}{8.314\times T}} = 10^{8}\, e^{-\frac{75\times10^3}{8.314\times T}}$$

Taking log on both sides, we get

$$2.303 \times 10 - \frac{150 \times 10^3}{8.314\text{T}} = 2.303 \times 8 - \frac{75 \times 10^3}{8.314T}$$

$$2.303 \times (10 - 8) = \frac{(150 - 75) \times 10^3}{8.314 \times T}$$

$$2.303 \times 2 = \frac{75 \times 10^3}{8.314 \times T}$$

$$T = \frac{75 \times 10^3}{2.303 \times 2 \times 8.314} = 1958.5\,\text{K}$$

Problem 3.5 For two parallel reactions of the same order, the rate constants are k_1 and k_2 and the energies of activation are E_1 and E_2, respectively. Prove that apparent overall energy of activation $E = \dfrac{k_1E_1 + k_2E_2}{k_1 + k_2}$.

Solution Let x moles of first product are formed. The number of moles of other product will be $1–x$.

Energy of activation per mole of $A = E_1$

For x mole, energy of activation = xE_1

Similarly, the energy of activation for product B = $(1 - x)\,E_2$

Thus
$$E = xE_1 + (1 - x)\,E_2$$

again
$$\frac{[\text{Product A}]}{[\text{Product B}]} = \frac{k_1/(k_1 + k_2)}{k_2/(k_1 + k_2)} = \frac{x}{(1 - x)}$$

When one mol of reactant disappears x mol of A and $(1 - x)$ moles of B are formed
$$E = \frac{k_1}{k_1 + k_2}E_1 + \frac{k_2}{k_1 + k_2}E_2 = \frac{k_1E_1 + k_2E_2}{k_1 + k_2}$$

Problem 3.6 If the initial concentration of A is 2.0 mol dm^{-3} and k_1 and k_2 are 0.30 and 0.15 min^{-1}, respectively, at what time the concentration of B in the following reaction will be maximum:

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

Also calculate the maximum concentration of B.

Solution

$$\text{Time (max)} = \frac{\ln k_1 - \ln k_2}{k_1 - k_2} = \frac{\ln(0.30) - \ln(0.15)}{(0.30) - (0.15)} = \frac{0.60}{0.15} = 4\,\text{min}$$

$$[\text{B}]_{\text{max}} = [\text{A}]_0\left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1-k_2}} = 2.0\left(\frac{0.15}{0.30}\right)^{\frac{0.15}{0.30-0.15}} = 1.0\,\text{mol dm}^{-3}$$

3.4 Steady-State Treatment

Many reactions which seem to be quite simple are indeed very complex. The reactions proceed in different steps. In such stepwise complex reactions, the overall reaction rate is determined by the slowest step among different steps. Various intermediate or unstable species are produced in different steps. Thus, a reaction involving many steps will lead to complex equations. In order to express the overall rate of a complex reaction in terms of the individual rate constants, a special treatment is required. In simple procedure, the intermediates such as the atoms and free radicals, the concentrations of which are necessarily low, are assumed to have a constant concentration during the course of reaction. According to steady-state treatment, it may be assumed that the rate of formation of intermediate is equal to its rate of disappearance, or

$$\text{net } \frac{d[\text{Intermediate}]}{dt} = 0$$

This way, simple expressions for the concentration of intermediates can be obtained and hence an equation for the overall rate can be derived.

3.5 Chain Reactions

Many reactions proceed through series of self repeating steps involving formation of active species called free radicals, as intermediates. These species either regenerate themselves or produce other active species that can carry on the reaction and are responsible for the formation of products. Such reactions are called chain reactions.

The chain reaction, in general, involves following three steps:

(*a*) *Initiation step:* In this step the intermediate or free radicals which are responsible to carry on the reaction, are formed from the ordinary molecules. For example in the reaction of H_2 and Br_2, at the first stage, the molecules of bromine are dissociated into atoms

$$Br_2 \rightarrow Br + Br \text{ (chain initiation)} \qquad \text{(i)}$$

(*b*) *Propagation step:* The initiation step is followed by reactions leading to the formation of the product with simultaneous generation of one or more reactive species. Such steps are called *propagation steps*

$$Br + H_2 \rightarrow HBr + H \qquad \text{(ii)}$$

$$H + Br_2 \rightarrow HBr + Br \qquad \text{(iii)}$$

Br atom which leads to the formation of HBr in steps (ii) and (iii) is also required to continue the cycle. These self-propagating steps are likely to continue through repeated generation of chains of H and Br atoms. Thus, for any initial Br atom, the formation of a large number of HBr would result.

(*c*) *Termination step:* The removal of the active species from the participation in the propagation steps results in breaking of the chain and stopping of the reaction. This step is called *termination step*. For example, when two Br atoms come together to unite into a Br_2 molecule, the chain is broken and stopped

$$Br + Br \rightarrow Br_2 \quad \text{(termination step)} \qquad \text{(iv)}$$

In any controlled chain reaction steps (*a*) to (c) are essentially present. However, in some chain reactions, a step, which may inhibit the process, may also be involved. This step is called *inhibition step*. For example, in Br_2

and H_2 reaction, a collision between H atom and HBr inhibit the process and inhibition step is also present

$$\mathrm{H + HBr \rightarrow H_2 + Br} \quad \text{(inhibition step)} \qquad \text{(v)}$$

3.5.1 Rate Determination

Let us consider a general chain reaction

$$\mathrm{A} \xrightarrow{k_i} n\dot{F} \qquad \text{(initiation)} \qquad \text{(i)}$$

$$\dot{\mathrm{F}} + \mathrm{B} \xrightarrow{k_\mathrm{p}} \dot{\mathrm{F}} + \mathrm{P} \qquad \text{(propagation)} \qquad \text{(ii)}$$

$$\dot{\mathrm{F}} + \dot{\mathrm{F}} \xrightarrow{k_t} \mathrm{F}_2 \qquad \text{(termination)} \qquad \text{(iii)}$$

Now,

$$\text{Rate of initiation} = \frac{d[\dot{\mathrm{F}}]}{dt} = -\frac{d[\mathrm{A}]}{dt} = nk_i[\mathrm{A}] \qquad (3.26)$$

$$\text{Rate of propagation} = \frac{d[\mathrm{P}]}{dt} = k_\mathrm{p}[\dot{\mathrm{F}}][\mathrm{B}] \qquad (3.27)$$

which is also rate of formation of product

$$\text{Rate of termination} = 2k_t[\dot{\mathrm{F}}] \qquad (3.28)$$

For determination of the rate of formation of product, the concentration of intermediate free radical, i.e. $[\dot{\mathrm{F}}]$ must be known. For determination of $[\dot{\mathrm{F}}]$, the steady state approximation with respect to $[\dot{\mathrm{F}}]$ can be applied, since it is usually present in very small concentrations. According to steady state approximation, the rate of formation of intermediate must be equal to rate of its disappearance.

Since $\dot{\mathrm{F}}$ is formed in above steps (i) and (ii) and disappears in steps (ii) and (iii), therefore

$$nk_i\,[\mathrm{A}] + k_p[\dot{\mathrm{F}}][\mathrm{B}] = k_p[\dot{\mathrm{F}}][\mathrm{B}] + 2k_t[\dot{\mathrm{F}}]^2$$

Hence,
$$[\dot{\mathrm{F}}] = \left(\frac{nk_i[\mathrm{A}]}{2k_t}\right)^{1/2} \qquad (3.29)$$

On substituting the value of $[\dot{\mathrm{F}}]$ in equation (3.27), the rate of propagation step can be given as

$$\text{Rate of propagation} = k_p\left(\frac{nk_i}{2k_t}\right)^{1/2}[\mathrm{A}]^{1/2}[\mathrm{B}] \qquad (3.30)$$

3.5.2 Reaction between H_2 and Br_2

Consider the following reactions:

$$Br_2 \xrightarrow{k_i} Br + Br \tag{i}$$

$$Br + H_2 \xrightarrow{k_{p_1}} HBr + H \tag{ii}$$

$$H + Br_2 \xrightarrow{k_{p_2}} HBr + Br \tag{iii}$$

$$H + HBr \xrightarrow{k_{\text{inh}}} H_2 + Br \tag{iv}$$

$$Br + Br \xrightarrow{k_t} Br_2$$

Rate of formation of product

$$\frac{d[\text{HBr}]}{dt} = k_{p_1}[\text{Br}][\text{H}_2] + k_{p_2}[\text{H}][\text{Br}_2] - k_{\text{inh}}[\text{H}][\text{HBr}] \tag{a}$$

For determination of rate of reaction, [Br] and [H] must be known and can be determined by applying steady state approximation with respect to [H] and [Br], respectively.

On applying the steady state approximation with respect to [H], we get

$$k_{\text{p}_1}[\text{Br}][\text{H}_2] = k_{\text{p}_2}[\text{H}][\text{Br}_2] + k_{\text{inh}}[\text{H}][\text{HBr}] \tag{b}$$

or

$$[\text{H}] = \frac{k_{\text{p}_1}[\text{Br}][\text{H}_2]}{k_{\text{p}_2}[\text{Br}_2] + k_{\text{inh}}[\text{HBr}]} \tag{c}$$

Applying the steady state with respect to [Br], we get

$$k_{\text{i}}[\text{Br}_2] + k_{\text{p}_2}[\text{H}][\text{Br}_2] + k_{\text{inh}}[\text{H}][\text{HBr}] = k_{\text{t}}[\text{Br}]^2 + k_{\text{p}_1}[\text{Br}][\text{H}_2] \tag{d}$$

From equations (b) and (c), we get

$$k_{\text{i}}[\text{Br}_2] = k_{\text{t}}[\text{Br}]^2$$

or

$$[\text{Br}] = \left(\frac{k_{\text{i}}}{k_{\text{t}}}\right)^{1/2}[\text{Br}_2]^{1/2} \tag{e}$$

Substituting the value of [Br] in equation (c), the value of [H] becomes

$$[\text{H}] = \frac{k_{\text{p}_1}(k_{\text{i}}/k_{\text{t}})^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2]}{k_{\text{p}_2}[\text{Br}_2] + k_{\text{inh}}[\text{HBr}]} \tag{f}$$

Again, from equations (a) and (b), we get

$$\frac{d[\text{HBr}]}{dt} = 2k_{\text{p}_2}[\text{H}][\text{Br}_2] \tag{g}$$

Substituting the value of [H] from equation (f), the rate of reaction becomes

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_{\text{p}_1} k_{\text{p}_2} (k_\text{i}/k_\text{t})^{1/2} [\text{Br}_2]^{3/2} [\text{H}_2]}{k_{\text{p}_2} [\text{Br}_2] + k_{\text{inh}} [\text{HBr}]}$$

or
$$\frac{d[\text{HBr}]}{dt} = \frac{2k_{\text{p}_1} k_{\text{p}_2} (k_\text{i}/k_\text{t})^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2]}{1 + k_{\text{inh}} [\text{HBr}]/k_{\text{p}_2} [\text{Br}_2]} \tag{3.31}$$

3.5.3 Chain Length

The average number of chain propagation steps taking place for every single chain carrier generated in the initiation step is called the *chain length* and can be measured by determining the ratio of overall rate of propagation reaction to the rate of initiation step, i.e.

$$\text{Chain length} = \frac{\text{Rate of propagation}}{\text{Rate of initiation}} \tag{3.32}$$

3.5.4 Chain Transfer Reactions

Sometimes in chain reactions, the active species are free radicals, which are initially formed and reacts with a reactant molecule to give a new active species. This active species in turn reacts again with a reactant molecule to form yet another new active species. This way, at every stage of propagation, a new active species of higher molecular weight is formed. The mutual combination of two chain carriers or inactivation of a chain carrier may cause the termination of the chain. Such type of reactions are called *chain transfer reactions*. Polymerization involving free radicals in propagation are good examples of such reactions. The general mechanism is given as

$$\dot{\text{F}}_2 \xrightarrow{k_\text{i}} \dot{\text{F}} + \dot{\text{F}} \qquad \text{initiation}$$

$$\left.\begin{array}{l} \dot{\text{F}} + \text{A} \xrightarrow{k_{\text{p}1}} \text{A}\dot{\text{F}} \\ \text{A}\dot{\text{F}} + \text{A} \xrightarrow{k_{\text{p}2}} \text{A}_2\dot{\text{F}} \\ \cdots\cdots\cdots\cdots\cdots \\ \text{A}_{n-1}\dot{\text{F}} + \text{A} \xrightarrow{k_{\text{p}n}} \text{A}_n\dot{\text{F}} \end{array}\right\} \qquad \text{propagation}$$

$$\text{A}\dot{\text{F}} + \text{A}\dot{\text{F}} \xrightarrow{k_\text{t}} (\text{AF})_2 \qquad \text{termination}$$

3.5.5 Branching Chain Explosions

Some reactions proceed explosively. The explosion are of two types (i) thermal explosion and (ii) explosion depends on chain reaction. The basic reason for a thermal explosion is the exponential dependence of reaction rate on the temperature. In an exothermic reaction, if the evolved energy cannot escape, the temperature of the reaction system increases and this accelerates the rate of reaction. The increase in reaction rate produces heat at an even greater rate. As the heat cannot escape, hence the reaction is even faster. This process continues and an explosion occurs.

The other basic type of explosion depends on a chain reaction. In some chain reactions, each chain carrier produces more than one free radical in propagation steps resulting in a rapid increase in the concentration of active species with time with a consequent rapid increase in the reaction rate. This in turn would further increase the production of free radicals. The reaction thus occurs instantaneously and an explosion takes place. The chain is called to *branch* when an active species or chain carrier produces more than one free radical or carrier, e.g.

$$\mathrm{H_2 \rightarrow H + H} \qquad \text{(chain initiation)} \qquad \text{(a)}$$

$$\left.\begin{array}{l} \mathrm{H + O_2 \rightarrow OH + O} \\ \mathrm{O + H_2 \rightarrow OH + H} \end{array}\right\} \qquad \text{(chain branching)} \qquad \text{(b)}$$

$$\mathrm{OH + H_2 \rightarrow H_2O + H} \qquad \text{(chain propagation)} \qquad \text{(c)}$$

In (b) and (c), it can be seen that from each H atoms, two radicals O and H are produced which propagate the chain. Thus, a branching of chain occurs. When reactions proceed to some extent, the amount of free radicals would be very large and an explosion would occur. The free radicals may also be destroyed mainly by collision with the walls.

Below a certain pressure, the reaction takes place slowly and smoothly. At low pressure, the active species or radicals reach the surface easily and get destroyed. The rate of destruction of radicals counter balances the increase of formation of radicals from branching of the chain. Hence, the reaction proceeds smoothly.

On increasing the pressure, the rate of diffusion of the radicals to the walls decreases and therefore the rate of destruction of radicals also slows down while the rate of propagation and branching increases. Thus due to a considerable rise in concentration of radicals the rate of reaction increases enormously leading to an explosion. This is called *lower explosion limit* and depends upon the size and shape of the vessel.

On further increasing the pressure, the radicals more readily destroy internally in the gas than at the walls. This results in the removal of the active species or radicals and any increase in production of radicals is again counter balanced. The reaction, therefore, proceeds smoothly. The third limit is due to thermal explosion. In exothermic reactions when the reaction is carried out in closed space, the heat generated cannot be dissipated. The reaction rate suddenly becomes very rapid and a thermal explosion occurs. These limits are shown in Fig. 3.2

3.5.6 Kinetics of Branching Chain Explosion

Let n be the number of chain carrier or radicals formed from each initial radical ($\dot{\mathrm{F}}$) which is produced from the reactant A. Then the mechanism, in general, will be as follows:

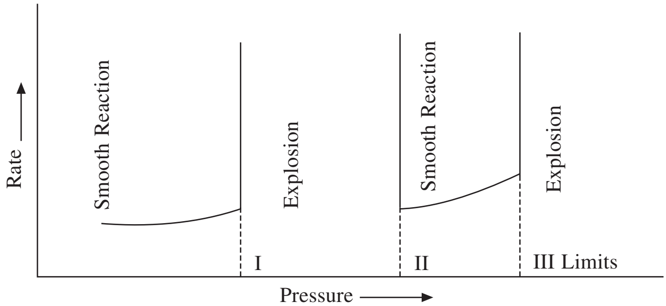


Fig. 3.2 Explosion in branching chain reactions.

$$A \xrightarrow{k_i} \dot{F}$$

$$A + \dot{F} \xrightarrow{k_p} P + n\dot{F}$$

$$\dot{F} \xrightarrow{k_t} \text{Destruction}$$

The termination constant k_t involves two rate constants, i.e. rate constants, due to gas phase destruction k_g and rate constant due to wall destruction k_w. For smooth reaction the steady state conditions with respect to $\dot{F}$ should prevail.

On applying the steady state conditions with respect to $\dot{F}$, we get

$$k_i[A] + nk_p\,[A][\dot{F}] = k_p[A][\dot{F}] + k_t[\dot{F}]$$

or

$$[\dot{F}] = \frac{k_i[A]}{k_t + k_p[A](1-n)} \tag{3.33}$$

For reactions, where $n = 1$

$$[\dot{F}] = \frac{k_i[A]}{k_t} = k''[A] \tag{3.34}$$

When $n > 1$, the branching of chain is involved. If n is large enough so that $k_t = k_p\,[A]\,(n-1)$, $[\dot{F}]$ tends to infinity and explosion occurs.

At low pressure k_w is large and $(k_w + k_g)$, i.e. $k_t >> k_p\,[A]\,(1-n)$, i.e. rate of destruction is greater than rate of formation of intermediate species and reaction occurs smoothly.

At high pressure, when k_w falls, the rate of formation of reactive species becomes large, i.e., $k_p\,[A]\,(1-n) > k_t$ and explosion occurs. Further increase in pressure lowers the value of k_w but k_g will increase and again the condition of $(k_w + k_g) >> k_p\,[A]\,(1-n)$ prevails which slows down the rate.

3.5.7 Free Radical Chains

Rice, Hetzfeld and others explained the kinetic laws governing many organic reactions on the basis of chain propagation through free radicals. For example, the thermal decomposition of acetaldehyde, decomposition of ethane etc.

(*a*) *Thermal decomposition of acetaldehyde*: The following mechanism in which formation of methyl radical is involved in initiation step has been proposed for thermal decomposition of acetaldehyde:

$$\begin{array}{rll}
\text{(i)} & CH_3CHO \xrightarrow{k_1} \dot{C}H_3 + \dot{C}HO & \text{initiation} \\
\text{(ii)} & \dot{C}HO \xrightarrow{k_2} CO + H & \\
\text{(iii)} & H + CH_3CHO \xrightarrow{k_3} H_2 + \dot{C}H_3CO & \\
\text{(iv)} & \dot{C}H_3CO \xrightarrow{k_4} CH_3 + CO & \multirow{2}{*}{\} \text{ propagation}} \\
\text{(v)} & \dot{C}H_3 + CH_3CHO \xrightarrow{k_5} CH_4 + CH_3CO & \\
\text{(vi)} & 2\dot{C}H_3 \xrightarrow{k_6} C_2H_6 & \\
\text{(vii)} & \dot{C}H_3 + \dot{C}H_3CO \xrightarrow{k_7} CH_3COCH_3 & \} \text{ termination} \\
\text{(viii)} & 2\dot{C}H_3CO \xrightarrow{k_8} CH_3COCOCH_3 &
\end{array}$$

Applying the steady state treatment for CHO and H, we get

$$k_1[CH_3CHO] = k_2[\dot{C}HO]$$

and
$$k_2[\dot{C}HO] = k_3[H][CH_3CHO]$$

Therefore,

$$[H] = k_1/k_3 \qquad \text{(a)}$$

From steady state treatment for $[\dot{C}H_3]$ and $[\dot{C}H_3CO]$, we get

$$k_1[CH_3CHO] + k_4[\dot{C}H_3CO] = k_5[CH_3][CH_3CHO] + k_6[\dot{C}H_3]^2 + k_7[\dot{C}H_3][CH_3CO] \qquad \text{(b)}$$

and

$$k_3[H][CH_3CHO] + k_5[\dot{C}H_3][CH_3CHO] = k_4[\dot{C}H_3CO] + k_7[\dot{C}H_3]\,[\dot{C}H_3CO] + k_8[\dot{C}H_3CO]^2 \qquad \text{(c)}$$

It is probable that the $\dot{C}H_3$ radical is the most abundant chain carrier and therefore, neglecting steps (vii) and (viii), the equation may be written as

$$k_1[CH_3CHO] + k_4[\dot{C}H_3CO] = k_5[\dot{C}H_3][CH_3CHO] + k_6[\dot{C}H_3]^2 \qquad \text{(d)}$$

$$k_3\left(\frac{k_1}{k_3}\right)[CH_3CHO] + k_5[\dot{C}H_3][CH_3CHO] = k_4[\dot{C}H_3CO] \qquad \text{(e)}$$

where $[H] = k_1/k_3$ (equation (a)).

From equations (d) and (e), we get

$$[\dot{C}H_3] = \left\{\frac{2k_1[CH_3CHO]}{k_6}\right\}^{1/2} \tag{f}$$

The rate of disappearance of acetaldehyde may be given as

$$-\frac{d[CH_3CHO]}{dt} = k_1[CH_3CHO] + k_3[H][CH_3CHO] + k_5[\dot{C}H_3][CH_3CHO]$$

$$= k_1[CH_3CHO] + k_3(k_1/k_3)\,[CH_3CHO]$$

$$+ k_5\left\{\frac{2k_1[CH_3CHO]}{k_6}\right\}^{1/2}[CH_3CHO]$$

$$= 2k_1[CH_3CHO] + k_5\left(\frac{(2k_1)}{k_6}\right)^{1/2}[CH_3CHO]^{3/2} \tag{g}$$

If step (i) is relatively slow, the rate law (g) reduces to

$$-\frac{d[\text{acetaldehyde}]}{dt} = k''\,[CH_3CHO]^{3/2} \tag{h}$$

where $k'' = k_5\left(\frac{2k_1}{k_6}\right)^{1/2}$.

Therefore, the order of the reaction is 1.5, which has been observed experimentally.

(*b*) *Decomposition of ethane*: Pease (1928) proposed the following chain radical mechanism for decomposition of ethane:

(i) $C_2H_6 \xrightarrow{k_1} \dot{C}H_3 + \dot{C}H_3$ (initiation)

(ii) $\dot{C}H_3 + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5$

(iii) $C_2H_5 \xrightarrow{k_3} C_2H_4 + H$

(iv) $H + C_2H_6 \xrightarrow{k_4} C_2H_5 + H_2$ } (propagation)

(v) $H + C_2H_5 \xrightarrow{k_5} C_2H_6$ (termination)

Applying steady state conditions for $[CH_3]$, we get

$$k_1[C_2H_6] = k_2\,[\dot{C}H_3]\,[C_2H_6]$$

Therefore $$[\dot{C}H_3] = k_1/k_2 \tag{a}$$

Again applying steady state conditions for $[C_2H_5]$ and $[H]$, we get

$$k_2[\dot{C}H_3][C_2H_6] + k_4[H][C_2H_6] = k_3[C_2H_5] + k_5[H][C_2H_5] \tag{b}$$

and $$k_3[C_2H_5] = k_4[H]\,[C_2H_6] + k_5[H]\,[C_2H_5] \tag{c}$$

From equations (a), (b) and (c), we can get

$$2k_5\ [\mathrm{H}]\ [\mathrm{C_2H_5}] = k_1[\mathrm{C_2H_6}] \tag{d}$$

and

$$k_3\ [\mathrm{C_2H_5}] = k_1\ [\mathrm{H}]\ [\mathrm{C_2H_6}] \tag{e}$$

Dividing equation (d) by (e), we get

$$\frac{2k_5}{k_3} = \frac{1}{[\mathrm{H}]}$$

or

$$[\mathrm{H}] = \left(\frac{k_3}{2k_5}\right)^{1/2} \tag{f}$$

Therefore, $[\mathrm{C_2H_5}]$ can be obtained as

$$[\mathrm{C_2H_5}] = \frac{k_1}{k_3}[\mathrm{H}][\mathrm{C_2H_6}] \quad \text{(from equation (e))}$$

$$= \frac{k_1}{k_3}\left(\frac{k_3}{2k_5}\right)^{1/2}[\mathrm{C_2H_6}] \tag{g}$$

Now, rate of reaction is given as

$$\frac{d[\mathrm{C_2H_4}]}{dt} = k_3[\mathrm{C_2H_5}]$$

$$= k_3\frac{k_1}{k_3}\left(\frac{k_3}{2k_5}\right)^{1/2}[\mathrm{C_2H_6}] \quad \text{(from equation (g))}$$

$$= k_1\left(\frac{k_3}{2k_5}\right)^{1/2}[\mathrm{C_2H_6}] = k[\mathrm{C_2H_6}] \tag{h}$$

where $k = k_1\ (k_3/2k_5)^{1/2}$. Hence, the reaction is first order.

3.5.8 Chain Length and Activation Energy in Chain Reactions

The chain length of chain reaction is defined as follows:

$$\text{Chain length} = \frac{\text{Rate of overall reaction}}{\text{Rate of initiation}}$$

For example, in case of thermal decomposition of acetaldehyde

$$\text{Chain length} = \frac{k_5(2k_1/k_6)^{1/2}[\mathrm{CH_3CHO}]^{3/2}}{k_1[\mathrm{CH_3CHO}]} = k_5\left(\frac{2}{k_1k_6}\right)^{1/2}[\mathrm{CH_3CHO}]^{1/2}$$

The energy of activation in such chain reactions can be evaluated from those of the individual steps in the process. For example, in decomposition of acetaldehyde, we have

$$-\frac{d[\text{acetaldehyde}]}{dt} = k_5\left(\frac{2k_1}{k_6}\right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

$$= \sqrt{2}.A_5.e^{-E_5/RT}\left(\frac{A_1e^{-E_1/RT}}{A_6e^{-E_6/RT}}\right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2} \text{ (can be written as)}$$

where A_1, A_5 and A_6 are frequency factors and E_1, E_5 and E_6 are the activation energies for the corresponding steps (i), (v) and (vi), respectively.

Or

$$-\frac{d[\text{acetaldehyde}]}{dt} = \sqrt{2}.A_5\left(\frac{A_1}{A_6}\right)^{1/2} e^{-(2E_5+E_1-E_6/2RT)}[\text{CH}_3\text{CHO}]^{3/2}$$

Therefore, E_{act} for overall reaction is

$$E_{\text{overall}} = \tfrac{1}{2}\ [2E_5 + E_1 - E_6]$$

Problem 3.7 (Chain Reaction) The thermal decomposition of acetone is found to follow the rate law as

$$-\frac{d[\text{acetone}]}{dt} = \left(\frac{k_\text{i}}{k_\text{t}}\right)^{1/2} k_\text{p}[\text{acetone}]$$

and E_{act} for initiation, propagation and termination steps are 350, 200 and 50 kJ mol^{-1}, respectively. Calculate overall E_{act}.

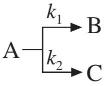
Solution

$$(E_{\text{act}})_{\text{overall}} = \frac{1}{2}[(E_{\text{act}})_{\text{ini}} - (E_{\text{act}})_{\text{termi}}] + (E_{\text{act}})_{\text{pro}} = \frac{1}{2}[350 - 50] + 200$$

$$= 150 + 200 = 350 \text{ kJ mol}^{-1}$$

EXERCISES

1. Determine the values of rate constants k_1 and k_2 in the following reactions:

   (a) 

   (b) $\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C}$

   (c) $\text{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{B}$

2. Discuss the mechanism of the following reaction

$$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$$

   and show that

$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k''[\text{HBr}]/[\text{Br}]}$$

3. What is meant by steady state approximation? Determine the rate law, i.e. $\frac{d[\mathrm{P}]}{dt}$ in the following reaction, using the steady state approximation:

$$\mathrm{A + B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{I_1}$$

$$\mathrm{I_1 + C} \xrightarrow{k_3} \mathrm{I_2}$$

$$\mathrm{I_2} \xrightarrow{k_4} \mathrm{P}$$

What will be $\frac{d[\mathrm{P}]}{dt}$ if,

(i) $k_2 >> k_3$
(ii) $k_3 >> k_2$

4. Following is the decomposition of O_3 in the mechanisms

$$\mathrm{O_3 \rightleftharpoons O_2 + O \ (fast)}$$

$$\mathrm{O + O_2 \rightarrow 2O_2 \ (slow)}$$

Show that $-\frac{d[\mathrm{O_3}]}{dt} = k\frac{[\mathrm{O_3}]^2}{\mathrm{O_2}}$.

5. In reaction

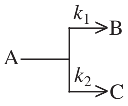
$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

show that $$[\mathrm{B}]_{\max} = [\mathrm{A}]_o\left(\frac{k_2}{k_1}\right)^{k_2/(k_1-k_2)}$$

and $$t_{\max} = \frac{\ln(k_1/k_2)}{k_1 - k_2}$$

where $t_{\max}$ is the time at which concentration of B is maximum.

6. In reaction



show that [B] : [C] = $k_1 : k_2$.

7. A reaction has following mechanism:

$$\mathrm{A + B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{I_1 + I_2 \ (fast)}$$

$$\mathrm{I_1 + B} \xrightarrow{k_3} \mathrm{P_1 + I_2 \ (slow)}$$

$$\mathrm{2I_2} \xrightarrow{k_4} \mathrm{P_2}$$

where A and B are reactants, P_1 and P_2 are products, I_1 and I_2 are reaction intermediates. Find rate of reaction in terms of reactants and total order of reaction.

8. For reaction $\mathrm{A} \xrightarrow{k_1} \mathrm{B} \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \mathrm{C}$; k_2 is twice the value of k_3. Show that at the completion of reaction the ratio [B] : [C] will be 1/3 : 2/3.

9. Consider the following mechanism:

$$H_2\text{ (Para)} \xrightarrow{k_1} 2H^0\text{ (initiation)}$$

$$H^0 + H_2\text{ (Para)} \xrightarrow{kp} H_2\text{ (ortho)} + H^*\text{ (propagation)}$$

$$H^0 + H^0 \xrightarrow{k_i} H_2\text{ (termination)}$$

Determine the rate of propagation, chain length and E_{act} for the reaction.

10. One mole of reaction gives two moles of the product $\left(A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2B\right)$, where $k_f = 2.0 \times 10^{-2}\ s^{-1}$ and $k_b = k_f$. If the initial concentration of reaction, i.e. $[A]_0 = 2.0$ mol dm^{-3}, at what time the concentration of product will be 1.0 mole dm^{-3}.

4

Theories of Reaction Rate

4.1 Equilibrium and Rate of Reaction

The feasibility (i.e. direction and extent of the chemical change) and mechanism (i.e. study of rate and factors effecting it) are two important aspects, which should be distinguished clearly while considering a chemical reaction. There is no simple connection between the two aspects. For a general reaction

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium constant is defined as

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K_c does not depend on concentrations but depends on temperature. At the given temperature, if the equilibrium concentrations of C and D are higher than those of A and B and indicates high value of K_c, then A and B have reacted to a considerable extent. On the other hand, if K_c is small, there will be little of C and D at equilibrium. Thus, the extent of chemical reaction is determined by equilibrium constant and is not related in any simple way to the rate or velocity of reaction with which the chemical change takes place. The reaction between two reactants may occur to almost completion, but the time for even very small fraction of the molecules to react may be extremely long.

The theory of equilibrium is treated on the basis of thermodynamics considering only the initial and final states. Time or intermediate states have no concern. However, there is a close relationship between the theory of rates and the theory of equilibria, in spite of there being no general relation between equilibrium and rate of reaction. A good approximation of equilibrium can be regarded between the reactants and activated state and the concentration of activated complex can, therefore, be calculated by ordinary equilibrium theory and probability of decomposition of activated complex and hence the rate of reaction can be known.

4.2 Partition Functions and Statistical Mechanics of Chemical Equilibrium

Partition function Q per unit volume of a molecule represent the energy increase at absolute zero temperature when molecule reacts and is defined as

$$Q = \Sigma_{\mathrm{i}}\, g_{\mathrm{i}} e^{-e_{\mathrm{i}}/k_{\mathrm{b}}T} \tag{4.1}$$

where k_{b} is the Boltzmann constant, e_{i} is the energy with respect to zero point energy for a given energy state of the molecule and g_{i} the number of states corresponding to that level. Since the energy include electronic E_{e}, transitional E_{t}, vibrational E_{v} and rotational energy E_{r}, we have

$$e_{\mathrm{i}} = E_{\mathrm{e_i}} + E_{\mathrm{t_i}} + E_{\mathrm{r_i}} + E_{\mathrm{v_i}} \tag{4.2}$$

The partition function, therefore, becomes

$$Q = \sum_{\mathrm{i}} g_{\mathrm{e_i}} e^{-E_{e_{\mathrm{i}}}/k_{\mathrm{b}}T}\, g_{\mathrm{t_i}} e^{-E_{\mathrm{t_i}}/k_{\mathrm{b}}T}\, g_{\mathrm{v_i}} e^{-E_{\mathrm{v_i}}/k_{\mathrm{b}}T}\, g_{\mathrm{r_i}} e^{-E_{\mathrm{r_i}}/k_{\mathrm{b}}T} \tag{4.3}$$

Equation (4.3) can be written as

$$Q = q_{\mathrm{e}}^{\mathrm{e}} q_{\mathrm{t}}^{\mathrm{t}} q_{\mathrm{r}}^{\mathrm{r}} q_{\mathrm{v}}^{\mathrm{v}} = Q_{\mathrm{e}} Q_{\mathrm{t}} Q_{\mathrm{r}} Q_{\mathrm{v}} \tag{4.4}$$

where q_{e}, q_{t}, q_{r} and q_{v} are partition functions for each degree of freedom for electronic, translational, rotational and vibrational changes, respectively, and e, t, r and v are respective degrees of freedom.

The partition function has thus been factorised so that each term may be evaluated separately. The partition function for electronic energy is given by

$$Q_{\mathrm{i}} = \sum_{i} g_{\mathrm{e_i}} e^{-E_{e_i}/k_{\mathrm{b}}T} \tag{4.5}$$

At ordinary temperatures the excited energy levels of an atom or molecule are usually too high to make significant contribution to the partition function. If the lowest state is singlet state, the statistical weight g_{e} is unity. Thus if lowest state is taken as the zero level, the other levels are sufficiently high and the partition function is approximately unity.

For translation motion, the partition functions of each degree of freedom is given by

$$q_{\mathrm{t}} = \frac{(2\pi m k_{\mathrm{b}} T)^{1/2}}{h} \cdot l \tag{4.6}$$

where h is Planck's constant and l the distance in x-direction through which the molecule of mass m is allowed to move. For 3 degrees of freedom of translation, the product of such three functions is the partition function per unit volume for translational motion and is given by

$$Q_{\mathrm{t}} = \frac{(2\pi m k_{\mathrm{b}} T)^{3/2}}{h^3} \tag{4.7}$$

The rotational partition function is given as

$$Q_r = \frac{8\pi^2 I k_b T}{h^2} \tag{4.8a}$$

(for linear molecule which has only 2 degrees of rotational freedom) where I is the moment of inertia of the molecule and

$$Q_r = \frac{8\pi^2 (8\pi^3 ABC)^{1/2} (k_b T)^{3/2}}{h^3} \tag{4.8b}$$

(for non-linear molecule which has 3-degrees of rotational freedom) where A, B and C are the moment of inertia about three mutually perpendicular axis.

A molecule consisting of N atoms has $3N$ total degrees of freedom. Out of these $3N$ degrees of freedom, three relate to translational motion and 2 or 3 (depending on linear or nonlinear molecule, respectively) relate to rotational energy. Remainder degrees of freedom, i.e. $3N - 5$ in case of linear molecule and $3N-6$ in case of nonlinear molecule apply for vibrational energy. In diatomic molecule, which will be linear, there will be 3 degrees of freedoms for translational motion, 2 for rotational motion and $3N - 5$, i.e. $(3 \times 2) - 5 = 1$ degree of freedom for vibrational motion. The partition function for vibrational motion is

$$Q_v = \overset{i}{\Sigma}(1 - e^{-h\nu/k_b T})^{-1} \tag{4.9}$$

where ν is the vibrational frequency/sec. For a diatomic molecule partition function consists of a single function, i.e.

$$q_v = (1 - e^{-h\nu/k_b T})^{-1} \tag{4.10}$$

Table 4.1 gives the expressions for partition functions and approximate order of magnitude.

Table 4.1 Partition functions

Motion	Degree of freedom	Partition function	Order of magnitude
Translational	3	$(2\pi m k_b T)^{1/2}/h^3$	10^{24}-10^{25}
Rotational linear	2	$8\pi^2 I k_b T/h^2$	10-10^2
Non linear	3	$8\pi^2(8\pi^3 ABC)^{1/2}(k_b T)^{3/2}/h^3$	10^2-10^3
Vibrational	1	$(1 - e^{-h\nu/k_b T})^{-1}$	1-10
Restricted rotation	1	$(8\pi^2 I k_b T)^{3/2}/h$	1-10

The equilibrium constant, for a general reaction

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

in terms of partition function may be written as

$$K_c = \frac{Q_C^c \, Q_D^d}{Q_A^a \, Q_B^b} \, e^{-E_0/RT} \tag{4.11}$$

where Q's are the partition functions per unit volume of the molecules A, B, C and D and E_0 is the energy increase at the absolute zero when a moles of A react with b moles of B, to give c moles of C and d moles of D, all substances being in their standard states.

Since the energy is the amount of energy that the reactant must acquire at 0°K, before they can react, E_0 is the hypothetical energy of activation at this temperature. The partition functions in this expression must be evaluated with respect to zero point levels of the respective molecules.

4.3 Partition Functions and Activated Complex

Let us consider a equilibrium between reactants and activated complex as follows:

$$\mathrm{A} + \mathrm{B} \xrightleftharpoons{K^{\neq}} X^{\neq}$$

• Number of atoms	N_A	N_B	$(N_A + N_B)$
• Total degree of freedom	$3N_A$	$3N_B$	$3(N_A + N_B)$
• Translational degree of freedom	3	3	3
• Rotational degree of freedom	2	2	2 (for linear molecules)
	3	3	3 (for linear molecules)
• Vibrational degree of freedom	$3N_A - 5$	$3N_B - 5$	$3(N_A + N_B) - 6$ (linear mole)
	$3N_A - 6$	$3N_B - 6$	$3(N_A + N_B) - 7$ (non-linear mole)

The equilibrium constant for formation of activated complex ($K^{\neq}$) is given by

$$K^{\neq} = \frac{[X^{\neq}]}{[\mathrm{A}][\mathrm{B}]} \tag{4.12}$$

This equilibrium constant in terms of the appropriate partition functions can be written as

$$K^{\neq} = \frac{Q^{\neq}}{Q_A Q_B} e^{-E_0/RT} \tag{4.13}$$

In activated complex, one degree of vibration has been considered of a different character from the rest, since it corresponds to a very loose vibration which allows the complex to dissociate into products. Hence, this vibrational degree of freedom will vanish during the dissociation of complex into the products. In case of activated complex the vibrational degrees of freedom, therefore, have been taken as $3(N_A + N_B) - 6$ (when molecule is linear) or $3(N_A + N_B) - 7$ (when molecule is nonlinear) in place of $3(N_A + N_B) - 5$ or $3(N_A + N_B) - 6$.

Since the vibrational partition function is given by $(1 - e^{-h\nu/k_bT})^{-1}$, the value of this function when $\nu \to$ zero, becomes

$$\lim_{\nu \to 0} \frac{1}{1 - e^{-h\nu/k_bT}} = \frac{1}{1 - (1 - h\nu/k_bT)} = \frac{k_bT}{h\nu} \tag{4.14}$$

where only first term has been taken in expansion.

The term $k_bT/h\nu$ should be included in the equilibrium constant given by equation (113). Therefore, the equation becomes

$$K^{\neq} = \frac{[X^{\neq}]}{[A][B]} = \frac{k_bT}{h\nu} \frac{Q^{\neq}}{Q_AQ_B} e^{-E_0/RT} \tag{4.15}$$

The concentration of activated complex is given by the following equation:

$$[X^{\neq}] = \frac{k_bT}{h\nu} \frac{Q^{\neq}}{Q_AQ_B} e^{-E_0/RT} [A][B] \tag{4.16}$$

4.4 Collision Theory

According to collision theory, the collision between the reactant molecules is the first step in the chemical reaction. The rate of reaction will be proportional to the number of collisions per unit time between the reactant, but it has been observed that not every collision between the reactant molecules results in a reaction. When we compare the calculated number of collisions per second with the observed reaction rate, we find that only a small fraction of the total number of collisions is effective. There can be following reasons why a collision may not be effective.

(i) During the collisions some of the molecules having low energy (less than the energy of activation) are not capable of undergoing transformation. This can be understood with the help of energy-reaction coordinate diagram shown in Fig. 4.1.

If the sufficient energy ($\approx E_{act}$) has been provided to the reactants and the reactants have reached at energy level A, i.e. energy of activated complex, the collision between the reactants will result in the formation of activated complex and the activated complex would yield the products. However, if reactants are not having sufficient energy (i.e. they are at energy level B), the collision between the reactants would not result in the formation of activated complex. Therefore, the collision will be ineffective. Thus, only those collisions, in which reactant molecules have sufficient energy ($\geq E_{act}$) are useful collisions.

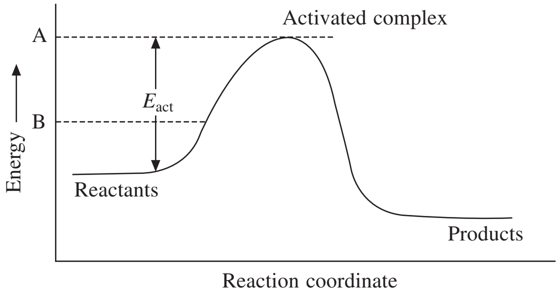


Fig. 4.1 Energy-reaction coordinate diagram.

(ii) The molecules are not properly orientated or aligned during the collisions. The importance of the proper orientation of molecules during the collision may be considered with the following example (Fig. 4.2) where alignment (a) leads to reaction while alignment (b) does not. In case (b), the molecule ⒷⒷ is not properly oriented and one B atom is far away and not capable of forming bond with any atom of A.

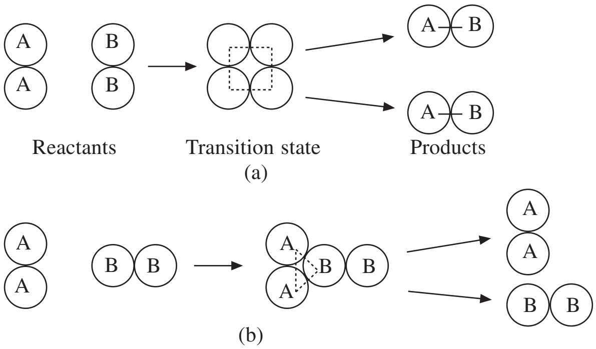


Fig. 4.2

On the basis of above discussions we can express the rate as the product of three factors as

$$\begin{array}{l}\text{Number of}\\ \text{effective}\\ \text{collisions}\\ \text{cc/sec}\end{array} = \left\{\begin{array}{l}\text{Total}\\ \text{number of}\\ \text{collisions/}\\ \text{cc/sec}\end{array}\right\} \times \left\{\begin{array}{l}\text{Fraction of}\\ \text{collisions that}\\ \text{have sufficient}\\ \text{energy } (\geq E_{act})\end{array}\right\} \times \left\{\begin{array}{l}\text{Fraction of}\\ \text{collisions that}\\ \text{have proper}\\ \text{orientation}\end{array}\right\}$$

or

Rate = {Collision frequency} × {Energy factor} × {Orientation factor}

4.4.1 Collision Frequency

If we take three molecules of reactant A and three molecules of reactant B in a container, each molecule of reactant A can collide with three molecules of reactant B and the total number of collisions between reactants A and B will be 3 × 3 = 9. The number of collisions is, therefore, proportional to the product of number of molecules of reactants, i.e.

No. of collisions ∝ (No. of molecules of A) × (No. of molecules of B)

Now let us consider the reaction between two gases A and B.

Let n_A and n_B be the number of molecules per unit volume of gases A and B, respectively. Let m_A and m_B be the masses of molecules of A and B, respectively and σ_A and σ_B be their diameters. Again, let us assume that molecule of gas A is moving with a velocity u_A and colliding with the molecule of gas B which is stationary (Fig. 4.3).

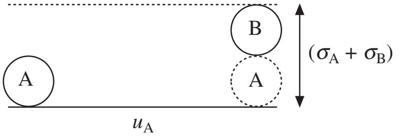


Fig. 4.3

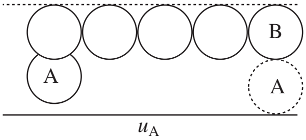


Fig. 4.4

In one second, molecule A travels a distance u_A and collides with molecule B. In traveling the distance u_A, molecule A not only collides with one molecule of B, but will collide with all the molecules of B, which are present in this distance.

Number of molecules of B present in distance $u_A = \pi\left(\frac{\sigma_A + \sigma_B}{2}\right)^2 u_A n_B$

Number of collisions/sec/cc when all the molecules of A collide with molecules of B $= \pi\left(\frac{\sigma_A + \sigma_B}{2}\right)^2 u_A n_B n_A$

However, in above derivation it has been assumed that molecules of B are stationary, which is not correct. Because the molecules of gases are moving with different velocities and cannot be assumed to be stationary. Thus, the average velocity of molecules u_A may be replaced by $\sqrt{8k_bT/\pi\mu}$, where k_b is Boltzmann's constant and μ the reduced mass given by

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$$

The number of collisions sec/cc, i.e. collision frequency may be given as

$$\text{Collision frequency} = \pi\left(\frac{\sigma_A + \sigma_B}{2}\right)\sqrt{\frac{8k_bT}{\pi\mu}}\, n_A n_B \qquad (4.17)$$

When the collision is between the molecules of a single reactant taking $\sigma_A = \sigma_B = \sigma$, $m_A = m_B = m$ and $n_A = n_B = n$, the equation reduces to

$$\text{Collision frequency} = 2\sigma^2 n^2 \sqrt{\pi k_b T/m} \qquad (4.18)$$

4.4.2 Energy Factor

At a given temperature the molecules of a substance have an average velocity and, therefore, an average kinetic energy. The average kinetic energy is characteristic of the substance. But all the molecules do not travel with the same velocity. Some molecules move faster than the average velocity while some move slower. The distribution of energy is shown in Fig. 4.5(a). The number of molecules with a particular velocity or energy is greatest for a velocity near the average and decreases as the velocity becomes longer or smaller than the average.

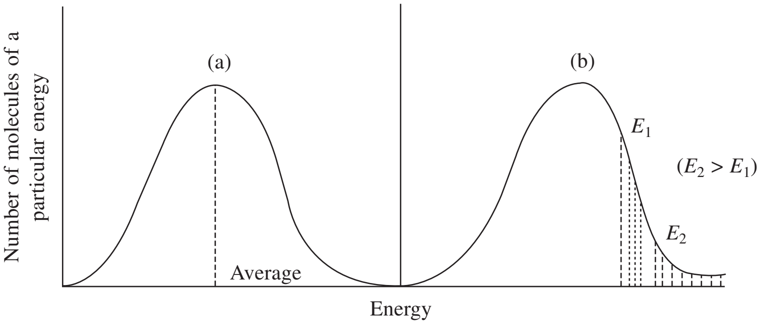


Fig. 4.5 Energy: (a) distribution and (b) collision.

The collisions of particular energies E_1 and E_2 are shown in Fig. 4.5(b). It is evident that greater the value of energy, smaller the number of molecules (hence the collisions) having that energy.

The proportion of molecules having a particular energy, at temperature T is given by the Boltzmann's factor (assuming only translational energy along two degrees of freedom) as

$$n_i/n_0 = \frac{\text{Number of molecules having energy } E_i}{\text{Total number of molecules}} = e^{-E_i/RT}$$

Therefore, if n_0 is total number of molecules of the reaction, the n number of molecules having energy $\geq E_{act}$ can be given as

$$n/n_0 = e^{-E_{act}/RT}$$

Since the number of collisions is directly proportional to the number of molecules, we get

$$Z/Z_0 = n/n_0 = e^{-E_{act}/RT}$$

where Z_0 is total collision and Z the effective collision in which molecules have energy $\geq E_{act}$. Thus

$$Z_{effective} = Z_0 e^{-E_{act}/RT} \tag{4.19}$$

and $e^{-E_{act}/RT}$ gives the fraction of collisions with energy $\geq E_{act}$.

A rise in temperature, of course, increases the average kinetic energy and average velocity as shown in Fig. 4.6.

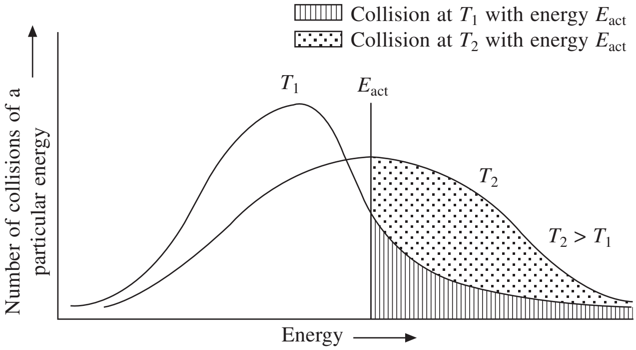


Fig. 4.6 Change in number of collisions with change in temperature.

An increase in temperature, for a given E_{act}, increases the fraction of sufficiently energetic collisions and hence increases the rate.

4.4.3 Orientation Factor

The kinetic energy of moving molecules is not the only source of energy needed for changes during the reaction. The other types of energies like vibrational energy (due to vibrations among the various atoms within the molecules), rotational energy (due to rotation of atoms with respect to each other) etc. may also be affected during the collision. Thus, the alignment of the atoms in the molecule at the time of collision is an important factor and should be considered at the time of collision. The orientation factor p (also called probability factor) depends upon the geometry of the particles and kind of reaction that is taking place. For simple atomic reactions it does not vary widely.

4.4.4 Rate of Reaction

On considering the collision frequency, energy and the probability factors discussed above, the rate of reaction by collision theory is given as

$$\text{Rate of reaction} = p \cdot z \cdot e^{-E_{act}/RT} \tag{4.20}$$

where p is the probability factor, z the collision frequency and $e^{-E_{act}/RT}$ the energy factor.

$$\text{Rate} = p\pi\left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\frac{8k_bT}{\pi\mu}}\, n_A n_B e^{-E_{act}/RT}$$

or

$$\frac{\text{Rate}}{n_A n_B} = p\pi\left(\frac{\sigma_A + \sigma_B}{2}\right)\sqrt{\frac{8k_bT}{\pi\mu}}\, e^{-E_{act}/RT}$$

or $$k\,(\text{rate constant}) = p\pi\left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\frac{8k_bT}{\pi\mu}}\, e^{-E_{act}/RT} \tag{4.21}$$

(Rate/n_An_B = Rate constant in cc/mol/sec).

Equation (4.21) gives the rate constant for a bimolecular reaction in terms of collision theory.

For simple atomic reactions ($p = 1$), the rate constant in cc/mole/sec can be given as

$$k = N\pi\left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\frac{8k_bT}{\pi\mu}}\, e^{-E_{act}/RT} \tag{4.22}$$

Comparing equation (4.22) with Arrhenius equation, i.e. $k = Ae^{-E_{act}/RT}$, the Arrhenius factor (or frequency factor) is given as

$$A = N\pi\left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\frac{8k_bT}{\pi\mu}}\ \text{liter mol}^{-1}\text{sec}^{-1} \tag{4.23}$$

The expression on right hand side of equation (4.23) is known as *collision number Z.* The frequency factor of the reaction is, therefore, identified with collision number. In reactions between two like molecules, the expression for the frequency factor becomes

$$A = 2N\sigma^2\sqrt{\frac{\pi k_bT}{m}} \tag{4.24}$$

4.4.5 Weakness of the Collision Theory

Although the collision theory of reaction rates is evidently satisfactory when applied to a number of reactions, it fails conspicuously in many cases such as rapid chain reactions, reactions involving complex molecules etc. The collision theory has been oversimplified and suffers from following weaknesses:

1. No attempt has been made to correlate the value of probability factor p with the structure and properties of the reacting molecules and it is also not possible to interpret the abnormally high rates that we sometimes observe. The value of p has been found to vary from unity to 10^{-9} when we move from simple atomic reaction to reactions involving complex molecules. There is no explanation in terms of collision theory for such a wide variation in the value of p.

Consider the reaction

$$A_2 + B_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2AB$$

From collision theory, we get

$$k_1 = p_1 Z_1 e^{-E_1/RT} \text{ (forward reaction)}$$

$$k_2 = p_2 Z_2 e^{-E_2/RT} \text{ (backward reaction)}$$

Then, the equilibrium constant

$$K = \frac{k_1}{k_2} = \frac{p_1 Z_1}{p_2 Z_2} e^{-(E_1 - E_2)/RT} \tag{4.25}$$

Again, the equilibrium constant in terms of free energy change is given as

$$K = e^{-\Delta G/RT} = e^{\Delta S/R} e^{-\Delta H/RT}, \ (\Delta G = \Delta H - T\Delta S) \tag{4.26}$$

where ΔG, ΔS and ΔH are the increase in free energy, entropy and enthalpy, respectively.

On comparing equations (4.25) and (4.26), we get

$$\frac{p_1 Z_1}{p_2 Z_2} e^{-(E_1 - E_2)/RT} = e^{\Delta S/R} e^{-\Delta H/RT} \tag{4.27}$$

If the molecules A_2, B_2 and AB are of comparable dimensions, $Z_1 = Z_2$ and also $e^{-(E_1-E_2)/RT} \approx e^{-\Delta H/RT}$. Therefore,

$$\frac{p_1}{p_2} = e^{\Delta S/R} \tag{4.28}$$

i.e. ratio of probability factor must be approximately equal to $e^{\Delta S/R}$ (entropy term). Therefore, the probability factor must be interpreted in terms of entropy consideration in a precise manner.

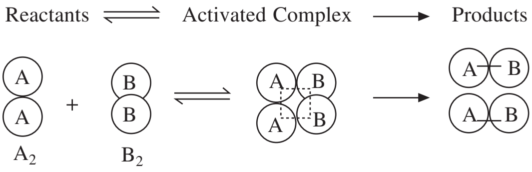
2. The reacting molecules might acquire the energy from translational, potential, vibrational and rotational energies. In collision theory, the molecules have been treated as hard spheres undergoing elastic collisions and in term $e^{-E_{\text{act}}/RT}$ only the translational energy involving two degrees of freedom has been considered. The whole kinetic energy is not involved. The molecules have a structure with rotational and vibrational degrees of freedom and they should be taken into account in considering the effective collision.

3. The intermolecular distance at which the reaction can occur may also be different from the collision diameter taken in the collision theory.

4. The collision theory is silent on the cleavage and formation of bonds involved in the reaction.

4.5 Transition State Theory

The transition state theory (also known as absolute reaction rate theory) was first given by Marcellin (1915) and then developed by Erying and Polanyi (1935). According to this theory, the reactant molecules are first transformed into intermediate transition state (also known as activated complex). The activated complex is formed by loose association or bonding of reactant molecules or by redistribution of energy. The activated complex is unstable and breaks into the products at a definite rate as follows:



1. The activated complex has been considered as a separate entity and there exists an equilibrium between reactants and activated complex.

$$A + B \overset{K^{\neq}}{\rightleftharpoons} X^{\neq} \rightarrow C + D$$

The concentration of activated complex can thus be obtained by applying the equilibrium conditions, i.e.

$$[X^{\neq}] = K^{\neq}\,[A][B] \tag{4.29}$$

where ≠ refers to the activated complex.

2. Energy of activation is the additional energy which should be supplied to the reactants in order to form activated complex or to reach at the peak of the energy barrier as shown in Fig. 4.7.

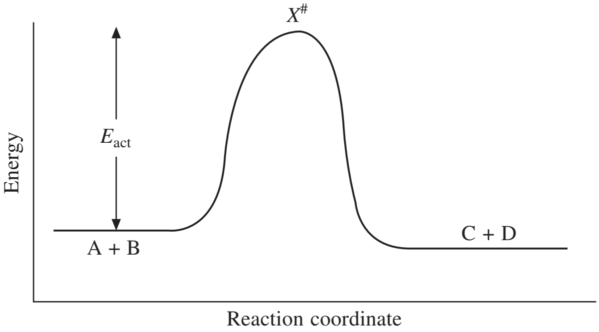


Fig. 4.7

3. One vibrational degree of freedom of activated complex is quite unstable and responsible for disrupting the activated complex (vibrating at the top of the barrier) into the products. The frequency of such vibration will be low and average energy will be of the order of k_bT, i.e.

$$E_{vib} = k_bT = h\nu$$

Therefore,

$$\nu = \frac{k_bT}{h} \tag{4.30}$$

where k_b and h are Boltzmann's and Planck's constants, respectively.

4. The rate at which the complex breaks up into the products, i.e. the rate of reaction depends on two factors: (i) concentration of the activated complex and (ii) frequency of vibration of activated complex. Hence,

$$\text{Rate of reaction} = [X^{\neq}]\,\nu \tag{4.31}$$

Substituting the values of $[X^{\neq}]$ and ν from equations (4.29) and (4.30), we get

$$\text{Rate of reaction} = \frac{k_b T}{h} K^{\neq} [\mathrm{A}][\mathrm{B}] \tag{4.32}$$

Now, if k is the rate constant for above reaction, we have

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \text{Products}$$

Experimentally

$$\text{Rate of reaction} = k[\mathrm{A}][\mathrm{B}] \tag{4.33}$$

Comparing equations (4.32) and (4.33), we get

$$k = \frac{k_b T}{h} K^{\neq} \tag{4.34}$$

Thus, rate constant for a reaction can be given by equation (4.34) in terms of equilibrium constant for the formation of activated complex $K^{\neq}$ which can be expressed either in terms of partition or thermodynamic functions.

4.5.1 Thermodynamic Approach

The equilibrium constant of a chemical reaction is related with standard free energy change ΔG^0 as

$$RT \ln K = -\Delta G^0 \tag{4.35}$$

Also $\Delta G^0 = \Delta H^0 - T\Delta S^0$ (Gibb's-Helmholtz relation).

Therefore,

$$K = e^{-(\Delta H^0 - T\Delta S^0)/RT} = e^{\Delta S^0/R} e^{-\Delta H^0/RT} \tag{4.36}$$

In the formation of activated complex, if $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are change in free energy, enthalpy and entropy, respectively, for one gram mole of the substance, then equilibrium constant

$$K^{\neq} = e^{-\Delta G^{\neq}/RT} \tag{4.37}$$

$$K^{\neq} = e^{\Delta S^{\neq}/R} e^{-\Delta H^{\neq}/RT} \tag{4.38}$$

Substituting the value of $K^{\neq}$ in equation (3.34), the rate constant

$$k = \frac{k_b T}{h} e^{-\Delta G^{\neq}/RT} \tag{4.39}$$

and
$$k = \frac{k_b T}{h} e^{\Delta S^{\neq}/R} e^{-\Delta H^{\neq}/RT} \tag{4.40}$$

Again, on taking the logarithms of equation (4.34) and differentiating with respect to T, we get

$$\ln k = \ln (k_b/h) + \ln (T) + \ln (K^{\neq})$$

or
$$\frac{d(\ln K)}{dT} = \frac{1}{T} + \frac{d(\ln K^{\neq})}{dT} \tag{4.41}$$

Again, from Arrhenius equation

$$k = Ae^{-E_{\text{act}}/RT}$$

where E_{act} is the energy of activation per mole for complex formation.

Or

$$\frac{d(\ln k)}{dT} = \frac{E_{\text{act}}}{RT^2} \tag{4.42}$$

By comparing equations (4.41) and (4.42), we get

$$\frac{E_{\text{act}}}{RT^2} = \frac{1}{T} + \frac{d(\ln K^{\neq})}{dT}$$

or
$$E_{\text{act}} = RT + RT^2 \frac{d(\ln K^{\neq})}{dT} \tag{4.43}$$

But $\frac{d(\ln K^{\neq})}{dT} = \Delta E^{\neq}/RT^2$ (Van't Hoft isochore).

Therefore,
$$E_{\text{act}} = RT + \Delta E^{\neq} \tag{4.44}$$

Again
$$\Delta E^{\neq} = \Delta H^{\neq} - \Delta nRT$$

where Δn is change in the number of molecules in going from reactants to activated complex.

Thus, equation (4.44) becomes

$$E_{\text{act}} = RT + \Delta H^{\neq} - \Delta nRT \tag{4.45}$$

If, $\Delta n = 1$, $E_{\text{act}} = \Delta H^{\neq}$ and the rate constant may be obtained by equation (4.40) replacing $\Delta H^{\neq}$ by E_{act}, i.e.

$$k = \frac{k_b T}{h} e^{\Delta S^{\neq}/R} e^{-E_{\text{act}}/RT} \tag{4.46}$$

In case $\Delta n \neq 1$, equation (4.45) may be written as

$$-\Delta H^{\neq} = -E_{\text{act}} - RT\,(\Delta n - 1)$$

and then rate constant would be

$$k = \frac{k_{\text{b}}T}{h}\, e^{\Delta S^{\neq}/R} e^{-E_{\text{act}}/RT} e^{-(\Delta n - 1)} \tag{4.47}$$

When $\Delta n = 0$, for unimolecular reaction

$$k = e\frac{k_{\text{b}}T}{h}\, e^{\Delta S^{\neq}/R} e^{-E_{\text{act}}/RT} \tag{4.48}$$

and when $\Delta n = -1$,

$$k = e^{2}\,\frac{k_{\text{b}}T}{h}\, e^{\Delta S^{\neq}/R} e^{-E_{\text{act}}/RT} \tag{4.49}$$

Thus, rate constant may be obtained by equations (4.47), (4.48) or (4.49) depending upon the value of Δn.

4.5.2 Partition Function Approach

While the concentration of activated complex in terms of partition functions is given as

$$[X^{\neq}] = \frac{Q^{\neq}}{Q_{\text{A}} Q_{\text{B}}} e^{-E_0/RT}\,[\text{A}][\text{B}]$$

The rate of reaction from transition state theory is given by equation (4.31) as

$$\text{Rate of reaction} = \{X^{\neq}\}\ \nu$$

Therefore, in terms of partition function

$$\text{Rate of reaction} = \frac{k_{\text{b}}T}{h}\frac{Q^{\neq}}{Q_{\text{A}} Q_{\text{B}}}\, e^{-E_0/RT}\,[\text{A}][\text{B}] \tag{4.50}$$

Now, experimentally the rate of reaction = k[A][B], where k is the rate constant.

Thus, the rate constant is given by equation (4.51)

$$k = \frac{k_{\text{b}}T}{h}\,\frac{Q^{\neq}}{Q_{\text{A}} Q_{\text{B}}}\, e^{-E_0/RT} \tag{4.51}$$

4.5.3 Comparison with Arrhenius Equation and Collision Theory

The rate constant for a reaction in terms of various theories is given as

$$k = Ae^{-E_{\text{act}}/RT} \text{ (Arrhenius equation)}$$

$$k = p \cdot ze^{-E_{\text{act}}/RT} \text{ (collision theory)}$$

$$k = e^{-(\Delta n-1)} \frac{k_b T}{h} e^{\Delta S^{\neq}/R} e^{-E_{act}/RT} \text{ (transition state theory)}$$

or
$$k = \frac{k_b T}{h} \frac{Q^{\neq}}{Q_A Q_B} e^{-E_0/RT}$$

Thus, comparison of these theories gives

$$A = pz = e^{-(\Delta n-1)} \frac{k_b T}{h} e^{\Delta S^{\neq}/R} \tag{4.52}$$

where A is the frequency factor and p the Steric factor.

Generally, at ordinary temperatures,

$$\frac{k_b T}{h} \approx 10^{13} \text{sec}^{-1} \text{ and } z \approx 10^{14} \text{ cc mol}^{-1}\text{sec}^{-1} \text{ and } e^{-(\Delta n-1)} \approx 10$$

Therefore,

$$p \cdot 10^{14} \approx 10.10^{13} e^{\Delta S^{\neq}/R}$$

or
$$p \approx e^{\Delta S^{\neq}/R} \tag{4.53}$$

Thus, the steric factor may be explained with the help of entropy change. When two molecules come together to produce the activated complex, the total translational degrees of freedom are reduced (from 6 to 3) and rotational degrees of freedom also diminish. This is compensated by an increase in vibrational degrees of freedom. But the definite orientation in forming the activated complex necessarily reduced the entropy, i.e. $\Delta S^{\neq}$ is negative. This decrease in entropy is small when reaction takes place between simple atoms. The calculated value of $k_b T/h \cdot e^{\Delta S^{\neq}/R}$ corresponds to collision frequency ($A \approx Z, p \approx 1$). However, there would be a large decrease in entropy when reaction involves large polyatomic molecules. The value of p being smaller (varies from 1 to 10^{-9}), the value of A would also be lower than collision frequency.

4.5.4 Explanation for Steric Factor in Terms of Partition Function

If the contributions of single translational, rotational and vibrational degrees of freedom are written as q_t, q_r and q_v respectively, the total partition function Q for a molecule is expressed as

$$Q = q_t^t q_r^r q_v^v$$

where t, r and v are the number of the degrees of freedom contribution.

For a simple reaction, atom A + Atom $B \rightleftharpoons X^{\neq}$ (a linear molecule having two atoms). Partition functions, $Q_A = q_T^3$, $Q_B = q_T^3$, $Q^{\neq} = q_T^3 q_r^2$ $X^{\neq}$ will have one less degree of vibrational freedom and, therefore, rate constant is given by

$$k = \frac{k_b T}{h} \frac{q_T^3 q_r^2}{q_T^3 q_T^3} e^{-E_0/RT} \tag{4.54}$$

or
$$k = \frac{k_b T}{h}\,\frac{q_r^2}{q_T^3}\,e^{-E_0/RT} \approx 10^{10}\,e^{-E_0/RT}$$

4.5.5 Reaction between Polyatomic Molecules

Let us consider a complex reaction

$$A + B \rightleftharpoons X^{\neq}$$

where A is the nonlinear molecule having N_A atoms, B a nonlinear molecule having N_B atoms and $X^{\neq}$ a nonlinear molecule having $(N_A + N_B)$ atoms. Then the partition functions may be given as

$$Q_A = q_T^3 q_r^3 q_v^{3N_A-6}$$

$$Q_B = q_T^3 q_r^3 q_v^{3N_B-6}$$

$$Q^* = q_T^3 q_r^3 q_v^{3(N_A+N_B)-7}$$

The activated complex has always one degree of vibrational freedom less than a normal molecule with $(N_A + N_B)$ atoms. Now, the rate constant for complex reaction

$$k = \frac{k_b T}{h}\,\frac{q_T^3 q_r^3 q_v^{3(N_A+N_B)-7}}{h(q_T^3 q_r^3 q_v^{3N_A-6})(q_T^3 q_r^3 q_v^{3N_B-6})}\,e^{-E_0/RT}$$

or
$$k = \frac{k_b T}{h}\,\frac{q_v^5}{q_T^3 q_r^3}\,e^{E_0/RT}$$

or
$$k = \frac{k_b T}{h}\,\frac{q_r^2}{q_T^3}\left(\frac{q_v}{q_r}\right)^5 e^{-E_0/RT} \tag{4.55}$$

A comparison of equations (4.54) and (4.55) shows that the rate constant for a complex reaction differs from that obtained in simple atomic reaction by a factor of $(q_v/q_r)^5$. Since q_v is nearly unity, while q_r varies from 10 to 100 for a complex molecule, the ratio q_v/q_r, therefore, varies from 10^{-1} to 10^{-2} and $(q_v/q_r)^5$ varies from 10^{-5} to 10^{-10}. This factor may link to steric factor p. On comparing equation (4.55) with collision theory and Arrhenius equation, we get

$$A = pz = \frac{k_b T}{h}\,\frac{q_r^2}{q_T^3}\left(\frac{q_v}{q_r}\right)^5 \approx 10^{10}\,(p)$$

or
$$p = [q_v/q_r]^5$$

Steric factor p varies from 10^{-5} to 10^{-10} for complicated reactions. It may, therefore, be concluded that the reactions between polyatomic molecules are slower than expected on the rigid sphere model because several rotational degrees of freedom are lost, being replaced by vibrational degrees of freedom, which have a smaller probability associated with them.

Problem 4.1 The E_{act} and pre-exponential factor for a reaction

$$A_2 + B_2 \rightleftharpoons 2AB$$

are 15.5 kJ mol^{-1} and 10.9×10^{10} dm^3 $\text{mol}^{-1}\text{sec}^{-1}$, respectively. Calculate the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ at 1000 K.

Solution

$$\Delta H^{\neq} = E_{\text{act}} - 2RT = 15.5 \text{ kJ mol}^{-1} – 2(8.314\text{J mol}^{-1}\text{K}^{-1})(1000 \text{ K})$$

$$= –1.13 \text{ kJ mol}^{-1}$$

$$A = \frac{e^2 k_b T}{h} e^{\Delta S^{\neq}/R}$$

or

$$\Delta S^{\neq} = R \ln \frac{Ah}{k_b T}$$

$$= (8.314 \text{ J mol}^{-1}\text{K}^{-1}) \ln \left\{ \frac{(6.626 \times 10^{-34} \text{ Js})(10.9\ 10^{10} \text{dm}^3 \text{mol}^{-1} \text{sec}^{-1}) \times (1.00 \text{ mol dm}^3)}{(1.38 \times 10^{-23} \text{ Jk}^{-1})(1000\text{K})} \right\}$$

$$= - 60.3 \text{ Jk}^{-1} \text{ mol}^{-1}$$

Problem 4.2 It is assumed that the values of q_t, q_v and q_r for different molecules in reaction

Atom + Linear molecule (diatomic) ⟶ Nonlinear molecule

are equal. Calculate the value of Arrhenius factor A at 298°K for above reaction, if $q_t = 10^8$, $q_r = 10$ and $q_v = 1$.

Solution

$$\underset{\text{(Arrhenius equation)}}{k = Ae^{-E_{\text{act}}/RT}} = \underset{\substack{\text{(Transition state theory in terms of}\\\text{partition function)}}}{\frac{k_b T}{h} \cdot \frac{Q^{\neq}}{Q_A Q_B} e^{-E_{\text{act}}/RT}}$$

Therefore, $$A = \frac{k_b T}{h} \frac{Q^{\neq}}{Q_A Q_B}$$

Partition function: Atom $Q_A = q_T^3$

Linear molecule $\quad Q_{\mathrm{B}} = q_{\mathrm{t}}^3 q_{\mathrm{r}}^2 q_{\mathrm{v}}$

$Q^{\neq}$ (nonlinear triatomic molecule) = $q_{\mathrm{T}}^3 q_{\mathrm{r}}^3 q_{\mathrm{v}}^{(3-1)} = q_{\mathrm{t}}^3 q_{\mathrm{r}}^3 q_{\mathrm{v}}^2$

$$A = \frac{1.38 \times 10^{-23}\,\mathrm{Jk}^{-1}\,(298\ \mathrm{K})}{6.62 \times 10^{-34}\ \mathrm{Js}} \; \frac{(10^8)^3\,(10)^3\,(1)^2}{(10^8)^3\,(10^8)^3\,(10)^2\,(1)}$$

$$= 62.12 \times 10^{-8}\ \mathrm{sec}^{-1}$$

$$= 62.12 \times 10^{-8} \times 6.02 \times 10^{23}\ \mathrm{mol}^{-1}\ \mathrm{dm}^3\ \mathrm{sec}^{-1}$$

$$= 3.79 \times 10^{10}\ \mathrm{mol}^{-1}\ \mathrm{dm}^3\ \mathrm{sec}^{-1}$$

Problem 4.3 The value of $\Delta S^{\#}$ for a reaction has been obtained as $-80.5\ \mathrm{Jk}^{-1}\ \mathrm{mol}^{-1}$ at 400 K. Find the value of A for the reaction.

Solution From transition state theory

$$k = \frac{k_{\mathrm{b}} T}{h}\, e^{\Delta S^{\#}/R}\, e^{-E_{\mathrm{act}}/RT}$$

From Arrhenius equation

$$k = A e^{-E_{\mathrm{act}}/RT}$$

$$A = \frac{k_{\mathrm{b}} T}{h}\, e^{\Delta S^{\neq}/R} = \frac{1.38 \times 10^{-23}\,\mathrm{JK}^{-1}\mathrm{mol}^{-1} \times 400\ \mathrm{K}}{6.63 \times 10^{-34}\ \mathrm{Js}}\, e^{-80.5/8.314}$$

$$= 5.189 \times 10^{8}\ \mathrm{mol}^{-1}\ \mathrm{dm}^3\mathrm{s}^{-1}$$

Problem 4.4 The pre-exponential terms for a bimolecular gas reaction occurring at 350°C is $8.0 \times 10^{10}\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$. Calculate the entropy of activation.

Solution

$$k = A e^{-E_{\mathrm{act}}/RT} \qquad \text{(Arrhenius equation)}$$

$$k = \frac{K_{\mathrm{b}} T}{h}\, e^{1-\Delta n}\, e^{\Delta S^{\neq}/R}\, e^{-E_{\mathrm{act}}/RT} \qquad \text{(transition state theory)}$$

Therefore, $\quad A = \dfrac{k_{\mathrm{b}} T}{h}\, e^{1-\Delta n}\, e^{\Delta S^{\neq}/R}$

$$\Delta n = -1 \qquad \text{(for bimolecular reaction)}$$

$$A + B \rightleftharpoons X$$

$$\log A = \log\left(\frac{K_{\mathrm{b}} T}{h}\right) + \frac{\Delta S^{\neq}}{2.303 \times 8.314}$$

$$\Delta S^{\neq} = (2.303 \times 8.314)\left[\log(8.0 \times 10^{10}) - 0.8686 - \log\frac{1.37 \times 10^{-23} \times 623}{6.62 \times 10^{-14}}\right]$$

$$= -\ 58.89\ \text{kJ K}^{-1}\ \text{mol}^{-1}$$

Problem 4.5 Taking $q_t = 10^8$, $q_{\text{rot}} = 10$ and $Q_v = 1$, calculate the value of Arrhenius factor for the following reaction at 35°C:

$$\underset{\text{A}}{\text{Atom}} + \underset{\text{B}}{\text{Linear molecule}} \rightarrow \underset{\text{AB}}{\text{Nonlinear molecule}}$$

Solution

$$k = Ae^{-E_{\text{act}}/RT}$$

$$k = \frac{K_b T}{h}\frac{Q^{\neq}}{Q_A Q_B}e^{-E_{\text{act}}/RT} \qquad \text{(from transition state theory)}$$

Therefore,

$$A = \frac{K_b T}{h}\frac{Q^{\neq}}{Q_A Q_B}(\text{cm}^3\ \text{mol}^{-1}\text{s}^{-1})$$

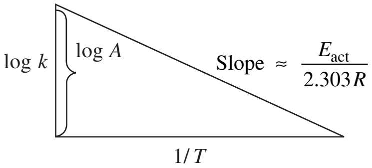
$$= \frac{1.38 \times 10^{-23}\ \text{JK}^{-1}(308\text{K})}{(6.62 \times 10^{-34}\ \text{Js})} \times \frac{(10^8)^3(10)^3 \cdot 1}{(10^8)^3(10^8)^3(10)^2(1)}$$

$$\times (10^{-3} \times 6.02 \times 10^{23})\ \text{dm}^3\ \text{mol}^{-1}\text{s}^{-1}$$

$$= 386.51 \times 10^8 = 3.86 \times 10^{10}\ \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$$

Problem 4.6 The plot of log k versus $1/T$, i.e. Arrhenius plot was linear with a negative slope 4.50×10^3 and intercept equal to 11.90 for a reaction. Calculate E_{act}, ΔH^* (at 25°C) and $\Delta S^{\neq}$.

Solution



$$\log k = \log A - \frac{E_{\text{act}}}{2.303RT}$$

$$E_{\text{act}} = 2.303 \times R \times \text{Slope}$$

$$= 2.303 \times 8.314 \times 4.50 \times 10^3 = 86.16\ \text{kJ mol}^{-1}$$

$$\Delta H^{\neq} = E_{\text{act}} - RT = 86.16 \times 10^3 - 8.314 \times 298$$

$$= 83.68\ \text{kJ mol}^{-1}$$

Again

$$A = \frac{k_b T}{h}e^{\Delta S^{\neq}/R}e^{1-\Delta n}$$

$$\log A = \log\left(\frac{k_b T}{h}\right) + \log(e^{-2}) + \frac{\Delta S^{\neq}}{2.303 \times 8.314}$$

$$\Delta S^{\neq} = (2.303 \times 8.314)\left[\log A - \log\left(\frac{k_b T}{h}\right) - 0.8686\right]$$

$$= (2.303 \times 8.314)\left[11.90 - \log\left(\frac{1.37 \times 10^{-23} \times 298}{6.62 \times 10^{-34}}\right) - 0.8686\right]$$

$$= -33.67 \text{ JK}^{-1}\text{mol}^{-1}$$

Problem 4.7 (Numerical based on collision theory) For unlike molecule

$$\text{Rate} = P\left(\frac{8\pi k_b T}{\mu}\right)^{\frac{1}{2}} d_{AB}^2 n_A n_b e^{-E_{act}/RT}$$

$$\text{Rate constant}(\text{cm}^3\,\text{mol}^{-1}\text{s}^{-1}) = P\left(\frac{8\pi k_b T}{\mu}\right)^{\frac{1}{2}} d_{AB}^2 e^{-E_{act}/RT}$$

$$\text{Rate constant}(\text{dm}^3\,\text{mol}^{-1}\text{s}^{-1}) = \frac{N_{av}}{10^3} \times \left(\frac{8\pi\pi R}{\mu}\right)^{\frac{1}{2}} d_{AB}^2 e^{-E_{act}/RT}$$

For like molecules, $n_A = n_B = n$ and $m_A = m_B = m$

$$\text{Rate} = 2P\left(\frac{\pi k_b T}{m}\right)^{\frac{1}{2}} d_{AB}^2 n^2 e^{-E_{act}/RT}$$

$$\text{Rate constant } (\text{cm}^3\ \text{mol}^{-1}\text{s}^{-1}) = 2P\left(\frac{\pi k_b T}{m}\right)^2 d_{AB}^2\, e^{-E_{act}/RT}$$

$$\text{Rate constant } (\text{dm}^3\text{mol}^{-1}\text{s}^{-1}) = 2\frac{N_{av}}{10^3}\left(\frac{\pi RT}{m}\right)^{\frac{1}{2}} d_{AB}^2\, e^{-E_{act}/RT}$$

Problem 4.8 Calculate the rate constant for decomposition of HI at 500 K, if energy of activation is 130.0 kJ mol^{-1} and collision diameter of HI is 3.5 Å.

Solution Since at every collision two molecules of HI decompose

$$k = 2 \times 2 \times \frac{N_{av}}{10^3}\left(\frac{\pi RT}{m_A}\right)^{\frac{1}{2}} d_{AB}^2\, e^{-E_{act}/RT}$$

$$= 4 \times \frac{6.023 N_0^{23}}{10^3}(3.5 \times 10^{-8})^2\left(\frac{22}{7} \times \frac{8.314 \times 10^{7500}}{128}\right)^{\frac{1}{2}} e^{-\frac{15000}{8.314\times 500}}$$

$$= 0.2553 \times 10^{10} = 2.55 \times 10^9 \text{ mol}^{-1}\text{ dm}^3\text{ s}^{-1}$$

4.6 Unimolecular Reactions and the Collision Theory

In the unimolecular reactions which are also of the first order, only one molecule takes part in the reaction. The process of activation in unimolecular reactions, if caused by collisions should ordinarily lead to second order reactions. How then the observed rate of reaction could be of first order. If however, the activation is by absorption of the radiant energy, this problem can be avoided. But many unimolecular reactions take place under conditions where there is no absorption of radiant energy. For example

$$C_4H_8 \xrightarrow{\text{Conversion}} 2C_2H_4$$

$$C_2H_5NH_2 \xrightarrow{\text{Decomposition}} C_2H_4 + NH_3$$

$$(CH_3)_2O \rightarrow CH_2 + H_2 + CO_2$$

$$CH_3NC \xrightarrow{\text{Isomerization}} CH_3CN$$

Therefore, the view of absorption of radiant energy was found to be unsatisfactory and finally rejected. Lindemann (1922) offered a solution to the problem.

4.6.1 Lindemann's Mechanism

According to Lindemann's hypothesis, the activation by collision can still give rise to first order kinetics if the activated molecules decompose only slowly compared to the rate at which they are deactivated. There is a time-log between the moment of activation and the moment of decomposition and in such a case, a stationary concentration of the activated molecules gets built up. Since the activated molecules will be in equilibrium with the normal molecules, their concentration will be proportional to that of normal molecules. The activated molecules disappear through two parallel processes, i.e. through deactivation and decomposition, represented as follows:

$$A + A \xrightarrow{k_1} A^* + A \text{ (activated)} \qquad \text{(i)}$$

$$A^* + A \xrightarrow{k_1'} A + A \text{ (deactivation)} \qquad \text{(ii)}$$

$$A^* \xrightarrow{k_2} \text{Products (decomposition)} \qquad \text{(iii)}$$

Again, we get

$$\text{Rate of activation} = \frac{d[A^*]}{dt} = k_1[A]^2$$

$$\text{Rate of deactivation} = -\frac{d[A^*]}{dt} = k_1'[A^*]\,[A]$$

$$\text{Rate of decomposition} = -\frac{d[A^*]}{dt} = k_2\,[A^*]$$

Applying the steady state conditions with respect to A^*, as the concentration of A^* is very small, we get

$$k_1[\mathrm{A}]^2 = k_1'[\mathrm{A}^*][\mathrm{A}] + k_2[\mathrm{A}^*]$$

or
$$[\mathrm{A}^*] = \frac{k_1[\mathrm{A}]^2}{k_1'[\mathrm{A}] + k_2}$$

Again, the rate of reaction $= -\dfrac{d[\mathrm{A}]}{dt} = \dfrac{d[\text{Product}]}{dt} = k_2[\mathrm{A}^*]$

Substituting the value of $[\mathrm{A}^*]$, we get

$$\text{Rate of reaction} = \frac{k_1 k_2 [\mathrm{A}]^2}{k_2 + k_1'[\mathrm{A}]} \tag{4.56}$$

At sufficiently high concentration or pressure, where $k_1'[\mathrm{A}] >> k_2$ equation (4.56) reduces to

$$\text{Rate of reaction} = \frac{k_1 k_2 [\mathrm{A}]}{k_1'} \tag{4.57}$$

Under these conditions the reaction is first order. This happens when time lag is relatively large. At very low concentrations or pressure, where $k_2 >> k_1'[\mathrm{A}]$, equation (4.56) reduces to

$$\text{Rate of reaction} = k_1[\mathrm{A}]^2 \tag{4.58}$$

and the reaction will be second order.

This behavior has been observed in many unimolecular reactions. Many first order reactions have been found experimentally to tend to the second order at a very low pressure.

Further, equation (4.56) may be written as

$$k^1 = -\frac{1}{[\mathrm{A}]}\frac{d[\mathrm{A}]}{dt} = \frac{k_1 k_2 [\mathrm{A}]}{k_2 + k_1'[\mathrm{A}]} \tag{4.59}$$

where k^1 is the first order rate coefficient.

At higher concentration where deactivation is prominent, i.e. $k_1'[\mathrm{A}] >> k_2$

$$-\frac{1}{[\mathrm{A}]}\frac{d[\mathrm{A}]}{dt} = \frac{k_1 k_2}{k_1'} = \text{Constant}$$

at low concentrations, when $k_2 >> k_1'[\mathrm{A}]$, it becomes

$$-\frac{1}{[\mathrm{A}]}\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}]$$

Therefore, a plot of $-\dfrac{1}{[\mathrm{A}]}\dfrac{d[\mathrm{A}]}{dt}$ versus [A] will be a curve as shown in Fig. 4.8.

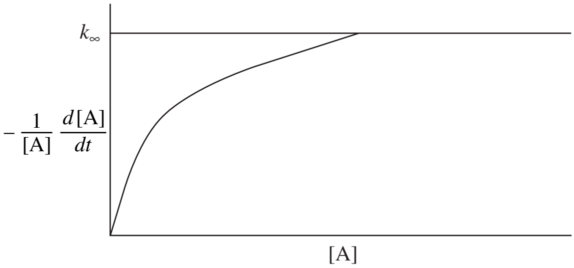


Fig. 4.8 Rate vs [A] for unimolecular reaction.

At high concentration, the curve is horizontal with the concentration axis while at low concentration $-\frac{1}{[A]}\frac{d[A]}{dt}$, i.e. first order rate coefficient increases proportionally with concentration.

The value of first order rate constant (k^1), i.e. k_1k_2/k_1 (say k_∞) at high concentration is determined from experiments and has also been calculated from simple collision theory (i.e. rate constant = $Ze^{-E_{\text{act}}/RT}$). In all cases it has been observed that rate constant dropped at much higher concentration than is actually observed. Since there can be no doubt about k_∞, which is an experimental quantity, the error must be in the estimation of rate constant.

Another difficulty with Lindemann's theory becomes apparent when equation (4.59) is considered from another point of view. Equation (4.59) may be written as

$$\frac{1}{k^1} = \frac{1}{k_1[A]} + \frac{k_1'}{k_1k_2} \tag{4.60}$$

According to equation (4.60) a plot $1/k^1$ versus 1/[A] should give a straight line with an intercept. However, deviations found from linearity are shown in Fig. 4.9.

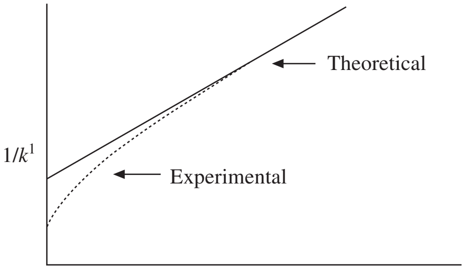


Fig. 4.9 Deviation in plot predicted by equation (4.60).

It is thus necessary to modify Lindemann's theory to explain the deviations. These deviations have been explained by theories proposed by Hinshelwood, Kassel, Rice and Ramsperger, and Slater.

4.6.2 Hinshelwood Treatment

The treatment of Hinshelwood and further modifications may be considered in terms of the following scheme:

$$A + M \rightleftharpoons A^* + M$$

$$A^* \rightarrow A^{\neq} \rightarrow \text{Product}$$

when M is any molecule (may be another A) that can transfer energy to A during collisions, A^* is an energized molecule and $A^{\neq}$ an activated molecule. A^* has acquired the energy it needs to become an activated molecule. However, it must undergo vibration before it converts to $A^{\neq}$. The process is represented in Fig 4.10.

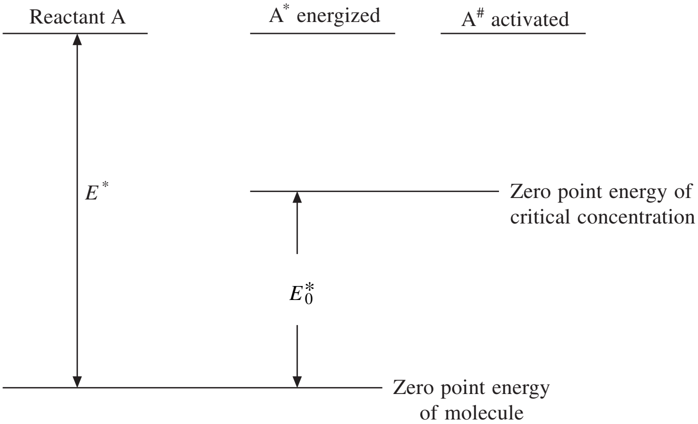


Fig. 4.10 Energy scheme for unimolecular reaction.

In Hinshelwood's treatment, the molecule A is allowed to acquire an amount of energy E_0^* at an enhanced rate. The rate at which A^* converts to $A^{\neq}$ is independent of that energy. Let us take the expression for first order rate constant given by Lindemann's theory, i.e.

$$k_1 = \frac{k_2 (k_1 / k_1')}{1 + (k_2 / k_1')[M]}$$

In case of Hinshelwood's modification both k_2 and (k_1 / k_1') have been treated as independent of E^*, i.e. amount of energy in the energized molecule. In Hishelwood's treatment the critical energy E_0^* is involved, not E^*.

Hinshelwood pointed out that the reaction $k = ze^{-E/RT}$ applies only if the energy is distributed among two degrees of freedom. Considering the distribution of energy among the S vibrational degrees of freedom, Hinshelwood derived the statistical expression, which gives the fraction of molecular having in excess of E_0^* as

$$f = \frac{1}{(S-1)!}\left(\frac{E_0^*}{k_b T}\right)e^{-E_0^*/k_b T} \tag{4.61}$$

and then he expressed that rate constant

$$k_1 = z_1 \frac{1}{(S-1)!}\left(\frac{E_0^*}{k_b T}\right)e^{-E_0^*/k_b T} \tag{4.62}$$

instead of simple expression $k_1 = ze^{-E_0^*/k_b T}$.

Thus, an addition factor which has appeared in equation (4.62) is $\frac{1}{(S-1)!}\left(\frac{E_0^*}{k_b T}\right)$ which may be greater than unity by many powers of 10 when S is sufficiently large.

Further equation (4.62) can be written in the form

$$k_1 \propto (T)^{1/2}\left(\frac{1}{T}\right)^{S-1} e^{-E_0^*/k_b T} \tag{4.63}$$

which on taking logarithms and then differentiating gives

$$\frac{d(\ln k_1)}{dT} = \frac{(3/2 - S)k_b T + E_0^*}{k_b T^2} \tag{4.64}$$

Again, the experimental activation energy is given by equation (4.65)

$$\frac{d(\ln k_1)}{dT} = \frac{E_{\text{exp}}}{k_b T^2} \tag{4.65}$$

where E_{exp} is the experimental energy per molecule. From (4.64) and (4.65) it follows that

$$E_0^* = E_{\text{exp}} + (S - 3/2)k_b T \tag{4.66}$$

Thus, E_0^* is higher than the experimental activation energy and can give much higher rates of activation and, therefore, much higher value of k_1/k_1' than simple collision theory.

However, the following difficulties still remain, which could not be explained on the basis of Hinshelwood's treatment.

1. According to Hinshelwood's proposal,

$$k_{\text{lim}} = \frac{k_1 k_2}{k_1'} = k_2' \frac{1}{(S-1)!}\left(\frac{E_0^*}{k_b T}\right)e^{-E_0^*/k_b T} \tag{4.67}$$

which indicates a strong temperature dependence of pre-exponential factor. There is no experimental evidence for it.

2. The explanation for the non-linearity in plot of $1/k_1$ versus $1/[\text{A}]$ is not given in Hinshelwood's theory.

3. The number of S required to give agreement with experiment usually was found to be only about one-half of the total number of vibrational mode. This has not been explained.

4.6.3 Rice and Ramsperger, and Kassel (RRK) Treatment

Rice and Ramsperger and independently Kassel proposed the theories to explain unimolecular reaction, in which both (k_2) and (k_1/k_1') have been treated as dependent on the energy of an individual energized molecule E^*. These theories jointly are referred as RRK theory. According to the theory the expression for the first order rate constant given by Lindemann theory i.e.

$$k_1 = \frac{k_2(k_1/k_1')}{1 + (k_2/k_1')[\mathrm{M}]}$$

can be written as

$$dk_1 = \frac{k_2(E^*)f(E^*)}{1 + (k_2(E^*)/k_1')\,[\mathrm{M}]}dE^* \tag{4.68}$$

where $k_2(E^*)$ shows that k_2 is a function of E^*, k_1/k_1' replaced by f is also a function of E^* and $f(E^*)$ is known as *distribution function*.

In equation (4.68), dk_1 is a canonical rate constant, relating to energized molecule having energy between E^* and $E^* + dE^*$. The expression can be integrated between the limits from minimum energy (E_0^*) to infinity to get the ordinary rate constant k_1, i.e.

$$k_1 = \int_{E_0^*}^{\infty} \frac{k_2(E^*)f(E^*)}{1 + (k_2(E^*)/k_1')[\mathrm{M}]}dE^*$$

The theories of Rice and Ramsperger, and Kassel are very similar and based on the assumption that k_2 will be a function of energy possessed by the energized molecule A^*. It has been postulated that the rate constant k_2 for decomposition of the active molecule increases with the energy possessed by the molecule in its various degrees of freedom. At high pressure, where there is a greater number of highly activated molecules, the rate, therefore, will be higher than predicted by the simple theory. It is supposed that on every vibration, there is reshuffling of energy between the normal modes, and after a number of vibrations the critical energy E^* may be found in one particular normal mode (referred as critical mode) and then the reaction occurs.

The larger the energy E possessed by the excited molecule, greater is the chance that necessary amount E^* can pass into critical mode and greater is, therefore, the rate of reaction. On the basis of quantum model, they obtained the rate which the required energy passes into the particular degree of freedom and is proportional to $(E - E^*/E)^{S-1}$, where S is the degree of vibrational freedom, E the total energy of molecule and E^* the minimum energy that a molecule must have for reaction to take place. Therefore, the rate constant k_2 can be obtained as

$$k_2 = k^{\neq}\left(\frac{E - E^*}{E}\right)^{S-1} \tag{4.69}$$

$k^{\neq}$ is the rate constant corresponding to the free passage of the system over the potential energy barrier. When E is sufficiently large, the energized molecule is essentially an activated molecule and therefore can convert immediately into the final state, i.e. k_2 is large. The variation of k_2 with E is shown schematically in Fig. 4.11.

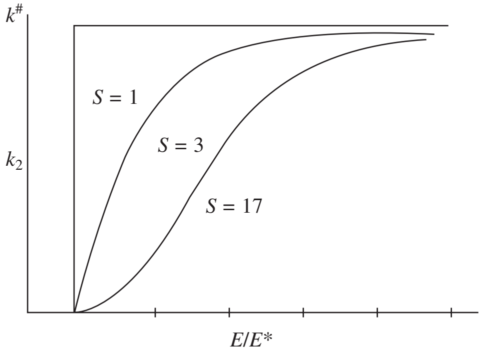


Fig. 4.11 Variation of k_2 with E/E^*.

The expression for k_∞ has also been obtained by Kassel and is given by

$$k_\infty = k^{\neq} e^{-E^*/k_\text{b}T} \tag{4.70}$$

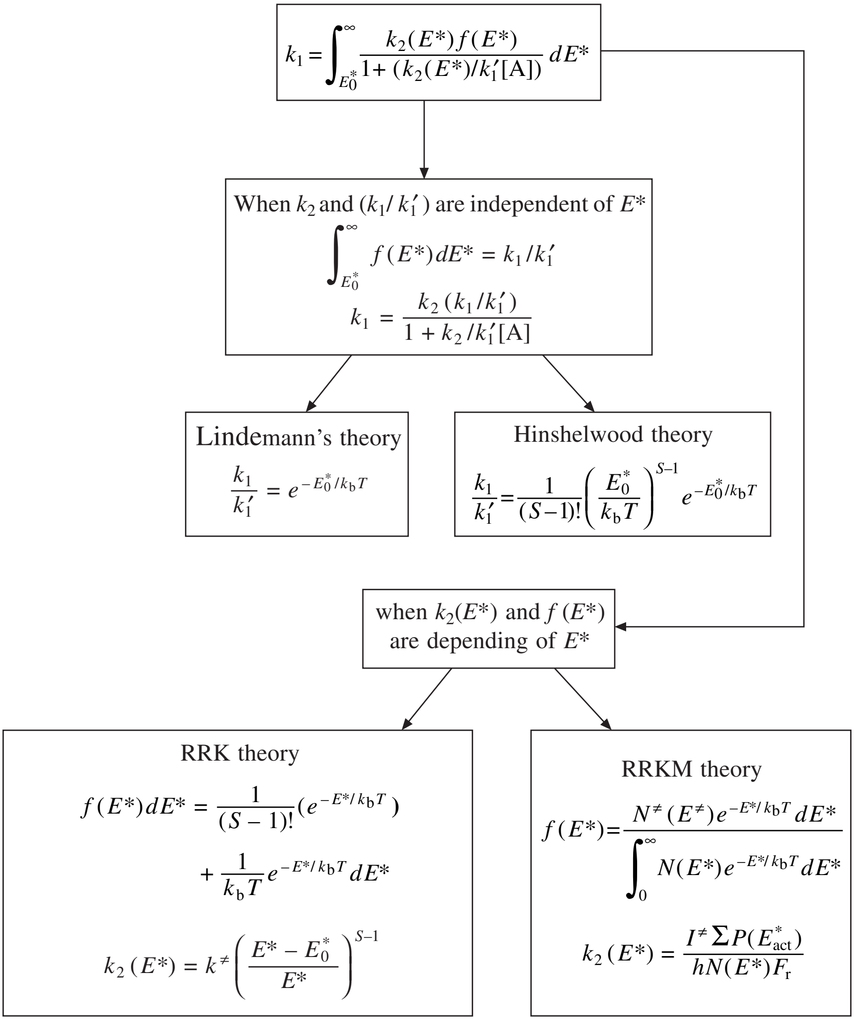
Therefore, according to this theory, $K^{\neq}$ would be equal to $k_\text{b}T/h$ provided the partition functions are same in the initial and activated states.

Therefore, in the treatment of Kassel and that of Rice and Ramasperger the only condition for energization is that the molecule must acquire the critical amount of energy E^*.

Any molecule that has acquired this energy will, unless it is deenergized by collision, pass through the activated state into final state. $k^{\neq}$ in above expressions is readily the frequency of energy redistribution.

4.6.4 Marcus Treatment

Marcus developed a quantum mechanical formulation of Kassel-Rice-Ramsperger theories in which zero point energies have been taken into account (see flow chart). However, due to lack of data for individual molecules it is difficult to apply the theory of Rice-Ramsperger-Kassel-Marcus (RRKM) to many reactions, but wherever it has been applied, it has been proved very satisfactory.



Flow Chart

4.6.5 RRKM Theory

This theory, developed by extending the Rice-Ramsperger-Kassel (RRK) theory by Marcus, is known as *RRKM theory*. Only a brief account of the theory is given here. In RRKM theory the initial degrees of freedom of A^* and $A^{\neq}$ have been designated as either active or inactive (adiabatic). It has been assumed that active modes exchange energy freely while inactive mode remains in the same quantum states during the reaction. Thus, inactive energy that remains in the same quantum state during the course of reaction and, therefore, cannot contribute to the breaking of bonds. During the formation of activated molecule $A^{\neq}$, the zero point energy, which is the energy of overall translation and rotation, is remained preserved as such and, therefore, is inactive. The vibrational energy and energy of internal rotational are active.

In RRKM theory, $k_2(E^*)$ and distribution functions $f(E^*)$ are represented as

$$f(E^*)dE^* = \frac{N(E^*)e^{-E^*/k_bT}dE^*}{\int_0^\infty N(E^*)e^{-E^*/k_bT}dE^*} \tag{4.71}$$

and

$$k_2(E^*) = \frac{I^{\neq}\Sigma P(E_{\text{act}})}{hN(E^*)F_r} \tag{4.72}$$

where $N(E^*)$ is the density of states, i.e. nuclear of states pursuit having energy between E^* and $E^* + dE^*$, $I^{\neq}$ is the statistical factor, $\Sigma P(E^*_{\text{act}})$ in number of vibrational-rotational quantum states of activated molecule, F_r is a factor introduced to correct the fact that the rotations may not be same in the activated molecule as in the energized molecule.

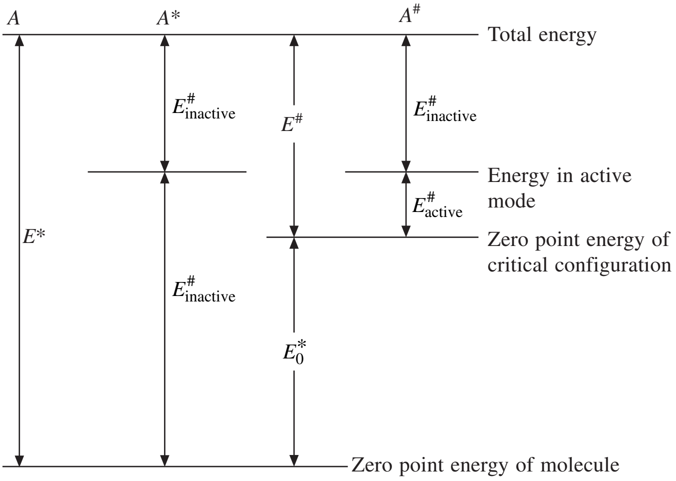


Fig. 4.12 Energy scheme for RRKM theory.

Vibrational frequencies for various normal modes must be estimated and active as well as inactive energies should be decided. Numerical methods may be used to calculate rate constant k_1 at various concentrations obtained by RRKM theory. The rate constant has been found to be same as given by conventional transition state theory, i.e.

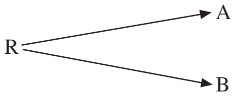
$$k_{1(\text{lim})} = \frac{k_{\text{b}}T}{h}\frac{Q^{\neq}}{Q_{\text{A}}}e^{-E_0^*/k_{\text{b}}T}$$

where $Q^{\neq}$ and Q_{A} are partition functions for activated state and reactant, respectively. Thus, theory is able to explain the abnormally high pre-exponential factors that are sometimes obtained.

4.7 Kinetic and Thermodynamic Control

In many reactions under a given set of conditions, a reactant may undergo competing reactions to give different products. The products composition may be governed either by equilibrium thermodynamic or by competing rate of formation of product.

Let a reactant R gives two products A and B in two different steps as follows:



The energy profile for the reaction is shown in Fig. 4.13.

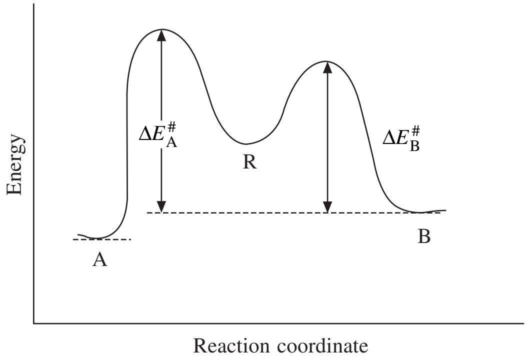
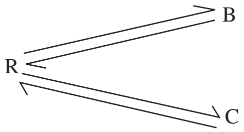


Fig. 4.13 Energy profile for competing reactions.

When both the steps are irreversible, product A is more stable (having lower energy) but product B will be formed in larger amount because it is formed with faster rate (low energy activation). The product is said to be kinetically controlled.

When the reactions are reversible as follows:



the product composition may be controlled either thermodynamically or kinetically.

Case I. If the reaction stopped well before the equilibrium has been established, the faster-formed product will be present in larger amount and the reaction will be kinetically controlled.

Case II. If the reaction is allowed to attain the equilibrium, the slower formed product A will be predominant, because product B (formed with faster rate) is first formed and converts back to reactants. While product A (which is formed with slower rate) is more stable and converts to reactant in much less amount. The product is called thermodynamically controlled.

Further the process depends on the reaction conditions, magnitude of $\Delta E_A^\#$ and $\Delta E_B^\#$ and stability of the products.

4.8 Hammond's Postulate

As the transition state (TS) has zero life-time, it is difficult to observe them directly. However, the information about the transition-state may be obtained on the basis of some inference. George S. Hammond (1955) laid out his postulate which may be stated as:

"If two states, as for examples, a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will involve only a small reorganization of the molecular structure".

Thus along the reaction coordinate, the species with similar energies, have similar structures.

With the help of Hammond's postulate the transition state can be assumed to be reasonably approximated by the structure of either the reactant, intermediate or product.

Consider the following three cases (Fig. 4.14):

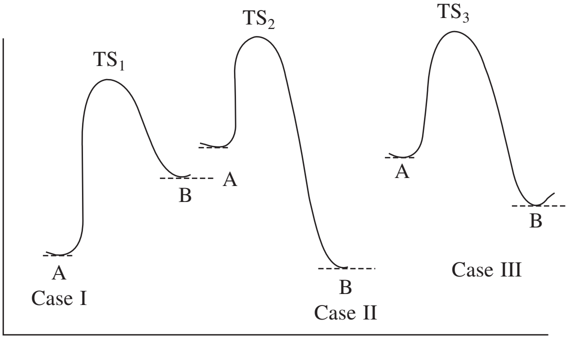


Fig. 4.14 Hammond's postulate.

Case I. Highly Endothermic Reaction

In highly endothermic reaction, the transition-state (TS_1) resembles product B.

Case II. Highly Exothermic Reaction

According to Hammond's postulate in highly exothermic reaction, the transition state (TS_2) resembles reactant A.

Case III. Slightly Exothermic Reaction

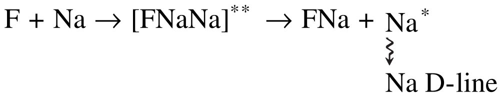
If reaction is slightly exothermic with a high activation energy, neither reactant nor product resemble transition state (TS_3).

Hammond postulate has been used to explain the effect of substituents on the rate of benzilic acid rearrangements, mechanism of electrophillic aromatic substitution reactions and reactions involving highly reactive intermediates such as carbonium ions and carbon ions.

4.9 Probing of the Transition State

We are aware of the fact that reactants go through a transition state before they convert into products. There was a feeling that the transition state of a chemical reaction could not be characterized directly in the laboratory because it won't be stable enough to be observed. Now the time has changed and it has become possible to characterize the transition state experimentally as well as theoretically.

Polanyi and coworkers (1980-83) monitored the 'wings' to the sodium D-line emission in the reaction



$$\mathrm{F + Na \rightarrow [FNaNa]^{**} \rightarrow FNa + } \underset{\text{Na D-line}}{\underset{\rightsquigarrow}{\mathrm{Na}^{*}}}$$

It was realized that the wings was six orders of magnitude lower in intensity than the D-line and the life-time of transition-state was around 10^{-12}s, about four order less than that of Na^*. In a subsequent experiment they also identified the transition state for the reaction

$$H + D_2 \rightarrow [HDD]^* \rightarrow HD + H$$

by velocity selected time of flight mass spectrometry. In their pump and probe experiment, the H atoms was generated from H_2S by pumping first laser (L_1). H atoms were reacted with D_2 to form $[HD_2]^*$ which in turn was probed by second laser (L_2) through resonantly enhanced multiphoton ionization. On variating the time delay between L_1 and L_2, they observed that the detected $[HD_2]^+$ came from $[HD_2]^*$. By varying the wave length of L_2, the probing of the transition state was possible.

Brooks and collaborators (1980-86) in a 3-beam experiments, crossed beams of K, $HgBr_2$ and $h\nu$ and monitored fluorescence from the product $HgBr^*$

$$\begin{tikzcd}
 & {[\mathrm{KHgBr_2}]^{+*}} \arrow[r] & \mathrm{KBr} + \mathrm{HgBr}^* \arrow[d, squiggly] \\
\mathrm{K} + \mathrm{HgBr_2} \arrow[r] & {[\mathrm{KHgBr_2}]^{\#}} \arrow[u, "(\mathrm{TS})"] & \mathrm{HgBr}
\end{tikzcd}$$

They also carried out a similar experiment with K, NaCl and $h\nu$ and monitored the D line emission from Na^*

$$\begin{tikzcd}
 & {[\mathrm{KClNa}]^{\#*}} \arrow[r] & \mathrm{KCl} + \mathrm{Na}^* \arrow[d, squiggly] \\
\mathrm{K} + \mathrm{NaCl} \arrow[r] & {[\mathrm{KClNa}]^{\#}} \arrow[u, "(\mathrm{TS})"'] & \mathrm{Na}
\end{tikzcd}$$

Witting and coworkers (1988) used laser (193 nm) to photo dissociate HBr in a $\{CO_2\text{-}HBr\}$ van der Waal complex and monitored the OH^- rotational distribution arising out of the reaction

$$H + CO_2 \rightarrow HO + CO$$

They observed that transition state is long lived with a life-time of ~1 ps.

At the end of the 1980s Zewail performed a series of experiments that were to lead to the birth of a new research field called femtochemistry. This could be described as using a high-speed camera to image molecules during the actual course of chemical reactions and trying to capture snap-shots of them just in the transition state. The camera was based on a new laser technology, with light flashed of some tens of femtoseconds (1 fs = 10^{-15} sec).

To achieve a "molecular movie" of a chemical reaction, Zewail mixed the reactants in the form of molecular beams in a vacuum chamber. In a simple case, a so-called unimolecular reaction step which concerns only one type of molecule, the reaction was started using a powerful pump pulse which excites the molecule to a higher energy state. The pump pulse was followed by a second (weaker) pulse. This pulse was timed to arrive at precise intervals after the reaction has been started, to reveal how long it takes for various molecular species to appear or vanish. The time interval between pulses can be varied simply by delaying the probe pulse by letting it travel a detour via some mirrors. The fingerprints and the time elapsing are then compared with theoretical simulations based on quantum chemical calculations on spectra and energies of the molecules in their various states.

In his first experiment (1987) Zewail studied the unimolecular disintegration of iodine cyanide into iodine atom and cyano radical: ICN → I + CN. They managed to observe a transition state corresponding to the I–C bond breaking. The whole reaction was over in 200 fs.

In another important experiment (1989) Zewail and his group studied the dissociation of sodium iodide (NaI): $Na^+ I^- \rightarrow Na + I$. The pump pulse excites the ion pair Na^+I^- which has an equilibrium distance of 2.8 Å between the nuclei to an excited from $[\text{Na–I}]^*$ which at this short bond distance assumes a covalent bonding character. However, its properties change when the molecule vibrates: when the Na and I atoms are at their outer turning points, 10-15 Å apart, the electron structure is ionic, $[\text{Na}^+\ldots\text{I}^-]^*$, as one electron has moved from Na to I. When the atoms move back together the bonding becomes covalent again: $[\text{Na–I}]^*$, and so forth. A critical point was observed during the vibration where the excited state and ground state are very close to each other. At this point there is a great probability that the excited $[\text{Na-I}]^*$ will either fall back to its ground state [Na-I] or decay into sodium and iodine atoms.

Zewail also studied bimolecular reactions, such as the reaction between hydrogen atoms and carbon dioxide: $H + CO_2 \rightarrow CO + OH$ which occurs in the atmosphere and during combustion, and which he showed was going via a long-lived (1000 fs) molecule HOCO. In a reaction between benzene and iodine (I_2), they observed that when the two molecules come close together they form a complex. The laser flash makes an electron from benzene jump over to the iodine molecule, which then becomes negatively charged while benzene becomes positively charged. The negative and positive charges attract each other. The bond between the two iodine atoms is stretched as the one closest to benzene is attracted toward benzene, the other then goes off and flies away. All happens within 750 fs.

Femtosecond studies being performed intensely the world over, using not only molecular beams but studying also processes on surfaces and clusters and in polymers. In addition, femtochemistry has been applied to the study of many important biological systems.

Besides the experimental studies, the theoretical approaches have also been developed to study the details of state-to-state chemistry to probing the transition-state. Polanyi and coworkers computed classical trajectories to follow the dynamics of

$$F + Na_2 \rightarrow FNa + Na$$

reaction on the excited state surface using London-Eyring-Polanyi-sato formations. The similar study were extended to predict the absorption spectrums of $(H_3^{\#})$ in $H + H_2$ collisions and the absorption spectrum of transition state in K + NaCl collisions.

A time-independent quantum mechanical study by Engel and coworkers (1985) gave qualitatively the same results as the time dependent analog and the quassi classical trajectory method. A quantum theory for probing transition-state absorption/emission has also been developed by Lee et al. (1989).

EXERCISES

1. Calculate the value of pre-exponential factor and rate constant at 298 K in following cases:

(a) Atom + Atom → Linear molecule
(b) Atom + Linear molecule → Nonlinear molecule
(c) Atom + Nonlinear molecule → Nonlinear molecule

Assuming that the values of q_t, q_r and q_v for different molecules are equal and 10^8, 10 and 1, respectively, for each degree of freedom.

2. The value of $\Delta S^{\neq}$ for a reaction is -160 J mol^{-1} K^{-1}, calculate the value of Arrhenius factor at 400 K.
3. The second order rate constant for a reaction $2A \rightarrow P$ is 2.0×10^{10} mol^{-1} dm^3 s^{-1} and $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the reaction and 190 kJ mol^{-1} and 15.0 Jmol^{-1} K^{-1}, respectively. Calculate the E_{act} and pre-exponential factor for the reverse reaction.
4. Compare the rate constant obtained from collision theory and transition state theory and prove that $\Delta H^{\neq} = E_{act} + \frac{1}{2}RT$.
5. Explain the following

   (a) The steric factor involved in collision theory may be interpreted in terms of $\Delta S^{\neq}$.
   (b) For reaction $A + B \rightarrow (AB)^{\#} \rightarrow A + B$ the entropy of activation is negative while for reverse reaction, i.e. $AB \rightarrow (AB)^{\neq} \rightarrow A + B$ the entropy of activation is positive.
   (c) Some reactions proceed with a very slow speed even though there is a large decrease in free energy.

6. If activation energy for a reaction is 100 kJ mol^{-1}, calculate the fraction of molecules which have energy $\geq E_{act}$.
7. Calculate pre-exponential factor and rate constant for the reaction

$$CH_3 + H_2 \rightarrow CH_4 + H$$

   at 100°C if collision diameter is 3.0×10^{-10} m and E_{act} of reaction is 20 kJ mol^{-1}.
8. With the help of transition state theory, prove that value of steric factor varies from 10^{-5} to 10^{-10} for complex reactions.
9. Explain that: (i) for gaseous reactions, the entropy of activation is generally negative and (ii) larger the decrease in entropy, smaller will be the value of Arrhenius factor.
10. Assuming $q_t = 10^8$, $q_r = 10$, $q_v = 1$ and $\frac{k_b T}{h} = 10^{13}$, calculate the value of rate constant for $n_A A + n_B B \rightarrow X^{\neq}$ in cc molecules^{-1} sec^{-1} and liter moles^{-1} sec^{-1}.

5

Kinetics of Some Special Reactions

5.1 Kinetics of Photochemical Reactions

There are certain reactions in which the activation may be carried out by electromagnetic radiations in visible and ultraviolet region having wavelength approximately between 100 to 1000 nm. These reactions are called *photochemical reactions*. A photon of radiation, referred to as quantum with energy $h\nu$ (ν being its frequency), is primary unit of radiation. When a photon from high energy electromagnetic radiations such as X- and γ-ray is used, the chemical processes are then called *radiolytic reactions*. The photochemical reactions are governed by two basic principles, viz. the Grotthus-Draper law and Einstein law of photochemical equivalence.

5.1.1 Grotthuss-Draper Law

This law states that only those radiations which are absorbed can be effective in producing the chemical change.

Although photochemical reaction is a result of absorption of light, it may not always lead to chemical change. Sometimes the absorption of photon may only increase the thermal energy or it may be reemitted (fluorescence).

5.1.2 Einstein Law of Photochemical Equivalence

In 1912, Einstein extended the concept of quantum theory of radiation to photochemical processes and stated that ‘each quantum of radiation absorbed by molecule activates one molecule in the primary step of a photochemical process’. This is known as *Einstein law of photochemical equivalence*.

According to this law, if every molecule so activated in primary absorption directly decomposes, the number of molecules taking part in chemical change would be equal to the number of quanta of energy absorbed. However, a molecule activated photochemically may initiate a sequence of reactions so that many reactant molecules through a chain mechanism would undergo chemical change. In such cases the number of molecules undergoing chemical changes will be many times of the quanta of energy absorbed.

The efficiency of a photochemical reaction is expressed in terms of quantum yield ϕ defined as

$$\phi = \frac{\text{Number of molecules reacting}}{\text{Number of quanta of radiation absorbed}} \tag{5.1}$$

For example, in the photolysis of HI,

$$HI + h\nu \rightarrow H + I$$

$$H + HI \rightarrow H_2 + I$$

$$2I \rightarrow I_2$$

absorption of photon leads to destruction of two HI molecule and ϕ is therefore equal to 2. In chain reactions a high value of quantum efficiency has been observed ($\sim 10^4$).

According to law of photochemical equivalence, the energy absorbed per mole E is given by

$$E = N_0 h\nu = \frac{N_0 hc}{\lambda} \text{ ergs per mole} \tag{5.2}$$

$$c = 3.0 \times 10^{10}\text{cm/sec; } h = 6.625 \times 10^{27} \text{ ergs-sec; } N_0 = 6.02 \times 10^{23}$$

$$E = \frac{1.196 \times 10^8}{\lambda} \text{ ergs per mole}$$

If λ is expressed in Å (1Å = 10^{-8}cm)

$$E = \frac{1.196 \times 10^{16}}{\lambda} \text{ ergs per mole} \tag{5.3}$$

$$= \frac{1.196 \times 10^{16}}{\lambda \times 4.184 \times 10^7} \text{ calories per mole}$$

$$= \frac{2.859 \times 10^5}{\lambda} \text{ k.cals per mole} \tag{5.4}$$

This energy which activates one mole of reactant is called *one Einstein*. As $E \propto 1/\lambda$, so one Einstein corresponding to UV radiations would involve more energy than that in the visible region.

5.1.3 Primary Process in Photochemical Reactions

The primary process consists of raising of the electronic quantum level of molecule by absorption of energy from photon. The excited molecule may then behave in different ways. The energy of the photon is transformed into heat and temperature of absorbing system is raised but the excited molecule may behave in other ways resulting in a chemical change.

The electronic transition which occurs on absorption of energy is accompanied with changes in vibrational and rotational quantum levels and is governed by Frank-Condon principle. The behavior of excited molecule can be understood from the potential energy curves as follows:

1. When an excited molecule also consists of a definite vibrational level as shown in Fig. 5.1(a), there shall be no direct dissociation of molecule and a fine structure in the electronic band spectra of the molecule will be observed. The excess energy, in usual course may be dissipated as heat or may give rise to fluorescence. But the molecule may retain its energy until it has not reacted with another molecule or transfer its energy to another molecule, e.g. decomposition of NOCl as follows:

$$\mathrm{NOCl} + h\nu \rightarrow \mathrm{NOCl}^*$$

$$\mathrm{NOCl}^* + \mathrm{NOCl} \rightarrow 2\mathrm{NO} + \mathrm{Cl_2}$$

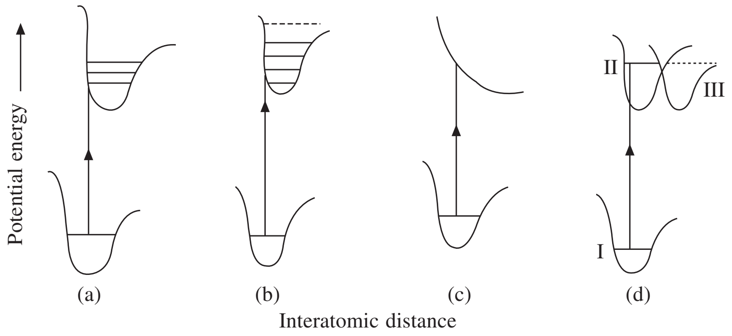


Fig. 5.1 Potential energy curves showing processes that can occur on absorption of radiation.

2. When a molecule raised to higher electronic state acquires a quantum level above the maximum stability level (Fig. 5.1(b)), the energy gained is higher than the binding energy of the molecule and the molecule will undergo dissociation in its first oscillation. The products of dissociation may start a chain reaction. In such a case, a continuum spectra will be observed, e.g. decomposition of HI or H_2–Cl_2 as follows:

$$\mathrm{HI} + h\nu \rightarrow \mathrm{H} + \mathrm{I}$$

$$\mathrm{H} + \mathrm{HI} \rightarrow \mathrm{H_2} + \mathrm{I}$$

$$\mathrm{I} + \mathrm{I} \rightarrow \mathrm{I_2}$$

$$\mathrm{Cl_2} + h\nu \rightarrow 2\mathrm{Cl}$$

$$\mathrm{Cl} + \mathrm{H_2} \rightarrow \mathrm{HCl} + \mathrm{H}$$

$$\mathrm{H} + \mathrm{Cl_2} \rightarrow \mathrm{HCl} + \mathrm{Cl}$$

3. When an excited molecule is in an electronic state which is quite

unstable (Fig. 5.1(c)), i.e. as soon as a photon is absorbed by the molecule, it breaks into atoms or radicals with different kinetic energy, a continuous spectrum without any fine structure is obtained. The products of dissociation may start secondary chemical changes or chain reactions as in 2 above.

4. Sometimes two higher electronic levels, stable state II and unstable state III may exist quite close to each other (Fig. 5.1(d)). By absorption of light, the molecule is raised to higher stable electronic state II. If the oscillations are relatively slow, there is a chance of the molecule of shifting from stable state II to unstable state III. If such a shift takes place, the molecule would dissociate producing atoms or radicals. The spectrum would show fine structure at lower levels of vibrations followed by a continuum. This is called *predissociation*.

5.1.4 H_2-Br_2 Reaction

The mechanism for reaction is as follows:

$$Br_2 + h\nu \rightarrow Br + Br;\ I_{obs}$$

$$Br + H_2 \rightarrow HBr + H;\ k_2$$

$$H + Br_2 \rightarrow HBr + Br;\ k_3$$

$$H + HBr \rightarrow H_2 + Br;\ k_4$$

$$Br + Br \rightarrow Br_2;\ k_5$$

The rate of formation of HBr is given as

$$\frac{d[\mathrm{HBr}]}{dt} = k_3[\mathrm{H}][\mathrm{Br_2}] + k_2[\mathrm{Br}][\mathrm{H_2}] - k_4[\mathrm{H}][\mathrm{HBr}] \qquad \text{(a)}$$

Under the steady state conditions, we have

$$\frac{d[\mathrm{H}]}{dt} = 0 \text{ and } \frac{d[\mathrm{Br}]}{dt} = 0$$

$$\frac{d[\mathrm{H}]}{dt} = k_2[\mathrm{H_2}][\mathrm{Br}] - k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{H}][\mathrm{HBr}] = 0 \qquad \text{(b)}$$

$$\frac{d[\mathrm{Br}]}{dt} = k_1 I_{abs} - k_2[\mathrm{H_2}][\mathrm{Br}] + k_3[\mathrm{H}][\mathrm{Br_2}] + k_4[\mathrm{H}][\mathrm{HBr}] - k_5[\mathrm{Br}]^2 = 0 \qquad \text{(c)}$$

On adding (b) and (c), we get

$$k_1 I_{abs} = k_5[\mathrm{Br}]^2$$

or

$$[\mathrm{Br}] = \left(\frac{k_1 I_{abs}}{k_5}\right)^{1/2} \qquad \text{(d)}$$

Substituting the value of [Br] in equation (b) and simplifying

$$[H] = \frac{k_2\left(\frac{k_1 I_{\text{abs}}}{k_5}\right)^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \qquad \text{(e)}$$

Again on substituting the values of [H] and [Br] in (a), the rate of reaction can be given as

$$\frac{d[HBr]}{dt} = \frac{2k_2\left(\frac{k_1 I_{\text{abs}}}{k_5}\right)^{1/2}[H_2]}{1 + k_4[HBr]/k_3[Br_2]} \qquad (5.5)$$

It is the same rate as given in thermal reaction given by equation (3.31). Thus, both in thermal and photochemical reactions, the primary process is the dissociation of Br_2 molecules. In spite of the chain mechanism, the quantum yield of H_2 and Br_2 reaction is very small, i.e. about 0.01 at ordinary temperature, although it increases as the temperature is raised. The reason is that the reaction immediately after initiation following the primary state, i.e.

$$Br + H_2 \rightarrow HBr + H$$

is an endothermic process and requires a high energy of activation. At ordinary temperature this reaction is so slow that most of bromine atoms recombine to produce molecules resulting in a low yield. As the temperature is raised, the rate of reaction increases and, therefore, quantum efficiency of the whole process also increases.

5.1.5 H_2 and Cl_2 Reaction

The quantum yield of H_2-Cl_2 combination is exceptionally high; it varies with the experimental conditions but is found to be between 10^4 and 10^6 in absence of O_2 with light of wavelength 4800 Å. The process occurs in the range 5460 to 4800 Å with an apparently lower efficiency because only a small proportion of light absorbed is capable of dissociating Cl_2 molecule. The mechanism can be proposed as

$$Cl_2 + h\nu \xrightarrow{k_1} 2Cl \qquad 1^{st}\text{ stage} \qquad \text{(i)}$$

$$\left.\begin{array}{l} Cl + H_2 \xrightarrow{k_2} HCl + H \\ H + Cl_2 \xrightarrow{k_3} HCl + Cl \end{array}\right] \text{chain reaction} \qquad \text{(ii, iii)}$$

$$Cl + \text{Wall} \xrightarrow{k_3} 1/2Cl_2 \qquad \text{termination} \qquad \text{(iv)}$$

Reaction (ii) between chlorine atom and hydrogen molecule is very rapid, since it is an exothermic process and has low energy of activation whereas corresponding reaction with bromine atom is very slow at ordinary temperature.

Applying the steady state treatment with respect to chlorine atom, we can get

$$k_1I_{\text{abs}} + k_3[\text{H}][\text{Cl}_2] = k_2[\text{Cl}][\text{H}_2] + k_4\,[\text{Cl}] \tag{a}$$

assuming that reaction (iv) is a first order reaction. Similarly, considering steady-state treatment with respect to hydrogen atom, we get

$$k_2[\text{Cl}][\text{H}_2] = k_3[\text{H}][\text{Cl}_2] \tag{b}$$

Hence, from (a) and (b)

$$k_1I_{\text{abs}} = k_4[\text{Cl}]$$

or

$$[\text{Cl}] = (k_1/k_4)\, I_{\text{abs}} \tag{c}$$

The rate of formation of HCl is given as

$$\frac{d[\text{HCl}]}{dt} = k_2\,[\text{Cl}][\text{H}_2] + k_3\,[\text{H}][\text{Cl}_2]$$

$$= 2k_2[\text{Cl}][\text{H}_2] \text{ (from equation (b))}$$

Substituting the value of [Cl] from equation (c), we get

$$\frac{d[\text{HCl}]}{dt} = \frac{2k_1k_2}{k_4}\, I_{\text{abs}}[\text{H}_2] \tag{5.6}$$

The rate law (5.6) is in agreement with experimental results. At high chlorine pressure, the termination step (iv) may be replaced by following equilibria

$$\text{Cl} + \text{Cl}_2 \rightleftharpoons \text{Cl}_3$$

$$2\text{Cl}_3 \rightleftharpoons 3\text{Cl}_2$$

This will lead to a different kinetic law. In presence of O_2, the following chain termination processes take place:

$$\text{H} + \text{O}_2 \rightarrow \text{HO}_2$$

$$\text{Cl} + \text{O}_2 + \text{HCl} \rightarrow \text{HO}_2 + \text{Cl}_2$$

HO_2 subsequently reacting to give products which do not propagate chains.

5.2 Oscillatory Reactions

Oscillations are familiar phenomena in mechanical systems and in electric circuits. Noyes and Field discussed the possibilities for concentration oscillations in closed systems and illustrated the principles by means of Oregonator model consists of the following five steps:

$$\text{A} + \text{Y} \rightarrow \text{X} \tag{i}$$

$$\text{X} + \text{Y} \rightarrow \text{P} \tag{ii}$$

$$\text{B} + \text{X} \rightarrow \text{ZX} + \text{Z} \tag{iii}$$

$$X + X \rightarrow Q \tag{iv}$$

$$Z \rightarrow fy \tag{v}$$

if [X] is always small. Because all the steps are irreversible, the free energy of the model system is indefinitely far removed from its equilibrium value. Species A and B are irreversibly consumed and P and Q are irreversibly produced. A stoichiometric factor is denoted by *f*. The species X, Y and Z are both consumed and produced, and their concentrations may oscillate depending upon the relative rates of production and consumption.

A chemical reaction can be designated as oscillatory, if repeated maxima and minima in the concentration of the intermediates can occur with respect to time (temporal oscillation) or space (spatial oscillation). A chemical system at constant temperature and pressure will approach equilibrium monotonically without overshooting and coming back. In such a chemical system the concentrations of intermediate must either pass through a single maximum or minimum rapidly to reach some steady state value during the course of reaction and oscillations about a final equilibrium state will not be observed. However, if mechanism is sufficiently complex and system is far from equilibrium, repeated maxima and minima in concentrations of intermediate can occur and chemical oscillations may become possible.

First model for oscillating system was proposed by Volterra for prey-predator interactions in biological systems and by Lotka for autocatalytic chemical reactions. Lotka's model can be represented as

$$A + X \xrightarrow{k_1} 2X \tag{i}$$

$$X + Y \xrightarrow{k_2} 2Y \tag{ii}$$

$$Y \xrightarrow{k_3} Z \tag{iii}$$

According to the above model, we have

$$\frac{d[X]}{dt} = k_1[A][X] - k_2[X][Y] \tag{5.7}$$

and

$$\frac{d[Y]}{dt} = k_2[X][Y] - k_3[Y] \tag{5.8}$$

The solution of these differential equations for [X] and [Y] indicate that the concentrations of intermediates of X and Y oscillate periodically with time. The concentrations of A and Z do not oscillate but rate of consumption of A and formation of Z do oscillate.

Oscillations of concentrations of intermediates can occur when one substance in a sequence of reactions is either an activator or an inhibitor for a reaction step that occurs earlier in the sequence. Such activation or inhibition can control intermediate forming steps and will be responsible for producing oscillation in the concentration of the intermediate. The important conditions required to generate oscillations in a chemical system are:

(i) Continuous flow of matter into system so as to keep [Reactant] constant.
(ii) A mechanism that allows coupled indirect feedback. Chemical oscillations generally operate by delayed feed back, e.g. autocatalytic steps (i) and (ii) in Lotka's mechanism.
(iii) System should be far from equilibrium, i.e. system should involve some irreversible steps.

5.2.1 Belousov-Zhabotinskii Reaction

An acidic bromate solution can oxidize various organic compounds and the reaction is catalyzed by species like cerous and manganous ions that can generate 1-equivalent oxidants with quite positive reduction potential. Belousov (1959) first observed oscillations in $[Ce^{IV}]/[Ce^{III}]$ during Ce (III) catalysed oxidation of citric acid by bromate ion. Zhabotinskii made extensive studies of both temporal and spatial oscillations and also demonstrated that instead of Ce (III), weak 1- equivalent reductants like Mn(II) and Fe (II) can also be used. The reaction is called Belousov-Zhabotinskii reaction. This reaction, most studied and best understood, can be represented as

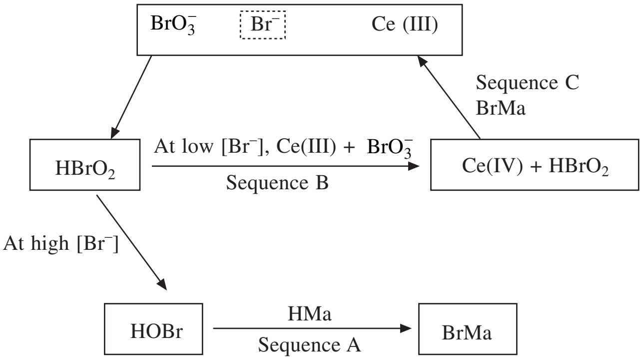
$$2H^+ + 2BrO_3^- + 3CH_2(COOH)_2 \rightarrow 2BrCH(COOH)_2 + 3CO_2 + 4H_2O$$

or $$HMa \rightarrow BrMa$$

$$3H^+ + 3BrO_3^- + 5CH_2(COOH)_2 \rightarrow 3BrCH(COOH)_2 + 4CO_2 + 5H_2O$$

An initial rapid change in concentration is followed by a long induction period and finally a series of oscillations in both $[Br^-]$ and [Ce (IV)]/[Ce(III)] are observed. These oscillations were followed potentiometrically.

Field and Noyes based on Oregonator model have proposed a mechanism involving three intermediates $HBrO_2$, Br^- and cerium (IV). The concentration of $HBrO_2$ changes between two limits whenever $[Br^-]$ passes through a critical value. Cerium (IV) is the intermediate which regenerates Br^-. The oscillations arise because of the switching from one reaction sequence to other. This is shown in Scheme A.



Scheme A

The series of elementary reactions can be divided into following three groups:

Sequence A

When solution contains sufficient amount of Br^-, reduction of BrO_3^- and bromination of malonic acid (HMa) take place by HOBr or Br_2 as follows:

$$2H^+ + BrO_3^- + Br^- \xrightarrow{\text{slow}} HBrO_2 + HOBr \tag{A_1}$$

$$HBrO_2 + Br^- + H^+ \xrightarrow{\text{slow}} 2HOBr \tag{A_2}$$

$$Br^- + HOBr + H^+ \xrightarrow{\text{fast}} Br_2 + H_2O \tag{A_3}$$

$$Br_2 + HMa \xrightarrow{\text{fast}} BrMa + H^+ + Br^- \tag{A_4}$$

Molecular bromine may or may not be an intermediate in this reaction. The overall reaction will be given by (A_1) + (A_2) + 3 (A_3) + 3 (A_4), i.e.

$$2Br^- + BrO_3^- + 3H^+ + 3HMa \rightarrow 3BrMa + 3H_2O \tag{a}$$

Sequence B

When [Br^-] is low, cerium (III) is oxidized to Ce (IV). The reaction is autocatalytic but inhibited by Br^- and, therefore, sequence B occurs only when system contains very low [Br^-].

$$BrO_3^- + HBrO_2 + H^+ \xrightarrow{\text{slow}} 2BrO_2^* + H_2O \tag{B_1}$$

$$H^+ + BrO_2^* + Ce^{III} \rightarrow HBrO_2 + Ce^{IV} \tag{B_2}$$

$$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+ \tag{B_3}$$

The overall reaction 2(B_1) + 4(B_2) + B_3, i.e.

$$BrO_3^- + 4\,Ce(III) + 5H^+ \rightarrow HOBr + 4Ce^{IV} + 2H_2O \tag{b}$$

constitute the sequence B.

Sequence C

When enough Ce^{IV} is produced by reaction (b), sequence C starts in which oxidation of HMa or BrMa starts.

$$BrMa + 4Ce^{IV} + 2H_2O \rightarrow Br^- + HCOOH + 2CO_2 + 4Ce^{III} + 5H^+$$

$$\text{or } HMa + 6Ce^{IV} + 2H_2O \rightarrow 6Ce^{III} + HCOOH + 2CO_2 + 6H^+ \tag{C_1}$$

$$HOBr + HCOOH \rightarrow Br^- + CO_2 + H^+ + H_2O \tag{C_2}$$

and overall reaction of sequence C will be (C_1) + (C_2), i.e.

$$BrMa + 4Ce^{IV} + HOBr + H_2O \rightarrow 2Br^- + 3CO_2 + 4Ce^{III} + 6H^+ \tag{c}$$

or $$HMa + 6Ce^{IV} + HOBr + H_2O \rightarrow 6Ce^{III} + 3CO_2 + 7H^+ + Br^-$$

The stoichiometric reaction for the oxidation of HMa is obtained by adding reaction (a), (b) and (c)

$$2BrO_3^- + 3HMa + 2H^+ \rightarrow 2BrMa + 2CO_2 + 2H_2O$$

which does not involve the concentrations of Br^- and Ce^{III} indicating that these species play a true catalytic role (Fig. 5.2).

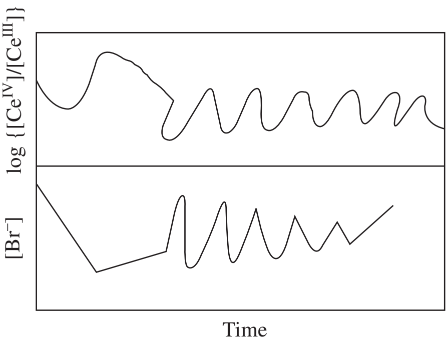


Fig. 5.2 Periodic behaviour in $[Br^-]$ and $[Ce^{IV}]/[Ce^{III}]$ in Belousov reaction.

5.3 Kinetics of Polymerization

A polymeric compound (polymer) is formed by the combination of numerous small units called *monomer* by appropriate chemical reactions. The high polymers are substances of very high molecular weight, which may occur in nature or may be synthesised. The degree of polymerization refers to the number of repeating units in the polymer chain and is related to the length of the chain. The molecular weight of the polymer is given by

$$\text{(Mol. wt. of polymer)} = \text{(Degree of polymerization)} \times \text{(Mol. wt. of repeating unit)}$$

Since the chain length may vary in any polymer, the average degree of polymerization is used.

For a substance to act as monomer, it should have two or more bonding or active sites (called *functional groups*, through which each can link to other monomers to form the polymer chain. The number of functional groups or bonding sites per monomer molecule is referred to as its functionality. Bifunctional monomers forms linear polymers which can be a straight or branched chain. When monomer is poly-functional, a three dimensional network containing both branches and cross links is possible. Since these monomers can undergo condensation or addition reactions, Carothers had originally classified the process as addition and condensation polymerizations. The addition polymers are formed by addition of monomers without any elimination and molecular weight of the polymer is an integral multiple of that monomer

$$n(CH_2 = CH_2) \rightarrow —(CH_2—CH_2)_n—$$

Addition polymerization may proceed through a free radical, cationic or anionic process. Condensation polymers, on the other hand, are formed by elimination of small molecules like that of water, alcohol or ammonia in the reaction of monomeric units, e.g.

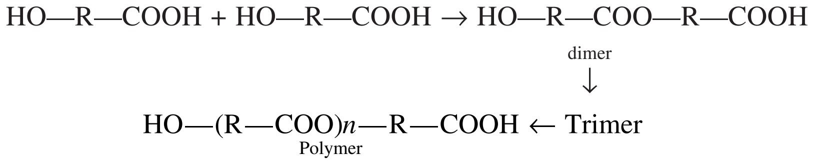
$$nH_2N—(CH_2)_6—NH_2 + nHOOC—(CH_2)_4—COOH$$

$$\rightarrow \left[HN—(CH_2)_6—NH—CO—(CH_2)_4—CO\right]_n + 2nH_2O$$

On the basis of polymerization mechanism, the processes of polymerization can be classified in two groups: (i) step growth polymerization and (ii) chain growth polymerization.

5.3.1 Step Growth Polymerization

In step growth polymerization, initially dimer formation takes place due to condensation, addition or ring opening etc., e.g.



$$\begin{array}{c} HO—R—COOH + HO—R—COOH \rightarrow \underset{\text{dimer}}{HO—R—COO—R—COOH} \\ \downarrow \\ \underset{\text{Polymer}}{HO—(R—COO)n—R—COOH} \leftarrow \text{Trimer} \end{array}$$

The dimer formed still has reactive groups. Hence, the polymerization will continue to take place in a stepwise fashion. Each step in this type of polymerization is identical and, therefore, the rate and mechanism of each step remains same as in the initial step. Polyestrification reactions are examples of step growth polymerization

$$HO—(CH_2)_5COOH \xrightarrow{\text{heat}} —[CO(CH_2)_5—O—]_n + (n-1)H_2O$$

or $$\text{Dicarboxylic acid} + \text{Diol} \rightarrow \text{Polymer} + \text{Water}$$

The water formed in the reaction is continuously removed from the reaction mixture by azeotropic distillation, in order to avoid reversible reaction between water and ester. The progress of reaction can be followed either by measuring the amount of water or by determining the amount of unreacted acid in aliquots withdrawn at regular intervals of time. The reaction can be carried out either in presence of a catalyst, i.e. a weak acid like p-toluene sulphonic acid (a strong acid can hydrolyse the polymer, formed) or in absence of the catalyst.

5.3.2 Polycondensation Reactions (in Absence of the Catalyst)

The rate of uncatalyzed polycondensation reaction follows the rate law

$$-\frac{d[\text{dicarboxylic acid}]}{dt} = k[\text{dicarboxylic acid}]^2[\text{diol}] \qquad (5.9)$$

The second order in acid arises as it acts both as reactant and the catalyst. If acid and diol are taken in equivalent concentrations, say c, the rate law can be written as

$$-\frac{dc}{dt} = kc^3 \tag{5.10}$$

On integrating the equation with the conditions that when $t = 0$, $c = c_0$, equation becomes

$$k = \frac{1}{2t}\left(\frac{1}{c^2} - \frac{1}{c_0^2}\right) \tag{5.11}$$

The fraction of the functional group that has reacted at any time t is given as

$$f = \frac{c_0 - c}{c_0} \quad \text{or} \quad c = c_0(1 - f) \tag{5.12}$$

Equation (5.11), therefore, can be written as

$$k = \frac{1}{2tc_0^2}\left(\frac{1}{(1 - f)^2} - 1\right) \tag{5.13}$$

According to equation (5.13), a plot of $1/(1 - f)^2$ versus time should be linear. This has been tested in many polyestrification reactions.

5.3.3 Acid Catalyzed Polycondensation Reaction

In case of acid catalyzed polyestrification reactions, the rate is given as

$$-\frac{d[\text{Acid}]}{dt} = k''[\text{dicarboxylic acid}][\text{catalyst}][\text{diols}] \tag{5.14}$$

Since concentration of catalyst remains constant, the rate law may be given as

$$-\frac{d[\text{Acid}]}{dt} = k[\text{dicarboxylic acid}][\text{diols}] \tag{5.15}$$

when $k = k''$ [catalyst].

Further, at equivalent concentrations of dicarboxylic acid and diol i.e. c, the rate law equation (5.15) becomes

$$-\frac{dc}{dt} = kc^2 \tag{5.16}$$

where k is a second order rate constant.

Integrating equation (5.16) under the conditions that $c = c_0$ at $t = 0$, and considering $c = c_0\,(1 - f)$, the rate equation is obtained as

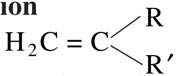
$$k = \frac{1}{tc_0}\left(\frac{1}{1 - f} - 1\right) \tag{5.17}$$

Thus, f may be given as

$$f = \frac{kc_0 t}{1 + kc_0 t} \tag{5.18}$$

Equation (5.18) has also been verified experimentally.

5.3.4 Chain Growth Polymerization

The unsaturated monomers of type  $H_2C = C\begin{smallmatrix} R \\ R' \end{smallmatrix}$ are bifunctional and their reactivity towards polymerization can be attributed to the π bond which undergo homolytic or heterolytic fission in presence of free radicals, cations or anions. Therefore, chain growth polymerization can progress through the following different mechanisms:

(i) Free radical polymerization
(ii) Cationic polymerization
(iii) Anionic polymerization

The polymerization proceeds in three distinct stages, viz. (i) initiation, (ii) propagation and (iii) termination. Initiation is the act of creating active centers in monomers. The activated monomers are the chain carrier species, i.e. these add on to the monomer to give another chain carriers. Such repeated sequence of monomers reacting with chain carriers contribute to growth of the polymer chain. These steps are known as *propagation steps* and will continue till the monomer is present in the system. However, these reactive chain carriers are deactivated and growth of polymer chain stops. This process is known as *termination process*.

5.3.5 Kinetics of Free Radical Polymerization

Free radical polymerization involves the generation of free radicals which propagate by addition of monomer molecules ultimately to give a large polymer molecule. It is generally carried out with a suitable initiator dissolved in the monomer solution.

Initiation: This is a two stage process, viz.

(i) Decomposition of initiator to give free radical

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}^\bullet \tag{i}$$

(ii) Attacking of free radical on monomer to give chain carrier

$$\mathrm{R}^\bullet + \mathrm{M} \xrightarrow{k_i} \mathrm{M}_1^\bullet \tag{ii}$$

The rate of dissociation of initiator is given as

$$-\frac{d[\mathrm{I}]}{dt} = k_\mathrm{d}[\mathrm{I}] = \frac{1}{2}\frac{d[\mathrm{R}^\bullet]}{dt} \tag{a}$$

$$\frac{d[\mathrm{R}^\bullet]}{dt} = 2k_\mathrm{d}[\mathrm{I}]$$

On applying the steady-state treatment with respect to [R$^\bullet$], we get

$$\frac{d[\mathrm{R}^\bullet]}{dt} = -\frac{d[\mathrm{R}^\bullet]}{dt}$$

$$2k_\mathrm{d}\,[\mathrm{I}] = k_\mathrm{i}[\mathrm{R}^\bullet][\mathrm{M}]$$

Now

$$\text{Rate of initiation} = \frac{d[\mathrm{M}^\bullet]}{dt} = k_\mathrm{i}\,[\mathrm{R}^\bullet][\mathrm{M}] = 2k_\mathrm{d}[\mathrm{I}] \tag{b}$$

if f is the factor which represents the fraction of free radical effective in initiation process, then we can write

$$\text{Rate of initiation} = 2k_\mathrm{d}f\,[\mathrm{I}] \tag{c}$$

Propagation: Initiation is followed by propagation represented as follows:

$$\mathrm{M}_1^\bullet + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{M}_2^\bullet \tag{iii}$$

$$\mathrm{M}_2^\bullet + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{M}_3^\bullet \tag{iv}$$

$$\mathrm{M}_{x-1}^\bullet + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{M}_x^\bullet \tag{v}$$

Since the radical reactivity is independent of chain length, all propagation steps are assumed to have same rate constant k_p. Therefore, rate of propagation may be represented as

$$\text{Rate of propagation} = k_\mathrm{p}\,[\mathrm{M}][\mathrm{M}^\bullet] \tag{d}$$

where [M] is concentration of monomer and [M$^\bullet$] the concentration of reactive free radical.

Termination: The final step is termination which may involve the combination of two growing chain carriers

$$\mathrm{M}^\bullet + \mathrm{M}^\bullet \xrightarrow{k_\mathrm{t}} \mathrm{M}_2 \tag{vi}$$

Rate of termination is given by

$$-\frac{d[\mathrm{M}^\bullet]}{dt} = 2k_\mathrm{t}\,[\mathrm{M}^\bullet][\mathrm{M}^\bullet] \tag{e}$$

where factor 2 shows that in any termination process, two radicals are involved.

For many cases the concentration of free radical becomes practically constant since the radical is formed and consumed at identical rates. Therefore, under steady state conditions

$$\text{Rate of initiation} = \text{Rate of termination}$$

$$2k_d f\,[\text{I}] = 2k_t\,[\text{M}^\bullet]^2$$

or

$$[\text{M}^\bullet] = \left(\frac{k_d f[\text{I}]}{k_t}\right)^{1/2} \tag{f}$$

Again, overall rate of monomer consumption is

$$-\frac{d[\text{M}]}{dt} = \text{Rate of initiation} + \text{Rate of propagation}$$

When a very long polymer is formed, the rate of propagation is much greater than the rate of initiation and therefore, overall rate of polymerization is same as the rate of propagation. Hence

$$\text{Rate of polymerization} = \frac{k_p k_d^{1/2}}{k_t^{1/2}} f^{1/2}\,[\text{I}]^{1/2}\,[\text{M}] \tag{5.19}$$

Thus, the rate of polymerization is proportional to [M] and $[\text{I}]^{1/2}$, if f is high and independent of M, i.e. if $f = 1$.

When the initiation efficiency $f << 1$, f becomes function of M and

$$\text{Rate of polymerization} = \frac{k_p k_d^{1/2}}{k_t^{1/2}} [\text{f}]^{1/2}\,[\text{M}]^{3/2} \tag{5.20}$$

Experimental Determination of Rate Constants

The decomposition of initiator can be followed by usual analytical methods and k_d can be determined. The efficiency factor f can be obtained by comparing the amount of initiator [I] decomposed with the number of polymer chain formed. The rate of polymerization can be determined by monitoring the change in a physical or chemical property of the system. Generally, dilatometry technique is used for determination of the rate of polymerization. Let the extent of polymerization be small and concentration of initiator be constant. Let r_0, r_t and r_∞ be the readings on dilatometer initially, at time t and at the completion of reaction, respectively. If reaction is first order in [M],

$$\text{Rate of polymerization} = k\,[\text{M}]$$

where k is first order rate constant given as

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{t}\log\left(\frac{r_0 - r_\infty}{r_t - r_\infty}\right) \tag{5.21}$$

Thus, a plot of $(r_0 - r_\infty / r_t - r_\infty)$ versus time will be linear and slope of the plot will give the value

$$k = \frac{k_p k_d^{1/2}}{k_t^{1/2}} \{f[\mathrm{I}]\}^{1/2}$$

Now, if k_d, f and [I] are known, $(k_p / k_t^{1/2})$can be evaluated. For calculating individual values of k_t and k_p one more relation can be obtained as follows.

Under the steady state condition, the average life time τ is given as

$$\tau = \frac{[\mathrm{M}^\bullet] \text{ at any time}}{\text{Rate of disappearance of } \mathrm{M}^\bullet} = \frac{[\mathrm{M}^\bullet]}{2k_t [\mathrm{M}^\bullet]^2} = \frac{1}{2k_t [\mathrm{M}^\bullet]} \tag{5.22}$$

The value of $\mathrm{M}^\bullet$ can be obtained from rate of polymerization.

$$\text{Rate of polymerization} = k_p\,[\mathrm{M}]\,[\mathrm{M}^\bullet]$$

Therefore, we get

$$\tau = \frac{k_p [\mathrm{M}]}{2k_t (\text{Rate of polymerization})} \tag{5.23}$$

From equation (5.23) k_p/k_t can be calculated.

Kinetic chain length is defined as the average number of monomers reacting with a given active centre from initiation to termination and is given by

$$n = \frac{\text{Rate of propagation}}{\text{Rate of initiation}} = \frac{k_p[\mathrm{M}][\mathrm{M}^*]}{2k_d f[\mathrm{I}]}$$

$$= \frac{k_p [\mathrm{M}]\{k_d f[\mathrm{I}]/k_t\}^{1/2}}{2k_d f[\mathrm{I}]} = \frac{k_p [\mathrm{M}]}{2k_t^{1/2} k_d^{1/2} \{f[\mathrm{I}]^{1/2}\}} \tag{5.24}$$

5.3.6 Cationic Polymerization

In anionic polymerization, the initiators are either Bronsted or Lewis acids. In Bronsted acid, H^+ is the effective catalyst while in Lewis, co-catalyst is involved to give catalytically active species, e.g.

$$\underset{\substack{\text{Lewis acid}\\(\mathrm{A})}}{\mathrm{BF_3}} + \underset{\substack{\text{co-catalyst}\\(\mathrm{RH})}}{\mathrm{H_2O}} \rightleftharpoons \underset{\substack{\text{active species}\\(\mathrm{H^+—\overline{A}R})\rightarrow}}{\mathrm{H^+[BF_3OH]^-}}$$

The mechanism of anionic polymerization, in general, may be represented as

$$\left.\begin{array}{l} \mathrm{A + RH} \overset{K}{\rightleftharpoons} \mathrm{H^+—\overline{A}R} \\ \mathrm{H^+—\overline{A}R + M} \xrightarrow{k_i} \mathrm{HM^+—\overline{A}R} \end{array}\right\} \quad \text{(initiation)}$$

$$\mathrm{HM_x^+—A\overline{R} + M} \xrightarrow{k_p} \mathrm{HM_{x+1}^+— \overline{A}R} \quad \text{(propagation)}$$

$$\mathrm{HM_x^+}\text{—}\mathrm{AR} \xrightarrow{k_t} \mathrm{M_x} + \mathrm{H^+}\text{—}\,\overline{\mathrm{A}}\mathrm{R} \qquad \text{(termination)}$$

We can give

$$\text{Rate of initiation} = k_i[\mathrm{H^+}\text{—}\overline{\mathrm{A}}\mathrm{R}][\mathrm{M}] = k_i\mathrm{K[A][RH]M} \qquad \text{(a)}$$

$$\text{Rate of termination } = k_t[\mathrm{HM_x^+}\text{—}\overline{\mathrm{A}}\mathrm{R}] \qquad \text{(b)}$$

It is a first order process under the steady state conditions,

$$\text{Rate of initiation} = \text{Rate of termination}$$

$$k_i\mathrm{K[A][RH][M]} = k_t[\mathrm{HM_x^+}\text{—}\overline{\mathrm{A}}\mathrm{R}]$$

Therefore

$$[\mathrm{HM_x^+}\text{—}\overline{\mathrm{A}}\mathrm{R}] = \frac{k_i K}{k_t}\,[\mathrm{A}][\mathrm{RH}][\mathrm{M}] \qquad \text{(c)}$$

Rate of polymerization = Rate of propagation

$$= k_p[\mathrm{M}][\mathrm{HM_x^+}\text{—}\overline{\mathrm{A}}\mathrm{R}] \;=\; \frac{K k_p k_i}{k_t}\,[\mathrm{A}][\mathrm{RH}][\mathrm{M}]^2 \qquad (5.25)$$

In absence of a co-catalyst, the initiation step will be

$$\mathrm{HA} + \mathrm{M} \xrightarrow{k_i} \mathrm{HM^+\,A^-}$$

and correspondingly the rate of polymerization may be obtained as

$$\text{Rate of polymerization} = \frac{k_p k_i}{k_t}\,[\mathrm{HA}][\mathrm{M}]^2 \qquad (5.26)$$

It has also been observed that only ion-pair and not the discrete ionic species are involved in the initiation process.

$$\text{The chain length} = \frac{\text{Rate of polymerization}}{\text{Rate of termination}}$$

$$= \frac{K k_p k_i / k_t [\mathrm{A}][\mathrm{RH}][\mathrm{M}]^2}{(k_i K)[\mathrm{A}][\mathrm{RH}][\mathrm{M}]} = (k_p / k_t)[\mathrm{M}] \qquad (5.27)$$

5.3.7 Anionic Polymerization

The polymerization of olefinic compounds like acrylonitrile, vinyl chloride, styrene, methylmethacrylate can be initiated by anion. The mechanism, in general, can be given as

$$\left.\begin{array}{l} \mathrm{AB} \xrightarrow{k} \mathrm{A^+} + \mathrm{B^-} \\ \mathrm{B^-} + \mathrm{M} \xrightarrow{k_i} \mathrm{M^-} \end{array}\right] \text{(initiation)}$$

$$M_n^- + M \xrightarrow{k_p} M_{n+1}^-] \qquad \text{(propagation)}$$

$$M_n^- + B \xrightarrow{k_t} M_n + B^-] \qquad \text{(termination by chain transfer)}$$

where *B* is the species involved in chain transfer process.

$$\text{Rate of initiation} = k_i[B^-][M] \tag{a}$$

$$\text{Rate of propagation} = k_p\,[M]\,[M_n]^- \tag{b}$$

$$\text{Rate of termination} = k_t\,[M_n^-][B] \tag{c}$$

Under the steady state conditions

$$\text{Rate of initiation} = \text{Rate of termination}$$

i.e.

$$k_i[B^-][M] = k_t[M_n^-][B]$$

Therefore

$$[M_n^-] = \frac{k_i}{k_t}\frac{[B^-]}{[B]}[M] \tag{d}$$

Again

$$\text{Rate of polymerization} = \text{Rate of propagation}$$

Thus, we can write

$$\text{Rate of polymerization} = k_p[M][M_n^-] = \frac{k_p k_i}{k_t}\frac{[B^-]}{[B]}[M]^2 \tag{5.28}$$

which shows that reaction is second order in monomer.

$$\text{Chain length} = \frac{\text{Rate of polymerization}}{\text{Rate of termination}}$$

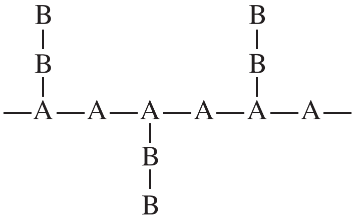
$$= \frac{(k_p k_i/k_t)[B^-][M]^2/[B]}{k_i[B^-][M]} = (k_p/k_t)[M]/[B] \tag{5.29}$$

5.3.8 Co-polymerization

The polymer prepared from same monomer is called *homopolymer*. If more than one monomer is used, the polymer obtained is called *copolymer* which may be of following four types depending on their structure arrangements:

(a) Alternating copolymer—when two structural units alternate in a linear fashion as ABABA . . . .
(b) Random copolymer—when the distribution is random as AABABB AAA . . . .
(c) Block copolymer—when alternations of substantial sequences appear in the chain as AAABBBAAABBB etc.

(d) Graft copolymer—when blocks of one monomer present as branches on the main backbone of the other polymer as



Polymer chains containing more than one type of monomer can be synthesised by selecting suitable monomers A and B and initiating the polymerization process using free radical or ionic initiators. The process is called *copolymerization*. The copolymer can exhibit better qualities than the parent homopolymer.

Let us consider a radical initiated copolymerization of two monomers M_1 and M_2. The four possibilities in which monomers M_1 and M_2 can add to radicals $M_1^\bullet$ and $M_2^\bullet$ are:

$$M_1^\bullet + M_1 \xrightarrow{k_{11}} \sim\!M_1\text{—}M_1^\bullet; \qquad \text{Rate} = k_{11}[M_1^\bullet][M_1]$$

$$M_1^\bullet + M_2 \xrightarrow{k_{12}} \sim\!M_1\text{—}M_2^\bullet; \qquad \text{Rate} = k_{12}[M_1^\bullet][M_2]$$

$$M_2^\bullet + M_1 \xrightarrow{k_{21}} \sim\!M_2\text{—}M_1^\bullet; \qquad \text{Rate} = k_{21}[M_2^\bullet][M_1]$$

$$M_2^\bullet + M_2 \xrightarrow{k_{22}} \sim\!M_2\text{—}M_2^\bullet; \qquad \text{Rate} = k_{22}[M_2^\bullet][M_2]$$

where k_{11} and k_{22} are the rate constants for self propagating and homoreactions. While k_{12} and k_{21} are rate constants for cross propagation, it has been assumed that the reactivity of any growing chain depends only on the end monomer unit carrying the free radical site and not on the length of the chain. Now, the disappearance of M_1 and M_2 can be given as

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^\bullet][M_1] + k_{21}[M_2^\bullet][M_1] \tag{a}$$

and
$$-\frac{d[M_2]}{dt} = k_{22}[M_2^\bullet][M_2] + k_{12}[M_1^\bullet][M_2] \tag{b}$$

Assuming a steady state, i.e. rate of disappearance of a particular chain end $M_1^\bullet$ is equal to its rate of formation, we get

$$k_{12}[M_1^\bullet][M_2] = k_{21}[M_2^\bullet][M_1]$$

or
$$\frac{[M_1^\bullet]}{[M_2^\bullet]} = \frac{k_{21}[M_1]}{k_{12}[M_2]} \tag{c}$$

From equations (a) and (b), we can get

$$\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_2]} = \frac{k_{11}[\mathrm{M}_1^\bullet][\mathrm{M}_1] + k_{21}[\mathrm{M}_2^\bullet][\mathrm{M}_1]}{k_{12}[\mathrm{M}_1^\bullet][\mathrm{M}_2] + k_{22}[\mathrm{M}_2^\bullet][\mathrm{M}_2]} = \frac{[\mathrm{M}_1]\{k_{11}[\mathrm{M}_1^\bullet]/[\mathrm{M}_2^\bullet] + k_{21}\}}{[\mathrm{M}_2]\{k_{12}[\mathrm{M}_1^\bullet]/[\mathrm{M}_2^\bullet] + k_{22}\}} \tag{d}$$

Substituting the value of $(\mathrm{M}_1^\bullet)/(\mathrm{M}_2^\bullet)$ from equation (c) into (*d*), we get

$$\frac{d[M_1]}{d[\mathrm{M}_2]} = \frac{[\mathrm{M}_1]\{k_{11}(k_{21}[\mathrm{M}_1]/k_{12}[\mathrm{M}_2]) + k_{21}\}}{[\mathrm{M}_2]\{k_{12}(k_{21}[\mathrm{M}_1]/k_{12}[\mathrm{M}_2]) + k_{22}\}}$$

$$= \frac{[\mathrm{M}_1]\{k_{11}[\mathrm{M}_1]/k_{12}[\mathrm{M}_2] + 1\}}{[\mathrm{M}_2]\{[\mathrm{M}_1]/[\mathrm{M}_2] + k_{22}/k_{21}\}}$$

Let $k_{11}/k_{12} = r_1$ and k_{22}/k_{21} as r_2

The relative reactivity ratios r_1 and r_2 are the ratios of rate constant for a given radical adding to its own monomer to the rate constant for its adding to the other monomer. For example when $r_1 > 1$, radical prefers to add to M_1 while if $r_1 < 1$, i.e. $\mathrm{M}_1^\bullet$ prefers to add to M_2. Now, we can write

$$\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_2]} = \frac{[\mathrm{M}_1]\{r_1[\mathrm{M}_1]/[\mathrm{M}_2] + 1\}}{[\mathrm{M}_2]\{k_{12}[\mathrm{M}_1]/k_{12}[\mathrm{M}_2] + k_{22}\}} = \frac{[\mathrm{M}_1]}{[\mathrm{M}_2]}\left\{\frac{r_1[\mathrm{M}_1] + [\mathrm{M}_2]}{[\mathrm{M}_1] + r_2[\mathrm{M}_2]}\right\} \tag{e}$$

If X_1 and X_2 are the mole fractions of monomers M_1 and M_2 being added to the growing chain at any time *t* and x_1 and x_2 are mole fractions of M_1 and M_2, respectively, in the feed, then

$$\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_2]} = \frac{X_1}{X_2} = X \text{ (say)}$$

and

$$\frac{[\mathrm{M}_1]}{[\mathrm{M}_2]} = \frac{X_1}{X_2} = x \text{ (say)}$$

Then equation (e) can be simplified as

$$X = x\left(\frac{r_1 x + 1}{x + r_2}\right) \tag{f}$$

or $$1 - X = 1 - x\left(\frac{r_1 x + 1}{x + r_2}\right) = \frac{x + r_2 - r_1 x^2 - x}{r_2 + x}$$

or $$(1 - X)\,(r_2 + x) = x + r_2 - \mathrm{r}_1 x^2 - x$$

$$r_2 + x - Xr_2 - xX = x + r_2 - r_1 x^2 - x$$

or $$x(1 - X) = r_2 X - r_1 x^2$$

$$\frac{x(1 - X)}{X} = r_2 - r_1\left(\frac{x_2}{X}\right) \tag{5.30}$$

According to equation (5.30) a plot of $\{x(1-X)/X\}$ against (x^2/X) should give a straight line with a slope ($= r_1$) and an intercept ($= r_2$). The values of r_1 and r_2 can be evaluated from this straight line. For different ratio of feed composition $[M_1]/[M_2]$, i.e. x, the polymerization is carried out keeping low percentage conversion.

The polymers are isolated and their composition is determined. This gives the value of x, i.e. instantaneous polymer composition ratio. Since X and x are different as polymerization progresses, the unreacted polymer ratio x will change resulting in a continuous change in the composition of the polymer formed. This is known as the *composition drift*.

The copolymerization depends on values of r_1 and r_2. The conclusions may be summarized as follows:

1. When $r_1 = 1$, $k_{12} = k_{11}$, i.e. rate constant for self-propagation and cross propagation are same, the radical $M_1^\bullet$ can add to M_1 or M_2 with equal probability.

2. When $r_1 \approx r_2 \approx 0$, self-propagation reactions are not taking place, $M_1^\bullet$ will add to M_2 and $M_2^\bullet$ will add to M_1. The formation of an alternating copolymers is expected.

3. When $r_1 < 1$ and $r_2 < 1$, the cross propagation reactions 12 and 21 are preferred to self-propagation reactions 11 and 22. M_2 can add to $M_1^\bullet$ and M_1 can add to $M_2^\bullet$ resulting in a copolymer formation. Predomination of one sequence depends on the values of r_1 and r_2 and feed ratio.

4. When $r_1 = r_2 = 1$, all four types of propagation reactions are equally possible. The copolymer will have same ratio of monomer as that of the monomer feed. A random copolymer is formed.

5. When both r_1 and $r_2 > 1$, a mixture of the two homopolymers is expected and it is possible to have block polymer.

6. When $r_1 > 1$ and $r_2 < 1$, the self-propagation reaction of type 11 and cross propagation reaction of type 21 are more probable. The copolymer formed will be richer in M_1. Similarly if $r_2 > 1$ and $r < 1$, copolymer will be richer in M_2.

5.4 Kinetics of Solid State Reactions

The solid state reactions are extremely complex due to intervention of many physical parameters and it becomes often necessary to make some generalizations in the complex reactions. The rate in solid state reactions cannot be defined in the same way as that for a homogeneous reactions because the concept of concentration in solid state reactions has no significance. The energy of activation in a solid state reaction has also no significance, except in some rare cases.

The lattice imperfections play an important role in reactions in solid state. The reactivity of solids are due to the defect or fault in the lattice. The more perfect a crystal is, the smaller is its reactivity. The defect may be point defect, dislocations, stacking faults, bulk defects etc.

The simple solid state reaction may involve either (i) the interfacial reaction or (ii) the diffusion of reactants to each other, as the rate determining step. For example, decomposition of a solid giving rise to another solid

$$\text{Solid} \rightarrow \text{Solid}$$

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

An interface is formed at the point where the decomposition takes place and the interfacial reaction becomes important.

When a gas or liquid involves in the reaction, for example, the oxidation of a metal surface

$$2Fe(s) + O_2(g) \rightarrow 2FeO(s)$$

The interface where the reaction takes place must be accessible to these reactants. In such cases, the diffusion of reactants to the reaction front becomes an important factor and diffusion of reactions to each other is rate determining step.

In reactions

$$\text{Solid (A)} + \text{Gas (B)} \rightarrow \text{Solid (AB)}$$

or
$$\text{Solid (A)} + \text{Liquid (B)} \rightarrow \text{Solid (AB)}$$

When the molar volume of product, i.e. solid (AB) is less than that of solid (A), the product layer will be porous and the rate determining step is the chemical process occurring at the interface of solid (A). Such reactions are also known as *topochemical reactions*. The rate of reaction may be determined by the available surface area of A. For example, if reaction involves spherical particle, the rate of reaction (i.e. $-dV/dt$, where V is the volume of particle at time t) is given as

$$-\frac{dV}{dt} = k(\text{surface area}) = k(4\pi r^2) \tag{5.31}$$

where r is radius of particle at time t.

Since, volume $V = \frac{4}{3}\pi r^3$

$$-\frac{d}{dt}\left(\frac{4}{3}\pi r^3\right) = 4\pi k r^2$$

or
$$-\frac{dr}{dt} = k \tag{5.32}$$

Thus, radius of the particle reduces at a constant rate.

In above reactions when molar volume of product (AB) is greater than that of reactant (A), the product (AB) will usually form a protected layer around (A), the diffusion process becomes the rate determining step. Since the diffusion is the rate controlling step in these reactions, according to Wagner's theory the rate of reaction is given by

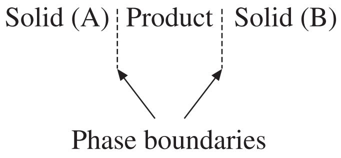
$$\text{Rate of reaction} = \frac{dx}{dt} = k/x$$

or

$$x^2 = 2kt \tag{5.33}$$

where constant k is proportional to diffusion coefficient. This is known as *parabolic law* and is frequently observed. Various other laws have also been obtained.

When a solid-solid reaction starts, a layer of product is formed between the two reactant phases and a single phase boundary converts into two different phase boundaries as



The product layer progressively becomes thicker until the original reactants are completely consumed. These reactions involve two steps: (i) the diffusion of reactants through the product layer and (ii) the reaction at the phase boundary. The relative rates of these steps determine the overall rate of reaction.

The experimental methods which give informations on the structure of the phases (for example, x-ray diffraction analysis of polycrystalline substances, diffuse reflectance spectra) may be used to follow the kinetics of solid-solid reactions.

Wagner gave a quantitative thermodynamic theory based on a simple addition reaction of type

$$AX + BX \rightarrow ABX_2$$

The theory is based on the assumptions that:

(i) the rate of reaction is determined by diffusion through the product layer.
(ii) only cations are mobile with no change in their mobility.
(iii) the mobility of cations corresponds to their transport fraction in an electrolysis experiment.
(iv) there is no appreciable electronic conduction.

The rate of reaction, determined as the sum of two individual particle currents, may be given as

$$\text{Rate} = -\frac{[A^+] + [B^+]Z_B}{1 + \dfrac{Z_B[B^+]V_B}{Z_A[A^+]V_A}} \int V_B[B^+]\,d\mu \tag{5.34}$$

where $[A^+]$ and $[B^+]$ are concentrations, Z_A and Z_B are valencies, V_A and V_B are mobilities of cations A and B, respectively, and l is diffusion length. On integration, the above expression shows that under the condition $V_B >> V_A$, the rate is proportional to transport number of A and in case $V_A >> V_B$ it is proportional to transport number of B. The theory has also been extended to cover the movement of anions i.e. diffusion of anions.

The progress of the reactions like

$$\text{Solid} + \text{Gas} \rightarrow \text{Gas}$$

or

$$\text{Solid} \xrightarrow{\text{Thermal decomposition}} \text{Gases}$$

can be studied thermogravimetrically. The amount of solid can be weighed at regular intervals of time. The reactions in which temperature is progressively changed at constant rate, can also be studied using thermogravimetry.

Let us consider the decomposition of a solid

$$\text{Solid} \rightarrow \text{Gases}$$

If α is the fraction of solid decomposed at time t, and the order of the reaction is one, the rate of disappearance of solid at any time t, may be given as

$$-\frac{d[\text{solid}]}{dt} = \frac{d\alpha}{dt} = k(1 - \alpha) \tag{a}$$

where k is rate constant.

Taking Arrhenius equation

$$k = k_\infty e^{-E_{\text{act}}/RT} \tag{b}$$

where k_∞ is the value of rate constant when temperature is infinite, i.e. upper limit for the rate constant.

Further, for a linear heating, the rate of heating may be given as

$$\theta = \frac{dT}{dt} \tag{c}$$

From equations (a), (b) and (c), we obtain

$$\frac{d\alpha}{(1 - \alpha)} = k_\infty \frac{1}{\theta} e^{-E_{\text{act}}/RT} dT \tag{5.35}$$

Taking logarithms of the integrated form of the equation (5.35), we get

$$\log\left[-\frac{\log(1 - \alpha)}{T^2}\right] = \log\left\{\frac{k_\infty R}{\theta E_{\text{act}}}\left(1 - \frac{2RT}{E_{\text{act}}}\right)\right\} - \frac{E_{\text{act}}}{2.303RT} \tag{5.36}$$

For usual values of E_{act} and nominal temperature range, the value of $\log\left\{\frac{k_\infty R}{\theta E_{\text{act}}}\left(1 - \frac{2RT}{E_{\text{act}}}\right)\right\}$ is constant and thus a plot of $\log\left[-\frac{\log(1-\alpha)}{T^2}\right]$ versus $1/T$ will be a straight line with a negative slope. From the slope the value of $E_{\text{act}}/2.303R$ (and hence E_{act}) may be obtained.

Considering the general reaction

$$-\frac{d[\text{solid}]}{dt} = \frac{d\alpha}{dt} = k_n(1-\alpha)^n \tag{5.37}$$

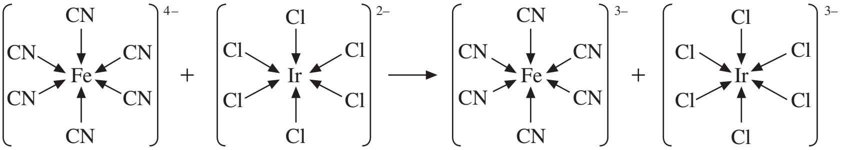
for n^{th} order of reaction, the order of reaction may also be determined.

5.5 Electron Transfer Reactions

Electron transfer reactions may follow two types of mechanism: (i) outer sphere mechanism and (ii) inner sphere mechanism.

5.5.1 Outer Sphere Mechanism

In principle, outer sphere mechanism involves electron transfer from reductant to oxidant when there is no change in the number or nature of the groups (coordination shells or spheres) attached to each of them. For example,



In outer sphere mechanism, one reactant becomes involved in the outer or second coordination sphere of the other reactant and an electron flows from the reductant to oxidant. It is also possible that the electron is transferred first to the solvent and then from the solvent to an ion.

Such reactions are observed in electron transfer reactions of substitutionally inert complexes. The mechanism involves three steps.

(i) Formation of complex between oxidant and reductant.
(ii) Chemical activation of complex, electron transfer and relaxation of the successor complex.
(iii) Dissociation of successor complex.

Step (ii) is generally the rate determining step; for example

$$\underset{\text{(Oxidant)}}{\mathrm{Fe}_{\mathrm{II}}^{2+}} + \underset{\text{(Reductant)}}{\mathrm{Fe}_{\mathrm{III}}^{3+}} \overset{K}{\rightleftharpoons} \underset{\text{(Complex)}}{\mathrm{Fe}_*^{2+} - \mathrm{Fe}_*^{3+}} \qquad \text{(i) formation of complex}$$

$$\underset{\text{(Complex)}}{\mathrm{Fe}_*^{2+} - \mathrm{Fe}_*^{3+}} \xrightarrow{k} \underset{\text{(Complex)}}{\mathrm{Fe}_*^{3+} - \mathrm{Fe}_*^{2+}} \qquad \text{(ii) transfer of electrons}$$

$$\underset{\text{(Complex)}}{\mathrm{Fe}_*^{3+} - \mathrm{Fe}_*^{2+}} \to \underset{\text{(Ions)}}{\mathrm{Fe}_{\mathrm{III}}^{3+} + \mathrm{Fe}_{\mathrm{II}}^{2+}} \qquad \text{(iii) separation of ions}$$

where asterisks represent the organized shells. The oxidant and reductant must structurally reorganize themselves before electron transfer so that energies of their transition states are equal.
Step (i) i.e. formation of complex is considered to be fast and rate is generally determined by step (ii). The rate may be given as,

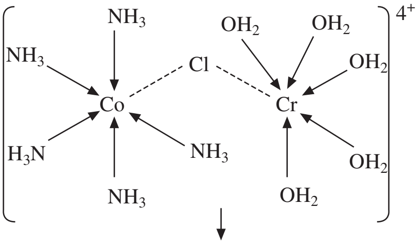
$$\text{Rate} = k\,K$$

Further electronic structure of oxidant and reductant, solvent reogranisation affects the rate of reaction.

5.5.2 Inner Sphere Mechanism

When two reactants (oxidant and reductant) spare a ligand in their primary coordination sphere, the electron is transferred across a bridging group and mechanism is known as inner sphere electron transfer mechanism. In this case the oxidant usually possesses at least one ligand capable of binding simultaneously to two metal ions. The other reactant is substitutionally labile i.e. one ligand must be replaced by bridging ligand. For example,

$[Co(NH_3)_5Cl]^{2+} + Cr(H_2O)_6^{2+} + 5H_2O \longrightarrow$



$[Co(H_2O)_6]^{2+} + [Cr(H_2O)_5Cl]^{2+} + 5\,NH_3$

According to Taube, the inner sphere mechanism can takes place when both oxidizing and reducing agents are substitution inert and when ligand transfer from oxidant to reductant is accompanied by electron transfer. The inner sphere electron transfer mechanism may be represented by the scheme

$$O - X + R - H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(Complex)}}{[O\text{---}X\text{---}R]} + H_2O \qquad \text{(i)}$$

$$\text{Complex} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} O^- + R\text{---}X^+ \qquad \text{(ii)}$$

where O is oxidant with a ligand X and R is reductant. The rate of reaction may be obtained as

$$\text{Rate} = \frac{k_1 k_3}{k_2 + k_3}\,[\text{Oxidant}][\text{Reductant}]$$

where k_1 is rate limiting and k_3 is rate determining. Thus, generally the reaction is second order being first order with respect to each oxidant and reductant.

The electronic structure of oxidant and reductant, nature of bridging ligand, formation as well as fission of complex are the factors which can effect the rate of the inner sphere electron transfer mechanism.

The outer sphere mechanism may take place in all redox active systems while inner sphere mechanism requires substitutionally labile reactants and products.

When oxidants and reductants change their oxidation state by an equal number of units, the reaction is known as complementary reaction. When the oxidant and the reductant change their oxidation state by a different number of units, the electron transfer reaction is known as a non-complementary reaction.

EXERCISES

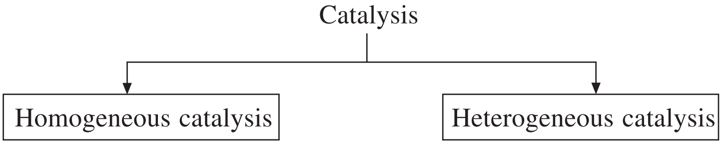
1. State and explain the 'law of photochemical equivalence' and 'quantum efficiency'.
2. Describe the primary process in photochemical reactions with help of suitable examples.
3. Discuss the kinetics of $H_2 + Cl_2 \rightarrow 2HCl$ reaction and explain why quantum yield of the reaction is exceptionally high?
4. Describe the 'Volterra model' for oscillatory reaction.
5. Give a brief account of Belousov-Zhabotinskii mechanism of oscillatory reaction.
6. Derive the equations for the rate of reaction and chain length of a free radical polymerization reaction.
7. Derive the equation for the rate of polymerization in (a) Anionic polymerization and (b) Cationic polymerization.
8. What is meant by relative reactivity ratios in copolymerization process? How the copolymerization depends on the relative reactivity ratios? Discuss.
9. Describe in brief, the kinetics of solid state reactions.
10. How the kinetics of thermal decomposition of a solid can be studied experimentally?

6

Kinetics of Catalyzed Reactions

6.1 Catalysis

In 1836, Berzelius observed that there are some substances, which increase the rate of reaction without changing themselves. He thought that such a substance loosens the bonds holding the atoms in reacting molecule and hence helps in increasing the rate of reaction. Such a process was called *catalysis* (Greek: *Kata* = wholly, *lein* = to loosen) and the substance called *catalyst*. A number of cases are now known in which a catalyst slows down (retards) the rate of reaction. In general, the catalyst may be defined as ‘a substance, which alters the rate of reaction, remaining itself chemically unchanged at the end of the reaction’.



Homogeneous catalysis	Heterogeneous catalysis
Catalysts and reactants in same phase	Catalyst and reactants in different phases
$\underset{(g)}{2SO_2} + \underset{(g)}{O_2} \xrightarrow{[NO]_g} \underset{(g)}{2SO_3}$	$\underset{(g)}{2SO_2} + \underset{(g)}{O_2} \xrightarrow{[Pt]_s} \underset{(g)}{2SO_3}$
$\underset{(vapor)}{CH_3CHO} \xrightarrow{[I_2]_{vapor}} \underset{(g)}{CH_4} + \underset{(g)}{CO}$	$\underset{(g)}{N_2} + \underset{(g)}{3H_2} \xrightarrow{[Fe]_s} \underset{(g)}{NH_3}$ (Haber Process)
$\underset{(l)}{Ester} + \underset{(l)}{H_2O} \xrightarrow{[H^+]_l} \underset{(l)}{Acid} + \underset{(l)}{Alcohol}$	$\underset{(g)}{CH_2 = CH_2} \xrightarrow{[Ni]_s} \underset{(g)}{CH_3 - CH_3}$
	$\underset{(l)}{2H_2O_2} \xrightarrow{[Pt]_s} \underset{(l)}{2H_2O} + \underset{(g)}{O_2}$

6.1.1 Positive Catalysis

The catalyst which increases the rate of a chemical reaction is called *positive catalyst* and the phenomenon is known as *positive catalysis*. Examples are

(i) $2KClO_3 \xrightarrow{[MnO_2]} 2KCl + 3O_2$

(ii) $4HCl + O_2 \xrightarrow{[CuCl_2]} 2H_2O + 2Cl_2$

(iii) $H_2O_2 \xrightarrow{[Pt]} H_2O + O$

(iv) Vegetable oil + $H_2 \xrightarrow{[Ni]}$ Vegetable ghee

6.1.2 Negative Catalysis

The catalyst which decreases the rate of reaction is called *negative catalyst* and phenomenon is called *negative catalysis*. Examples are

(i) $2H_2O_2 \xrightarrow{[Acetanilide]} 2H_2O + O_2$

(ii) $4CHCl_3 + 3O_2 \xrightarrow{[Alcohol]} 4COCl_2 + 2H_2O + 2Cl_2$

(iii) Knocking of petrol by tetraethyl lead

The negative catalysts are also known as *retarder* or *inhibitor*.

6.1.3 Auto Catalysis

When one of the product itself acts as a catalyst for that reaction, the phenomena is called *autocatalysis*. For example,

$$CH_3COOC_2H_5 + H_2O \xrightarrow{[HCl]} CH_3COOH^* + C_2H_5OH$$

$$2AsH_3 \xrightarrow{\text{Decomposition}} 2As^* + 3H_2$$

$$5C_2H_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{*2+} + 10CO_2 + 8H_2O$$

where * indicates the product acting as autocatalyst.

In autocatalytic reaction the graph plotted between the rate of reaction and time shows a sigmoid curve as shown in Fig. 6.1. As the product (catalyst) concentration increases the rate increases, and reaches to a maximum when the reaction is complete.

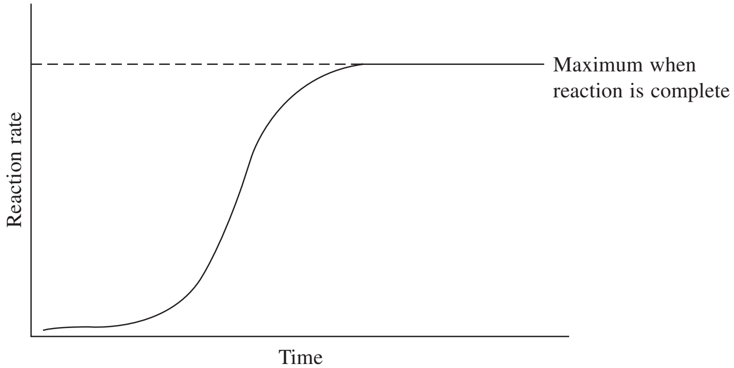


Fig. 6.1 Rate versus time plot for an autocatalytic reaction.

6.1.4 Induced Catalysis

When a reaction influences the rate of some other reaction which does not occur under ordinary conditions, the phenomenon is called *induced catalysis*. For example

1. Sodium arsenite does not oxidize in air while sodium sulphite oxidizes. When mixture of sodium arsenite and sodium sulphite is treated, both of them undergo simultaneous oxidation. Oxidation of sodium sulphite catalyses the oxidation of sodium arsenite.

2. Reduction of mercuric chloride with oxalic acid is slow whereas reduction of $KMnO_4$ by oxalic acid is fast. When mixture of mercuric chloride and oxalic acid is treated with $KMnO_4$, both get reduced simultaneously. Reduction of $KMnO_4$ induces the reduction of mercuric chloride.

6.1.5 Promoters

Sometimes the activity of a catalyst may be increased by addition of small amount of a second substance. The second substance, which though itself is not a catalyst, promotes the activity of a catalyst, is called the *promoter*.

For example, in reaction

$$N_2 + 3H_2 \xrightarrow[\text{Mo or } Al_2O_3]{[Fe]} 2NH_3$$

[Fe] is the catalyst and presence of Mo or Al_2O_3 increase the activity of iron and, therefore, acts as promoter. In reaction

$$CO + 2H_2 \xrightarrow[Cr_2O_3]{[ZnO]} CH_3OH$$

Cr_2O_3 acts as promoter and increases the activity of catalyst ZnO.

The phenomena of promotion is a common feature of heterogeneous catalysis. Generally, the presence of promoter increases the peaks and cracks on the surface of the catalyst and therefore is responsible for increasing the rate of reaction by increasing the activity of the catalyst.

6.1.6 Poisons

Sometimes the rate of a catalysed reaction is reduced by the presence of a small amount of same substance (may be as impurities in the reactants). Such a substance, which destroys the activity of a catalyst, is called *poison* and the process is called *catalytic poisoning*. For example, in reaction

$$2H_2 + O_2 \xrightarrow[CO]{[Pt]} 2H_2O$$

activity of catalyst Pt is poisoned by presence of CO. In reaction

$$N_2 + 3H_2 \xrightarrow[H_2S]{[Fe]} 2NH_3$$

presence of H_2S reduces the activity of Fe.

Poisoning of the catalyst by presence of a catalytic poison may be either due to chemical reaction between catalyst and poison (e.g. $Fe + H_2S \rightarrow Fe + H_2$) or poison may render surface of the catalyst unavailable for adsorption of reactants.

6.2 Theories of Catalysis

The two main theories of catalysis are: (i) intermediate compound formation theory and (ii) adsorption theory.

6.2.1 Intermediate Compound Formation Theory

According to this theory, the catalyst reacts with one of the reactants to give an intermediate, which reacts with another reactant to yield products and the catalyst as follows:

$$\text{A} + [\text{Catalyst}] \rightleftharpoons (\text{Intermediate})$$

$$\text{Intermediate} + \text{B} \rightarrow \text{Products} + [\text{Catalyst}]$$

For example

(i) $$2SO_2 + O_2 \xrightarrow{[NO]} 2SO_3$$

proceeds as

$$2NO + O_2 \rightarrow 2NO_2$$

$$NO_2 + SO_2 \rightarrow SO_3 + NO$$

(ii) $$C_6H_6 + CH_3Cl \xrightarrow{[AlCl_3]} C_6H_5CH_3 + HCl$$

proceeds as

$$CH_3Cl + AlCl_3 \rightarrow [CH_3]^+ [AlCl_4]^-$$

$$[CH_3]^+ [AlCl_4]^- + C_6H_6 \rightarrow C_6H_5CH_3 + AlCl_3 + HCl$$

6.2.2 Adsorption Theory

The heterogeneous catalysis e.g. gaseous reaction on a solid surface, is explained by this theory as follows:

$$A(g) + B(g) \xrightarrow{\text{Catalyst}} C(g) + D(g)$$

Generally, following four steps are involved in the heterogeneous catalysis:

(i) Diffusion of reactants at the surface of the catalyst.
(ii) Adsorption of reactants at the surface.
(iii) Reaction of reactants at the surface.
(iv) Desorption of products from the surface.

The reactants are adsorbed at the surface of the catalyst and held up at the surface by weak van der Waals forces (physical adsorption) or by partial chemical bonds (chemical adsorption). The catalyst surface have unbalanced chemical bonds on it. The reactant molecules are absorbed on the surface by these free bonds.

Thus, the surface provides the chances for reactants to combine and form activated complex and accelerate the rate of reaction. An increase in the surface area (increasing peaks, cracks, corners) of the catalyst increases the rate of reaction.

Out of the above four steps, steps (i) and (iii) are rapid and normally do not play any part in the overall rate determination of reaction. Mechanism of heterogeneous catalysis is discussed in Section 6.9.

6.3 Characteristics of Catalytic Reactions

The catalytic reactions are characterized by the following criteria:

1. During the reaction, the catalyst remains unchanged in mass and chemical composition at the end of reaction. However, the physical properties of the catalyst may change.

2. A very small quantity of the catalyst can produce an appreciable effect on the speed of reaction, e.g. an amount of ~10^{-6}-10^{-8} mol dm^{-3} of platinum group metal ions is sufficient to catalyse various redox reactions.

3. A catalyst cannot start a reaction but can only effect, i.e. decrease or increase the rate of reaction. Since the catalyst is reproduced at the end of reaction, it does not contribute any energy to the system. The free energy change thus will be same in presence or in absence of the catalyst. The catalyst works as an agent to find out an alternative path for the reaction.

4. The catalyst does not effect the final state of equilibrium. The equilibrium

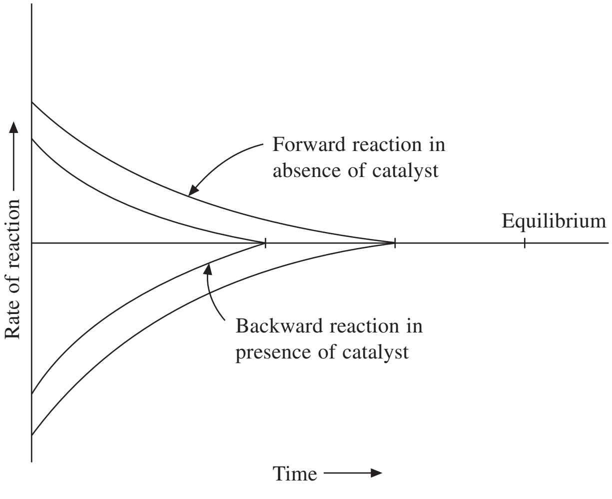


Fig. 6.2 State of equilibrium in absence as well as in presence of a catalyst.

constant $K = k_1/k_1'$, the ratio of rate constant for forward and backward reactions, remains same. The catalyst effects the rate constants for forward and backward reactions in same proportion and equilibrium reaches earlier without effecting equilibrium constant.

6.4 Mechanism of Catalysis

In enhancing the rate of a reaction, the catalyst does combine with a reactant forming an intermediate complex, which subsequently breaks up to yield the products along with the catalyst itself. The reactant with which the catalyst combines is often mentioned as a substrate. A general mechanism, which appears to apply to most of the catalytic reactions may be represented as follows:

$$S + C \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} X + Y \tag{a}$$

$$X + W \xrightarrow{k_2} P + C \tag{b}$$

where S and C represent the substrate and catalyst, respectively, X is the intermediate complex, Y some substance formed in addition to X and W is a molecule which reacts with the complex to give product P with elimination of the catalyst.

In surface catalysis, where X is an adsorption complex and Y and W are non-existent, the mechanism may be represented as follows:

$$S + C \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} X \tag{c}$$

$$X \xrightarrow{k_2} P + C \tag{d}$$

k_1' and k_2 are the first order rate constants while k_1 is a second order rate constant.

The species Y is also probably non-existent in most of the enzyme catalysed reactions involving only one substrate. In acidic or basic reactions, Y and W do, however, play roles. In acid catalysed reactions, where C is an acid, transfer of proton to S takes place giving Y as a conjugate base of C. W is a basic or amphoteric substance which accepts a proton from X. In base catalysis, Y is a conjugate acid to the base C while W transfers a proton to X and may be the solvent or another acidic substance. With regard to the stability of the intermediate complex X, the two possibilities, which may be considered, are:

(i) When rate of reconversion of complex into catalyst and the substrate is significantly greater than the rate with which it undergoes to give product (i.e. $k_1' >> k_2$), the concentration of the complex, i.e. [X] can be obtained by considering equilibrium (a) alone. And then rate can be calculated by multiplying [X] by k_2[W]. The complexes relevant to this type of catalysis are known as *Arrhenius complexes*.

(ii) When intermediate complex is much less stable species, i.e. rate of its conversion to products is not small compared with the reverse rate of reaction (a), it is then not possible to calculate the concentration of X by making use of equilibrium (a) alone because the rate of reaction (b) cannot be neglected.

The concentration of complex in such a case must be calculated by making the use of steady-state-treatment. This type of complex is known as a Van't Hoff complex.

Let us take a simple homogeneously catalyzed reaction

$$S + C \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} X \tag{e}$$

$$X \xrightarrow{k_2} P + C \tag{f}$$

The rate of formation of product, i.e. rate of reaction may be given as

$$\text{Rate of reaction} = k_2[X]$$

If intermediate complex is a Arrhenius complex i.e. $k_1' >> k_2$, the concentration of X can be determined from equilibrium (1), and we get

$$[X] = K[S][C]$$

where (equilibrium constant) $K = k_1/k_1'$ and, therefore,

$$\text{Rate of reaction} = k_2K[S][C] \tag{6.1}$$

However, if complex is of Van't Hoff type complex, [X] is determined by steady state treatment. On applying steady state conditions with respect to X, we get

$$k_1\,[S][C] = k_1'[X] + k_2\,[X]$$

or

$$[X] = \frac{k_1[S][C]}{k_1' + k_2}$$

and, therefore,

$$\text{Rate of reaction} = \frac{k_1k_2\,[S][C]}{k_1' + k_2} \tag{6.2}$$

However, when $k_1' >> k_2$, the rate law becomes same as in case of Arrhenius complex. Thus, the steady state treatment is the general one, and reduces to the equilibrium treatment (Arrhenius complex) when $k_1' >> k_2$.

The above rate laws clearly show that the rate is dependent on the catalyst concentration. For a given concentration of the catalyst, we may write

$$\text{Rate of reaction} = k''[S] \tag{6.3}$$

where $k'' = \dfrac{k_1k_2[C]}{k_1' + k_2}$ or $k_2K[C]$ (when $k_1' >> k_2$).

constant k'' is proportional to [C] and is known as catalytic coefficient for the catalyst.

6.5 Activation Energies of Catalyzed Reactions

The catalyst provides an alternative path for the transformation in which the required activation energy is reduced. Lesser activation energy permits larger amount of reaction in given time.

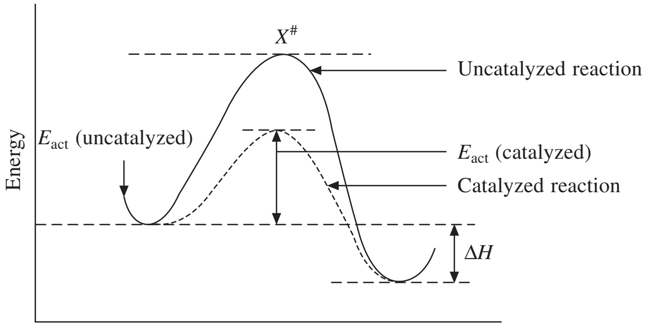


Fig. 6.3 Activation energies of uncatalyzed and catalyzed reactions.

Depending upon the system and conditions, the relationship between the overall activation energy of a catalyzed reaction and activation energies of the individual steps may be considered. For an Arrhenius complex, which is at equilibrium with reactants, at low substrate concentrations the rate of reaction is equal to k_2K[S][Catalyst] $(K = k_1/k_1')$, the overall activation energy is given by

$$E = E_1 + E_2 - E_{-1} \tag{6.4}$$

At higher substrate concentrations, where the rate is given by k_2 [Catalyst], the overall activation energy is given by

$$E = E_2 \tag{6.5}$$

In Vanť Hoff intermediate, where concentration of the catalyst is negligible compared with substrate concentration, at higher substrate concentration the rate is given by

$$\text{Rate} = \frac{k_1k_2}{k_1' + k_2}\,[\text{C}][\text{S}]$$

Now, if $k_2 >> k_1'$, we get

$$\text{Rate} = k_1\,[\text{C}][\text{S}]$$

and

$$\text{Activation energy } E = E_1 \tag{6.6}$$

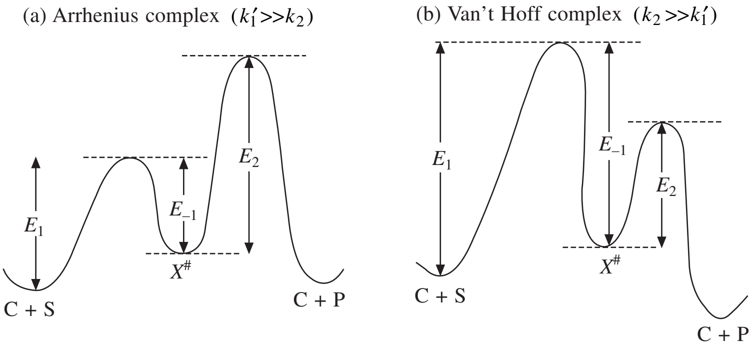
On the other hand, if $k_1' >> k_2$, we may write

$$\text{Rate} = \frac{k_1 k_2}{k_1'}[\mathrm{C}][\mathrm{S}]$$

therefore, overall energy is given by

$$E = E_1 + E_2 - E_{-1} \tag{6.7}$$

This, in fact, is the case of Arrhenius complex. These energies are represented in Fig. 6.4.



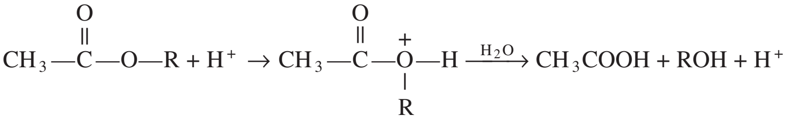
Rate controlling step is second barrier

Rate controlling step is first barrier

Fig. 6.4 Energy diagram for catalyzed reaction.

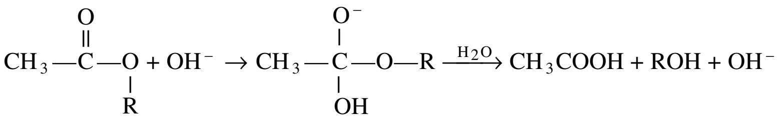
6.6 Acid Base Catalysis

There are certain reactions, e.g. inversions of sucrose and methane etc. in which the rate of reactions were found to be proportional to the concentration of H^+ ions. Similarly, there are reactions which are catalyzed by OH^- ions, e.g. conversion of acetone into diacetone alcohol or decomposition of nitroso-triacetoneamine. These are known as *specific hydrogen ion catalyzed* or *specific hydroxyl-ion catalyzed* reactions. Also there are some reactions in which both H^+ and OH^- ions act as catalysts probably along with water. The undissociated acid or base have negligible effect on the rate of reaction. The hydrolysis of ester is an example in which both H^+ and OH^- ions act as catalyst



$$\mathrm{CH_3}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\mathrm{R} + \mathrm{H^+} \rightarrow \mathrm{CH_3}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{R}}{|}}{\overset{+}{\mathrm{O}}}-\mathrm{H} \xrightarrow{\mathrm{H_2O}} \mathrm{CH_3COOH} + \mathrm{ROH} + \mathrm{H^+}$$

and



$$\mathrm{CH_3}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{R}}{|}}{\mathrm{O}} + \mathrm{OH^-} \rightarrow \mathrm{CH_3}-\underset{\underset{\mathrm{OH}}{|}}{\overset{\overset{\mathrm{O^-}}{|}}{\mathrm{C}}}-\mathrm{O}-\mathrm{R} \xrightarrow{\mathrm{H_2O}} \mathrm{CH_3COOH} + \mathrm{ROH} + \mathrm{OH^-}$$

Intermediate

If catalysis is effected simultaneously by H^+ and OH^- ions and reaction also occurs in absence of these ions, the rate of reaction may be written as,

$$\text{Rate} = k_{H_2O}[S] + k_{H^+}[H^+][S] + k_{OH^-}[OH^-][S] \tag{6.8}$$

where S is the substrate, k_{H^+} and k_{OH^-} are known as catalytic constants for H^+ and OH^- ions, respectively and k_{H_2O} is the rate constant in absence of the catalyst.

The first order rate constant is, therefore, given by

$$k = k_{H_2O} + k_{H^+}[H^+] + k_{OH^-}[OH^-] \tag{6.9}$$

Equation (6.9) can also be written in a more convenient form as

$$k = k_{H_2O} + k_{H^+}[H^+] + \frac{k_{OH^-} K_w}{[H^+]} \tag{6.10}$$

or

$$k = k_{H_2O} + \frac{k_{H^+} K_w}{[OH^-]} + k_{OH^-}[OH^-] \tag{6.11}$$

In most of the cases, one of these terms containing concentration is small compared with other terms and can be neglected.

For example, if reaction is carried out in 0.1N HCl, the term, $k_{H^+}[H^+]$ would be $k_{H^+} \times 10^{-1}$ while term $k_{OH^-} \times K_W/[H^+]$ would be $k_{OH^-} \times 10^{-13}$ which is negligible compared to $k_{H^+} \times 10^{-1}$ and, therefore, rate constant may be given as

$$k = k_{H_2O} + k_{H^+}[H^+]$$

or,

$$\log k = \log k_{H_2O} + \log k_{H^+} + \log[H^+]$$

or

$$\log k = \log k_{H_2O} + \log k_{H^+} - \text{pH} \tag{6.12}$$

Similarly, in 0.1N NaOH solution, the rate constant may be represented as

$$k = k_{H_2O} + \frac{k_{OH} K_w}{[H^+]}$$

or

$$\log k = \log k_{H_2O} + \log(k_{OH^-} \times K_w) - \text{pH} \tag{6.13}$$

Various possibilities that may arise in the reactions have been classified by Skrabal who plotted log k against the pH of the solution as shown in Fig. 6.5. Curve (a) represents a most general type of behavior for catalysis by H^+ and OH^- ions. The velocity in the intermediate region is equal to $k_{H_2O}[S]$ so that k_{H_2O} can also be determined directly from the rate in this region. A curve of the type a is given by the mutarotation of glucose, if k_{H_2O} is sufficiently

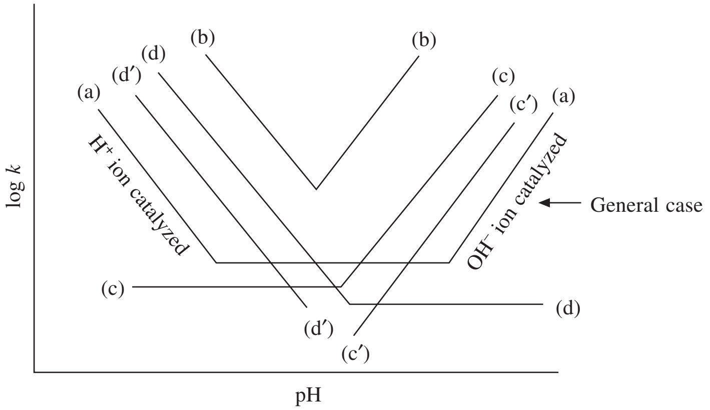


Fig. 6.5 Skrabal diagram: variation of rate constant with pH for acid base catalyzed reaction.

small, the horizontal part of the curve is not found. Two limbs of the curve intersects sharply (curve (b)) in case of hydrolysis of carboxylic esters.

If either k_{H^+} or k_{OH^-} is negligibly small, the corresponding sloping limb of the curve is found to be missing. If k_{H^+} is small, we obtain curve (c) and if k_{OH^-} is small, then we get curve (d). When uncatalyzed reaction, i.e. reaction in absence of catalyst is very slow and rate of reaction is negligible in absence of the catalyst, these curves will be simple straight lines with either a positive slope (curve (c) when k_{H_2O} is small and k_{H^+} is negligible) or with a negative slope (curve (d) when k_{H_2O} is small and k_{OH^-} is also small and negligible).

6.7 Enzyme Catalysis

Many chemical changes occurring in living processes are catalyzed by enzymes which are complex protein substances produced by living cells. Enzymes are often present in colloidal state and are very specific in their catalytic action. Zymase obtained from yeast catalyses the fermentation of dextrose but is ineffective in breakdown of cane sugar.

The mechanism of an enzymatic process may be represented as follows:

$$\text{Substrate (S)} + \text{Enzyme (E)} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(Complex)}}{\text{ES}} \qquad \text{(i)}$$

$$\text{(ES)} \xrightarrow{k_2} E + \text{Products (P)} \qquad \text{(ii)}$$

In the study of enzyme catalyzed reactions, the molar concentration of substrate is usually much greater than that of enzyme and, therefore, very little of substrate is bound to the enzyme. The total concentration of enzyme $[E]_T$ should be considered as the sum of the concentration of the enzyme and concentration of complex (ES), i.e.

$$[E]_T = [E] + [ES]$$

Applying the steady-state treatment with respect to complex, we get

$$k_1[\mathrm{E}][\mathrm{S}] - k_1'[\mathrm{ES}] - k_2[\mathrm{ES}] = 0$$

or
$$[\mathrm{ES}] = \frac{k_1[\mathrm{E}][\mathrm{S}]}{k_1' + k_2} \tag{6.14}$$

Again, [ES] can be determined in terms of $[\mathrm{E}]_\mathrm{T}$ as

$$[\mathrm{E}]_\mathrm{T} = [\mathrm{E}]\frac{k_1[\mathrm{E}][\mathrm{S}]}{k_1' + k_2}$$

or
$$[\mathrm{E}] = \frac{\{k_1' + k_2\}[\mathrm{E}]_\mathrm{T}}{k_1' + k_2 + k_1[\mathrm{S}]} \tag{6.15}$$

Hence, [ES] may be given as

$$[\mathrm{ES}] = \frac{k_1[\mathrm{S}][\mathrm{E}]_\mathrm{T}}{k_1' + k_2 + k_1[\mathrm{S}]} \tag{6.16}$$

Now, we can give

$$\text{Rate of reaction} = \frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}] \tag{6.17}$$

Substituting the value of [ES], we get

$$\text{Rate of reaction} = \frac{k_1k_2[\mathrm{E}]_\mathrm{T}[\mathrm{S}]}{k_1' + k_2 + k_1[\mathrm{S}]} = \frac{k_2[\mathrm{E}]_\mathrm{T}[\mathrm{S}]}{\frac{k_1' + k_2}{k_1} + [\mathrm{S}]} = \frac{k_2[\mathrm{E}]_\mathrm{T}[\mathrm{S}]}{k_\mathrm{m} + [\mathrm{S}]} \tag{6.18}$$

where $k_\mathrm{m} = (k_1' + k_2)/k_1$ is known as *Michaelis Menten constant.*

When [S] is sufficiently small, the rate law reduces to

$$\text{Rate of reaction} = \frac{k_2}{k_\mathrm{m}}[\mathrm{E}]_\mathrm{T}[\mathrm{S}] \tag{6.19}$$

and the reaction will show first order dependence with respect to substrate and a plot of rate versus [substrate] will be linear at lower substrate concentrations. At higher substrate concentrations, where [S] >> k_m, the rate law becomes

$$\text{Rate of reaction} = k_2[\mathrm{E}]_\mathrm{T} \tag{6.20}$$

and the reaction will be zero order with respect to the substrate and the plot of rate versus [substrate] will be horizontal to concentration axis as shown in Fig. 6.6. When [S] is quite high and k_m + [S] = [S], the rate will also be maximum, i.e. $(\text{Rate})_\text{max} = k_2[\mathrm{E}]_\mathrm{T}$. Again at this stage, the rate law may be written as

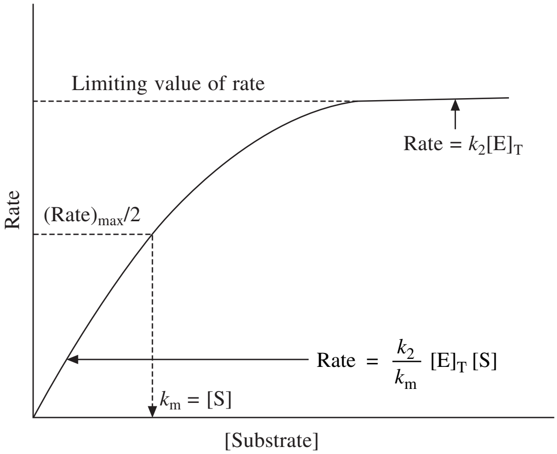


Fig. 6.6 Plot of rate versus [substrate] for enzyme catalyzed reaction.

$$\text{Rate of reaction} = \frac{(\text{Rate})_{\text{max}}[\text{S}]}{k_m + [\text{S}]} \tag{6.21}$$

Similarly, when $k_m = [S]$

$$\text{Rate of reaction} = \frac{1}{2}(\text{Rate})_{\text{max}} \tag{6.22}$$

Therefore, k_m (in mol dm^{-3}) is equal to the concentration of the substrate at which the initial rate is half of its maximum value. The value of k_m for an enzyme depends on the particular substrate and also on experimental conditions like pH, temperature, solvent, ionic strength etc. k_m gives an idea of strength of binding and saturation of enzyme and substrate.

The applicability of equation to experimental data may be tested as follows. Equation (6.18) may be written in its reciprocal form as

$$\frac{1}{\text{Rate}} = \frac{k_m + [\text{S}]}{k_2[\text{S}][\text{E}]_T} = \frac{k_m}{k_2[\text{S}][\text{E}]_T} + \frac{1}{k_2[\text{E}]_T} \tag{6.23}$$

Thus, a plot of 1/Rate versus 1/[S] would give a straight line with an intercept ($1/k_2[E]_T$) and a slope ($k_m/k_2[E]_T$). Therefore, the values of k_2 and k_m can be determined from the intercept and slope of the plot.

6.7.1 Influence of pH

When the pH is varied, the rates of enzyme catalyzed reaction shows a maximum value at certain pH called the *optimum* pH as shown in Fig. 6.7.

The influence of pH can be explained on the basis that the active center of the enzyme exists in three states of ionization as

$$\text{EH}_2 \xrightarrow{K_b} \text{EH} \xrightarrow{K_a} \text{E}$$

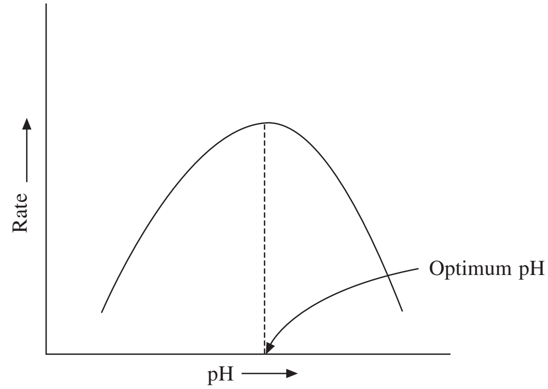


Fig. 6.7 Variation of rate of enzyme catalyzed reaction with pH.

EH_2 bears one more positive charge (or one less negative charge) than EH and EH has one more positive charge than E. For simplicity, charges have not been shown. K_a or K_b are the dissociation constants. Each of these three forms of enzyme can interact with the substrate to give the complex. The following mechanism may be proposed for reaction:

$$\begin{tikzcd}
EH_2 \arrow[r, equal, "K_b"] \arrow[d, equal] & EH \arrow[r, equal, "K_a"] \arrow[d, equal, "k_1"', "k_1'"] & E \arrow[d, equal] \\
EH_2S \arrow[r, equal, "K_b'"] & EHS \arrow[r, equal, "K_a'"] \arrow[d, "k_2"] & ES \\
 & EH + P &
\end{tikzcd}$$

It is assumed that it is the only (EHS) form of the complex which gives rise to products. In acidic solution, the equilibrium will lie over to left, EH_2S form of complex will dominate and rate of reaction will be low because EHS form is the reactive form.

In highly basic solution the ES form will be dominating and again the rate will be low. At some intermediate pH, when EHS is dominating, the rate will be maximum. Application of steady state treatment to this scheme of mechanism leads to a very complicated rate law and it is difficult to apply it to the experimental data.

A considerable simple form of rate equation has also been obtained assuming EH_2+S = EH_2S and E+S = ES equilibria to be unimportant and considering the following scheme:

$$\begin{tikzcd}
EH_2 \arrow[r, equal, "K_b"] & EH \arrow[r, equal, "K_a"] \arrow[d, equal, "k_1"', "k_1'"] & E \\
EH_2S \arrow[r, equal, "K_b'"] & EHS \arrow[r, equal, "K_a'"] \arrow[d, "k_2"] & ES \\
 & EH + P &
\end{tikzcd}$$

The application of steady state treatment to this scheme, gives the following rate equation:

$$\text{Rate} = \frac{k_2[\text{E}]_\text{T}[\text{S}]}{\left(1 + \dfrac{K_\text{a}}{[\text{H}^+]} + \dfrac{[\text{H}^+]}{K_\text{b}}\right)k_\text{m}\left(1 + \dfrac{K'_\text{a}}{[\text{H}^+]} + \dfrac{[\text{H}^+]}{K'_\text{b}}\right)[\text{S}]} \tag{6.24}$$

By measuring the rates over a range of [S] and pH, the values of k_2, k_m, K_a, K'_a, K_b and K'_b can be obtained.

6.8 Heterogeneous Catalysis

In heterogeneous catalyzed reaction, the surface of a solid serves as a catalyst while the reactants are in gaseous or liquid phase. One or more reactants get adsorbed on the surface of the solid. This phenomenon is similar to the formation of intermediate complex in homogeneous catalysis. In many cases, heat of adsorption leads to the activation of reactants and the reaction takes place easily. The surface thus provides an alternative path for the reaction to proceed with an accelerated rate. The reaction consists of the following four consecutive steps.

(i) Diffusion of reactants to the surface.
(ii) Adsorption of reactants on the surface.
(iii) Chemical transformation, i.e. reaction on the surface.
(iv) Desorption and diffusion of the products from the surface.

Steps (i) and (iv) are generally very fast and do not play any part in determination of rate of the reaction. The adsorption and desorption equilibria are easily attained. The concentration of reactant molecules on the surface is an important factor because the molecules which are adsorbed on the surface will undergo the chemical transformation. The concentration of the adsorbed molecules on the surface at any moment is proportional to the fraction of the surface (say θ) covered. Therefore, the rate of reaction will also then be proportional to the covered portion of the surface, i.e.

$$\text{Rate of reaction} \propto \theta = \beta\theta \tag{6.25}$$

where β is the proportionality constant.

In Langmuir adsorption isotherm, the fraction of the surface θ covered by adsorption has been related to the pressure P of the gas by relation

$$\theta = \frac{\alpha P}{1 + \alpha P} \tag{6.26}$$

where α is a constant.

Therefore, we can write

$$\text{Rate of reaction} = \frac{\alpha\beta P}{1 + \alpha P} \tag{6.27}$$

Let us now consider the reaction rates for some simple heterogeneous catalyzed reactions.

Case I. Dissociation of a single reactant on surface

When there is a single reactant, it is first adsorbed on the surface, activated and subsequently dissociates into products.

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

$$\text{Rate of reaction} = \beta\theta = \frac{\alpha\beta P}{1 + \alpha P} \tag{6.28}$$

When adsorption is low either due to very low pressure or due to low adsorption capacity of the surface and αP is negligible compared to unity, then

$$\text{Rate of reaction} = \alpha\beta P \tag{6.29}$$

i.e. rate of reaction is proportional to pressure and reaction will behave as first order.

However, when pressure is very high or adsorption capacity of surface is quite high, i.e. $\alpha P >> 1$,

$$\text{Rate of reaction} = \beta = \text{constant} \tag{6.30}$$

i.e. reaction rate is independent of pressure. At moderate pressure, when the adsorption is neither high nor low, the rate of reaction will be given by equation (6.28), which may be approximated to

$$\text{Rate of reaction} = kP^n \tag{6.31}$$

where n lies between 0 and 1, i.e. the order of reaction will be a fractional. These conditions are represented in Fig. 6.8.

Case II. When two reactants undergo change on the surface

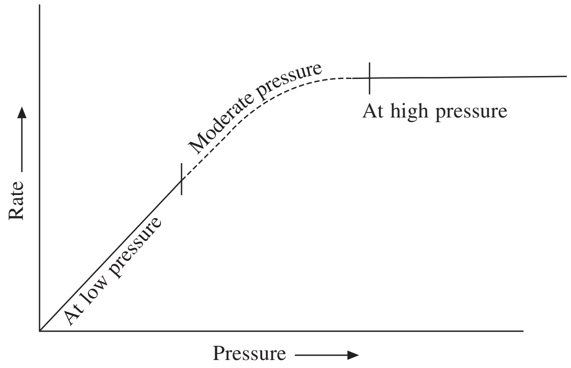


Fig. 6.8 Rate-pressure relationship for dissociation of single reactant on solid surface.

Let us consider a reaction in which two molecules A and B react on the surface adsorbed as

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

Let θ_1 and θ_2 be the fractions of surface covered by adsorption of A and B, respectively. Assuming that total area of surface for adsorption is 1 sq. cm, the surface portion remaining unaffected is = $(1 - \theta_1 - \theta_2)$.

Since the rate of adsorption and desorption should be equal, we get

$$k_1(1 - \theta_1 - \theta_2)p_1 = k_1'\theta_1 \quad \text{for A} \tag{a}$$

$$k_2(1 - \theta_1 - \theta_2)p_2 = k_2'\theta_2 \quad \text{for B} \tag{b}$$

where p_1 and p_2 are partial pressures of A and B, respectively, k_1, k_2 k_1' and k_2' are proportionality constants. Dividing equation (b) by (a), we get

$$\theta_2 = \frac{k_2 k_1' p_2}{k_1 k_2' p_1}\theta_1 \tag{c}$$

Substituting equation (c) in (a), we get

$$\theta_1 = \frac{k_1 p_1}{k_1' + k_1 p_1 + \dfrac{k_2 k_1'}{k_2'} p_2} \tag{d}$$

Substituting equation (c) in (b), we get

$$\theta_2 = \frac{k_2 p_2}{k_2' + k_2 p_2 + \dfrac{k_1 k_2'}{k_1'} p_1} \tag{e}$$

The rate of reaction will be

$$\text{Rate of reaction} = Z\theta_1\theta_2 \tag{6.32}$$

where Z is a constant.

The rate of reaction can be considered in different conditions as follows:

(i) When each gas is adsorbed very low, i.e. θ_1 and θ_2 are quite small, we get

$$\theta_1 = \frac{k_1 p_1}{k_1'} \text{ and } \theta_2 = \frac{k_2 p_2}{k_2'}$$

Thus

$$\text{Rate of reaction} = \frac{Z k_1 p_1 k_2 p_2}{k_1' k_2'} \tag{6.33}$$

Rate $\propto p_1 p_2$ suggests that rate will be of second order.

(ii) When one reactant (say A) is relatively more strongly adsorbed than the other (say B). In this case, θ_1 is much larger than θ_2. The term $k_2 p_2$ is small and negligible and hence θ_1 and θ_2 would be given as

$$\theta_1 = \frac{k_1 p_1}{k_1' + k_1 p_1} \text{ and } \theta_2 = \frac{k_2 p_2}{k_2' + \dfrac{k_1 k_2'}{k_1'} p_1} = \frac{k_1' k_2 p_2}{k_2'(k_1' + k_1 p_1)}$$

Hence,

$$\text{Rate of reaction} = Z\theta_1\theta_2 = \frac{Z k_1 k_1' k_2 p_1 p_2}{k_2'(k_1' + k_1 p_1)^2} = \frac{k p_1 p_2}{(1 + b p_1)^2} \qquad (6.34)$$

where $b = \dfrac{k_1}{k_1'}$. Such a complicated kinetics is being followed by reaction between CO_2 and H_2 on platinum.

(iii) When one reactant is very strongly adsorbed, we have,

$$\theta_2 = \frac{k_2 k_1' p_2}{k_1 k_2' p_1} \theta_1 \text{ (from equation (c))}$$

Rate of reaction = $Z\theta_1\theta_2$.

If A is adsorbed strongly, θ_1 will be almost unity and, therefore

$$\text{Rate of reaction} = Z\theta_2 = \frac{k_2 k_1' p_2}{k_1' k_2' p_1}\theta_1 = \frac{Z k_2 k_1'}{k_1 k_2'} \frac{p_2}{p_1} (\theta_1 = 1)$$

$$= k\frac{p_2}{p_1} \qquad (6.35)$$

Hence, the rate would be reduced at higher pressure p_1. The reaction of CO and O_2 on platinum follows such a kinetics.

It is important to note that adsorption does not necessarily lead to a catalytic reaction but the surface catalyzed reactions always occur through adsorption. In their catalytic action, the surfaces are specific in nature. Ni and Cu surfaces are very good catalysts for hydrogenation processes. The physical nature of a surface also influences its catalytic efficiency. Those atoms, which are at the peaks, edges etc. have high residual fields and are likely to have greater adsorption capacity. Taylor (1925) postulated that the adsorption and subsequent reaction takes place preferentially on certain parts of the surface, which are called *active centers*. The active center may constitute a small portion only of the total surface. Moreover, all active centers where adsorption occurs are not always catalytically effective.

6.9 Micellar Catalysis

The kinetics of organic reactions occurring at miceller surfaces formed from relatively simple surfactants have focused the attention of chemists because the reaction kinetics at micellar surfaces is an “interface” between physical and organic chemistry on one hand, and biochemistry and physiology on the other.

There are a number of structurally distinct classes of amphipathic molecules, which have various kinds of structures. The simplest amphipathic molecules have a straight chain of carbon atoms, usually 8-18 in number, to which is attached a polar group that may be anionic, cationic, zwitterionic or nonionic. For example

$CH_3(CH_2)_n—OSO_3^-$	Anionic
$CH_3(CH_2)_n—N^+(CH_3)_3$	Cationic
$CH_3(CH_2)_n—N^+(CH_3)_2—CH_2CH_2CH_2—OSO_3^-$	Zwitter-ionic
$CH_3(CH_2)_n$  $O—(CH_2CH_2O)_m—H$	Nonionic

A wide structural variation is possible within each class of molecules because both the length of the hydrophobic portion and the nature of the hydrophilic head group, as well as its position along the backbone, may be varied. The properties of the aggregates formed from these surfactants and the conditions under which they are formed depends on all these parameters. As the concentration of the surfactant in an aqueous solution is increased, many of the chemical and physical properties of the solution change rather abruptly (but continuously) over a concentration range known as the *critical micelle concentration* (CMC).

CMC is a characteristic narrow range of concentration at which micelles first become detectable. The value of CMC is dependent upon a large number of parameters like the total chain length, number of carbon-carbon double bonds, chain branching, various types of additives (polar, non-polar and electrolytes), temperature and pressure. An increase in hydrocarbon chain length and addition of strong electrolyte to ionic surfactant tends to decrease the CMC, while addition of C=C bonds and chain branching tends to increase CMC. A large number of experimental techniques have been utilized to determine the CMC value of the surfactants.

Over the narrow concentration range centering about the CMC, individual surfactant molecules form aggregates, usually containing 20-100 individual molecules. These aggregates are usually spherical, organized spherically so that the hydrophobic chains are hidden within the structure and thus isolated from the aqueous environment. The hydrophilic head groups are exposed on the micellar surface (Fig. 6.9).

The core of the micelle is composed of the hydrophobic chains of the surfactant molecules. Surrounding the core is the stern layer, or palisade layer, which is occupied by the regularly spaced charged head groups of the micelle together with a certain number of counter ions. The remainder counter ions are less tightly associated with the micelle and form a Gouy-Chapman layer, several hundred angstroms in thickness (Fig. 6.10).

The rate of various reactions is found to be influenced by the micelles

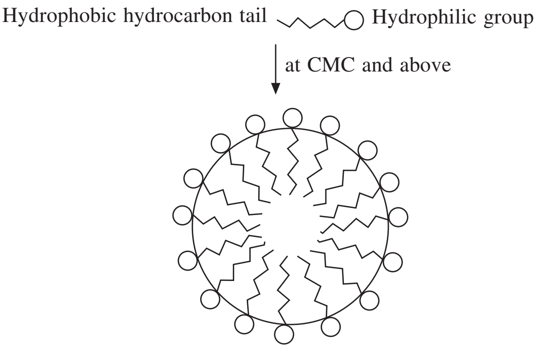
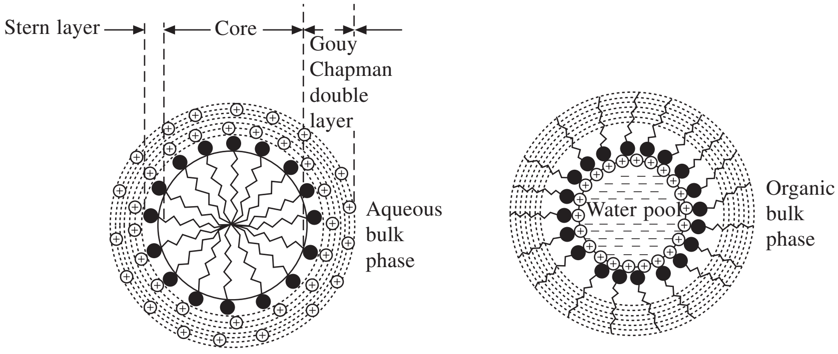


Fig. 6.9



(a) (b)

Fig. 6.10 Spherical cross-section of an idealized anionic: (a) normal micelle and (b) reverse micelle; (●) polar head group; (⊕) counter ion; (〰) the hydrocarbon chain.

formed from the surfactants. Fendler and Fendler (1975) have provided a comprehensive review of effort in this field. The micelle forming surfactants can be grouped into two classes. The first includes those cases in which the surfactant provides a medium for the reaction but does not participate directly in it. The second class includes those reactions in which the surfactant does participate directly in the reaction, either as a substrate or as a catalyst. In the former case, the surfactant is itself the substrate and is consumed in the course of the reaction; in the later case, the surfactant is transiently modified through interaction with substrate but is subsequently regenerated.

There are a number of bimolecular reactions for which the rate-surfactant profiles have been interpreted in terms of the distribution of surfactants between the aqueous and micellar pseudophase.

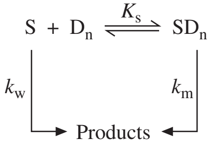
6.9.1 Models for Micellar Catalysis

From time to time various models have been developed to explain the micellar effect on the rate of reaction. Each model has its own strength and weakness.

The extent of solubilization of the substrate to the micelle can be related with the association constant or the binding constant. Some of the important models developed to explain the micellar effect are described briefly as follows:

(a) Menger and Portnoy's Model

In Menger and Portnoy's model, the variation of the rate constant with surfactant concentration has been treated on the basis of assumption that substrate 'S' is distributed between aqueous and micellar pseudo-phase given as follows:



This model leads to the following relationship for micellar catalysis:

$$\frac{1}{(k_\psi - k_w)} = \frac{1}{(k_m - k_w)} + \frac{1}{K_s(k_m - k_w)\{[D] - CMC\}} \tag{6.36}$$

where k_w and k_m are rate constants in aqueous phase and micellar medium, respectively, k_ψ is observed rate constant and K_s the binding constant of substrate with surfactant.

The linearity of the plot between $1/(k_\psi - k_w)$ and $1/\{[D] - CMC\}$ suggests the applicability of the model.

(b) Sepulveda Model

The binding constants for the association of the solute with the micelle can be evaluated with the help of model developed by Sepulveda and coworkers. According to the model, solute binds to micelles with following equilibrium:

$$S_a + D_m \overset{K_s}{\rightleftharpoons} S_m$$

for which equilibrium constant called *binding constant* is given as

$$K_s = \frac{[S_m]}{[S_a][D_m]} \tag{6.37}$$

where $[S_a]$ and $[S_m]$ are the substrate concentration expressed as molarities in terms of solution in the aqueous and micellar pseudophase, respectively, and $[D_m]$ is the total concentration of surfactant in micellar form, i.e. total concentration minus CMC.

The total substrate concentration $[S_t]$ and the total detergent concentration $[D_t]$ would be $\{[S_a]+[S_m]\}$ and $\{[S_m]+[D_m]+[CMC]\}$, respectively. The fraction of the substrate bounded to the micelle can be defined as

$$f = \frac{[\mathrm{S_m}]}{[\mathrm{S_t}]} \tag{6.38}$$

with the help of equations (6.37) and (6.38) and the total concentration of solutes, we get

$$\frac{f}{1-f} = K_\mathrm{s}([\mathrm{D_t}] - [\mathrm{S_t}]f) - K_\mathrm{s}[\mathrm{CMC}] \tag{6.39}$$

In general, $[\mathrm{S_t}] << [\mathrm{D_t}]$ and, therefore, equation (6.39) reduces to

$$\frac{f}{1-f} = K_\mathrm{s}[\mathrm{D_t}] - K_\mathrm{s}[\mathrm{CMC}] \tag{3.40}$$

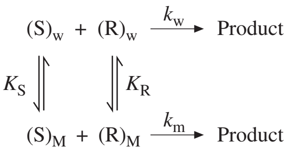
On plotting $\frac{f}{1-f}$ versus $[\mathrm{D_t}]$, a straight line is obtained with a slope equal to K_s (binding constant) and an intercept equal to $K_\mathrm{s}[\mathrm{CMC}]$. Experimentally, f can be determined from the equation

$$f = \frac{I - I_\mathrm{w}}{I_\mathrm{m} - I_\mathrm{w}} \tag{6.41}$$

where I, I_w and I_m are the absorbance in surfactant, water and when the solute is bonded to the micelle completely. Linearity of the plot $\frac{f}{1-f}$ versus $[\mathrm{D_t}]$ suggests the applicability of the model.

(c) Berezin Model

According to Berezin and coworkers, the observed rate constant k_ψ for the reaction under investigation may be made of two parts, i.e. k_w and k_m, which are due to partition of reactants in the aqueous phase and micellar pseudo-phase, respectively, as follows:



The apparent rate constant is given by the equation

$$k_\psi = \frac{k_\mathrm{w} + k_\mathrm{m} K_\mathrm{S} K_\mathrm{R} C}{(1 + K_\mathrm{S}\mathrm{C})(1 + K_\mathrm{R} C)} \tag{6.42}$$

where K_S and K_R are the binding constants for the substrate and the reactant, respectively and C the concentration of surfactant.

Assuming $k_\mathrm{w} << k_\mathrm{m} \cdot K_\mathrm{R}, K_\mathrm{s} C$, k_w can be neglected compared to the second term in the numerator of the equation and on rearranging, we get

$$\frac{1}{k_\psi} = \frac{1}{k_m K_S K_R C} + \frac{(K_S + K_R)}{k_m K_S K_R} + \frac{C}{k_m} \tag{6.43}$$

According to this equation, the plot of $1/k_\psi$ as function of C would show a minimum and the plot beyond C_{min} would be linear with a positive slope and positive intercept. However, at the optimum surfactant concentration corresponding to the maximum in the plot of k_ψ against [Surfactant], the following relationship is obtained.

$$C_{opt} = (K_S K_R)^{-1/2} \tag{6.44}$$

The linearity of the plot of $(1/k_\psi)$ against ([C]-CMC) showed the validity of the model. With the help of slope and intercept of the plot, the values of K_R, K_S and k_m can be computed.

(d) Piszkiewicz Co-operativity Model

A model analogous to the Hill model (for enzymatic reactions), which describes a more accurate dependence of the observed rate constants on surfactant concentration, was developed by Piszkiewicz. This model is applicable especially at low surfactant concentration and the data may be treated without reference to CMC. According to this model, a substrate (S) and n number of detergent molecules (D), aggregate to form critical micelle (D_nS), which may react to yield the product

$$nD + S \underset{K_D}{\rightleftharpoons} D_nS$$

$$D_nS \xrightarrow{k_m} \text{Product}$$

$$S \xrightarrow{k_w} \text{Product}$$

where K_D is the dissociation constant of micelle back to its free component and k_m the rate constant of reaction within the micelle.

According to the model, the observed rate constant has been expressed as a function of concentration of detergent as

$$k_\psi = \frac{k_m [D]^n + k_w K_D}{K_D + [D]^n} \tag{6.45}$$

where k_ψ is the observed rate constant and [D] the concentration of detergent. Equation (6.45) may be rearranged in the form

$$\log\left\{\frac{k_\psi - k_w}{k_m - k_\psi}\right\} = n \log [D] - \log K_D \tag{6.46}$$

According to equation (6.46), a plot of $\log \{(k_\psi - k_w)/(k_m - k_\psi)\}$ versus log [D] should be linear. The slope of the plot gives the value of n, which is also known as co-operativity index. At log $\{(k_\psi - k_w)/(k_m - k_\psi)\} = 0$, the value of n log [D] becomes equal to log K_D. Also at log$\{(k_\psi - k_w)/(k_m - k_\psi)\} = 0$, catalysis by detergent shows one half of its maximum effect on rate constant. The value of log [D] at this point is known as log $[D]_{50}$. With the help of the above linear plot we can calculate the values of co-operativity index n.

(e) Raghvan and Srinivasan's Model

Raghvan and Srinivasan developed a model, for bimolecular micellar catalysed reactions, which also predict constancy in k_{obs} values at high detergent concentration and may be used for evaluating the binding constants of reactants. They proposed the distribution of both reactant and nucleophile in aqueous and micellar phases. The product formation is assumed to result from decomposition of ternary complex involving substrate, nucleophile and micelle. After analyzing the data on the basis of this model, they concluded that almost all the nucleophile is present in the bulk phase.

$$n\mathrm{D} + \mathrm{S} \overset{k_1}{\rightleftharpoons} \mathrm{D}_n\mathrm{S}$$

$$\mathrm{D}_n\mathrm{S} + \mathrm{N} \overset{k_2}{\rightleftharpoons} \mathrm{D}_n\mathrm{S\,N}$$

$$\mathrm{D}_n\mathrm{SN} \overset{k_m}{\rightleftharpoons} \text{products}$$

$$\mathrm{S} + \mathrm{N} \overset{k_w}{\rightleftharpoons} \text{products}$$

where D, S and N are the detergent monomer, substrate and the nucleophile, respectively, while D_nS and D_nSN are the binary and ternary complexes, respectively. According to this model the observed rate constant in presence of surfactant is given as

$$k_\psi = \frac{k_w + k_m K_1 K_2 [D]^n}{1 + K_1[D]^n\{1 + K_2[S]_T\}} \tag{6.47}$$

Equation (6.47) may be rearranged in the form

$$\left(\frac{k_\psi - k_w}{k_\psi}\right)\frac{1}{[D]^n} = (K_1K_2)\left(\frac{k_m}{k_\psi}\right) - K_1\{1 + K_2[S]_T\} \tag{6.48}$$

Equation (6.48) predicts a linear relationship between $\{(k_\psi - k_w)/k_\psi)\,(1/[D]^n)\}$ and (k_m/k_ψ). The values of K_1 and K_2 (binding constants) can be evaluated with the help of intercept and slope of the linear plot of $\{(k_\psi - k_w)/k_\psi)\,(1/[D]^n)\}$ versus (k_m/k_ψ).

6.10 Phase Transfer Catalysis

The reactions between two substances which exist in two mutually insoluble phase are normally too slow to be of much practical importance. This is mainly because of the intrinsically low mutual solubility of the reactants in the opposite phases. A very effective and economical way of enhancing the rate of such reactions is to add a small catalytic quantity of another substance which can transport the reactant across the phase boundary in a form that has greater solubility in the target phase. This process is known as phase transfer catalysis. The *phase transfer catalysis* is similar to micellar catalysis.

The phase transfer catalysis not only promotes the reactions between the reagents which are mutually insoluble in immiscible phases, but also offers a number of process advantages such as, increase in rate of reactions, increase in product specificity, lowering of energy requirement, use of inexpensive solvents and catalysts, extraction of cations or even neutral molecules from one phase to another etc.

Onium salts, crown ethers, alkali metal salts or similar chelated salts, quaternary ammonium and phosphonium are some of the salts which have been widely used as phase transfer catalysts (PTC). The choice of phase transfer catalysts depends on a number of process factors, such as reaction system, solvent, temperature, removal and recovery of catalyst, base strength etc.

6.10.1 General Mechanism

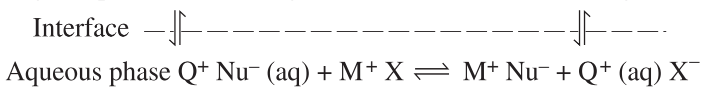
In general, there are two immiscible phases in reaction mixture, viz. an aqueous phase which contains a salt (a base or nucleophile) and the other an organic phase containing the substrate which is expected to react with the salt. When a phase transfer catalyst (usually contains a lipophilic cation) is added to the reaction mixture, the lipophilic cation (which has solubility in both aqueous and organic phases), exchanges anions with the excess of anions in the salt solution.

$$\underset{\substack{\text{(quaternary}\\ \text{salt, PTC)}}}{Q^+X^-_{(aq)}} + M^+Nu^-_{(aq)} \rightleftharpoons Q^+Nu^-_{(aq)} + M^+X_{(aq)}$$

Then a phase transfer equilibrium exists as

$$Q^+Nu^-_{(aq)} \rightleftharpoons Q^+Nu^-_{(org)}$$

Once nucleophile or base comes in nonpolar (organic) media, the displacement or deprotonation can take place with the product formation. The overall mechanism can be represented as follows:



Organic phase Q^+ Nu^- (org) + R – X $\rightarrow$ R – Nu + Q^+ (org) X

Interface

Aqueous phase Q^+ Nu^- (aq) + M^+ X $\rightleftharpoons$ M^+ Nu^- + Q^+ (aq) X^-

Stark's phase transfer catalytic cycle

In principle, a suitable PTC could transfer ions, free radicals and molecules from aqueous to organic phase. The anion transfer systems have been extensively investigated.

The rate of phase transfer catalyzed reaction depends on the following:

(a) Nature and rate of reaction in organic phase.
(b) Nature and solubility of phase transfer catalyst.
(c) Process of transfer of anion from aqueous to organic phase.

When $[X^-]$ and $[Nu^-]$ are constant in the aqueous phase by keeping the aqueous phase saturated with M^+X^- and M^+Nu^-, the Q^+Nu^- and Q^+X^- in organic phase will be in constant proportion.

Let

$$[Q^+Nu^-]_{org}/[Q^+X^-]_{org} = \theta \tag{6.49}$$

Again the total concentration of the catalyst in organic phase is

$$[Q]_{Total} = [Q^+X^-]_{org} + [Q^+Nu^-]_{org}$$

or

$$[Q]_{Total}/[Q^+X^-]_{org} = 1 + \frac{[Q^+Nu^-]_{org}}{[Q^+X^-]_{org}} = 1 + \theta \tag{6.50}$$

With the help of equations (6.49) and (6.50), we obtain

$$[Q^+Nu^-]_{org} = \frac{[Q]_{Total}\,\theta}{1 + \theta} \tag{6.51}$$

Now the rate of reaction in the organic phase is given by

$$-\frac{d[RX]}{dt} = k[RX][Q^+Nu^-]_{org} = k\frac{[RX][Q]_{Total}\,\theta}{1 + \theta} \tag{6.52}$$

where *k* is second order rate constant. The value of pseudo-first order rate constant may be obtained by integrating above equation as follows:

$$\ln\frac{[RX]_t}{[RX]_o} = \frac{k\cdot\theta[Q]_{Total}}{1 + \theta}\,t = -k_1 t \tag{6.53}$$

Thus the value of pseudo-first order rate constant is $k\,[Q]_{Total}\,\theta/(1 + \theta)$. The value of θ may be independently determined by analyzing organic phase for X^- and Nu^- ions.

From the values of θ, first order rate constant k_1 and $(Q)_{Total}$, we can also evaluate *k*.

6.10.2 Difference between Micellar and Phase Transfer-Catalyzed Reactions

The phase transfer catalysts are generally not surfactants. But the surfactants (small as well as large) are good phase transfer catalysts. The good phase transfer catalysts are partitioned into the organic phase of a two phase mixture and form emulsions or micelle dispersions in the aqueous phase. The rate of phase transfer catalysed reactions are directly proportional to [Catalyst] while in micellar catalysed reaction, the rates are generally low below the CMC of the surfactant and strongly dependent on [surfactant] at above its CMC. In some cases, rates may be also leveled off or even decrease after attaining a maximum value. There are some cases where a particular quaternary ammonium salt may behave as both a surfactant and a phase transfer catalyst or as either one depending on conditions of the reaction. The phase transfer catalyzed reactions are highly useful in synthetic applications while it is difficult to use micellar catalyzed reaction in synthetic application because of the difficulty in handling emulsions.

6.11 Kinetics of Inhibition

Certain constituents when added to the reaction mixture, slow down the rate of reaction. This phenomena is called *inhibition* and constituent called *inhibitor*. Such an effect is similar to the negative catalysis. But the constituent usually undergoes chemical change, inhibition is the preferred term. Inhibition may occur in chain reactions, enzyme catalysed reactions, surface reactions or many reversible or irreversible reactions. A trace amount of an inhibitor may cause a marked decrease in the rate of reaction. The inhibitor sometimes combines with a catalyst and prevents it from catalyzing the reaction.

6.11.1 Chain Reactions

In chain reactions, the inhibitor I_n interacts with free radical F^o and makes it unavailable for the propagation of chain, thus providing an extra termination step

$$F^\circ + I_n \xrightarrow{k_t'} \text{Inactive species}$$

The total rate of termination will be sum of rate of normal termination and rate of termination due to inhibitor.

Let us consider a general scheme

$A \xrightarrow{k_i} nF^\circ$ (i) (initiation)

$F^\circ + M \xrightarrow{k_p} M^\circ + L$ (ii) (propagation)

$F^\circ + X \xrightarrow{k_t} \text{Inactive species}$ (iii) (normal terminator)

$F^\circ + I_n \xrightarrow{k_t'} \text{Inactive species}$ (iv) (terminator due to inhibitor)

The rate of propagation is given as

$$\text{Rate} = k_p\,[F^\circ]\,[M] \tag{6.54}$$

With the help of steady-state approximation, [F°] can be obtained as

$$[F°] = \frac{nk_i[A]}{k_t[X] + k_t'[I_n]}$$

Therefore,

$$\text{Rate of propagation} = \frac{nk_i k_p[A][M]}{k_t[X] + k_t'[I_n]} \qquad (6.55)$$

Rate law (6.55) clearly indicates the retardation of rate on increasing the concentration of inhibitor.

6.11.2 Enzyme Catalyzed Reactions

In enzyme catalyzed reactions the inhibitor may interact in various ways either reversibly or irreversibly. In irreversible inhibition, the inhibitor associates with enzyme and block the active site of the enzyme or form a unstable complex with enzyme and thus retards the rate of reaction.

In reversible inhibition, the inhibitor may bind or associate to enzyme or enzyme-substrate complex. Depending on the binding/combination inhibitor, the reversible inhibition may be of three types.

(a) Competitive Inhibition

When the inhibitor and substrate are structurally similar, the inhibitor forms a complex or associate with enzyme and decrease the rate of enzyme catalyzed reaction by reducing the proportion of enzyme-substrate complex as follows:

$$E + S \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} ES \qquad \text{(i)}$$

$$E + I_n \overset{k_I}{\rightleftharpoons} EI_n \qquad \text{(ii)}$$

$$ES \overset{k_2}{\rightleftharpoons} E + \text{Product} \qquad \text{(iii)}$$

The total concentration of enzyme $[E]_T$ may be given as

$$[E]_T = [E] + [ES] + [EI_n]$$

where $[ES] = \frac{k_1[E][S]}{k_1' + k_2}$ (from steady-state condition with respect to ES) and

$$[EI_n] = K_I\,[E]\,[I_n] \qquad \text{(from equilibration)} \qquad \text{(iv)}$$

Thus [E] at any time, in terms of $[E]_T$ may be obtained as

$$[E] = \frac{[E]_T[k_1' + k_2]}{(k_1' + k_2') + k_1[S] + K_I(k_1' + k_2)[I_n]}$$

Now

$$\text{Rate of reaction} = k_2\,[\text{ES}] = \frac{k_1 k_2\,[\text{S}][\text{E}]_\text{T}}{(k_1' + k_2)\{1 + k_\text{I}\,[\text{I}_\text{n}]\} + k_1\,[\text{S}]}$$

or

$$\text{Rate} = \frac{k_2\,[\text{S}][\text{E}]_\text{T}}{k_\text{m}(1 + k_\text{I}\,[\text{I}_\text{n}]) + [\text{S}]} \tag{6.56}$$

where $k_\text{m} = \dfrac{k_1' + k_2}{k_1}$ = Michaelis-Menten constant.

Equation (2) in form of Lineweaver-Burk plot can be written as

$$\frac{1}{\text{Rate}} = \frac{1}{k_2\,[\text{E}]_\text{T}} + \frac{k_\text{m}\,(1 + k_\text{I}\,[\text{I}_\text{n}])}{k_2\,[\text{E}]_\text{T}}\,\frac{1}{[\text{S}]} \tag{6.57}$$

or

$$\frac{1}{\text{Rate}} = \frac{1}{k_2\,[\text{E}]_\text{T}} + \frac{k_\text{m}'}{k_2\,[\text{E}]_\text{T}}\,\frac{1}{[\text{S}]}$$

where $k_{\text{m}'} = k_\text{m}\ (1 + K_\text{I}[\text{I}_\text{n}])$, i.e. Michaelis-Menten constant in presence of inhibitor. From equation (6.57) it is clear that rate law is same as that for simple enzyme catalysed reaction, except that value of k_m is increased by a factor $(1 + K_\text{I}\ [\text{I}_\text{n}])$. With the help of slope and intercept of the plot of (1/Rate) versus 1/[S], the values of k_2 and $k_{\text{m}'}$ can be determined. Knowing the value of k_m (in absence of inhibitor) the value of k_I can also be evaluated.

(b) Uncompetitive Inhibition

In uncompetitive inhibition, the inhibitor combines with enzyme-substrate complex to form an uncreative complex (InES) as follows:

$$\text{E} + \text{S} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \text{ES} \tag{i}$$

$$\text{E} + \text{I}_\text{n} \overset{K_\text{I}}{\rightleftharpoons} \text{I}_\text{n}\text{ES} \tag{ii}$$

$$\text{ES} \xrightarrow{k_2} \text{E} + \text{Products} \tag{iii}$$

By applying the steady state approximation with respect to ES, we get

$$[\text{ES}] = \frac{k_1[\text{E}][\text{S}]}{k_1' + k_2}$$

and also

$$[\text{I}_\text{n}\text{ES}] = K_\text{I}[\text{ES}][\text{I}_\text{n}] \text{ from equilibrium} \tag{ii}$$

Therefore, the total concentration of E may be given as

$$[\text{E}]_\text{T} = [\text{E}] + [\text{ES}] + [\text{I}_\text{n}\text{ES}] = [\text{E}]\left\{1 + \frac{k_1[\text{S}]}{(k_1' + k_2)} + \frac{k_1 K_1\,[\text{S}][\text{I}_\text{n}]}{k_1' + k_2}\right\}$$

or $$[\mathrm{E}] = \frac{[\mathrm{E}]_\mathrm{T}(k_1' + k_2)}{(k_1' + k_2) + k_1[\mathrm{S}] + k_1 K_1 [\mathrm{S}][\mathrm{I_n}]}$$

and

$$[\mathrm{ES}] = \frac{k_1 [\mathrm{S}][\mathrm{E}]_\mathrm{T}}{(k_1' + k_2) + k_1[\mathrm{S}] + k_1 K_1 [\mathrm{S}][\mathrm{I_n}]}$$

Therefore, the rate of reaction is given as

$$\text{Rate} = k_2\,[\mathrm{ES}]$$

$$\text{Rate} = \frac{k_2 [\mathrm{S}][\mathrm{E}]_\mathrm{T}}{k_\mathrm{m} + [\mathrm{S}]\{1 + K_\mathrm{I}[\mathrm{I_n}]\}} \tag{6.58}$$

where $k_\mathrm{m} = (k_1 + k_2)/k_1$.

The above equation in the form of Lineweaver-Burk plot may be written as

$$\frac{1}{\text{Rate}} = \frac{k_\mathrm{m}}{k_2 [\mathrm{S}][\mathrm{E}]_\mathrm{T}} + \frac{\{1 + K_\mathrm{I}[\mathrm{I_n}]}{k_2 [\mathrm{E}]_\mathrm{T}}$$

or $$\frac{1}{\text{Rate}} = \frac{1}{k_2 [\mathrm{E}]_\mathrm{T}} + \frac{k_{\mathrm{m}'}}{k_2 [\mathrm{E}]_\mathrm{T}} \frac{1}{[\mathrm{S}]} \tag{6.59}$$

where $k_{\mathrm{m}'} = \dfrac{k_\mathrm{m}}{\{1 + k_1[\mathrm{I_n}]}$.

The values of k_2 and $k_{\mathrm{m}'}$ can be determined with the help of slope and intercept of the plot.

(c) Noncompetitive Inhibition

In noncompetitive inhibition the inhibitor combines with the free enzyme or with {enzyme-substrate} complex. The inhibitor combines at different active sites of the enzyme and does not compete with the substrate for the same active site

$$\mathrm{E + S} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \tag{i}$$

$$\mathrm{E + I_n} \overset{K_\mathrm{I}}{\rightleftharpoons} \mathrm{I_nE} \tag{ii}$$

$$\mathrm{ES + I_n} \overset{K_\mathrm{I}'}{\rightleftharpoons} \mathrm{I_nES} \tag{iii}$$

$$\mathrm{ES} \xrightarrow{k_2} \mathrm{E + Products} \tag{iv}$$

In such a case, the enzyme molecule is deformed to such an extent that either the formation of complex (ES) does not take place at its normal rate or if it is formed, complex does not decompose at its normal rate. At a fixed concentration of the inhibitor, the extent of inhibition may be minimized by an increase in [S].

The rate law for the above mechanism may be obtained as

$$\text{Rate} = \frac{k_2[\text{S}][\text{E}]}{k_\text{m}(1 + K_\text{I}[\text{I}_\text{n}]) + [\text{S}](1 + K_\text{I}'[\text{I}_\text{n}]} \tag{6.60}$$

It can be observed that when I_nES is not at all formed, the above rate law reduces as equation (6.56), while if I_nE is not formed at all, the rate law reduces to that for uncompetitive inhibition as equation (6.58).

6.11.3 Inhibition in Surface Reactions

When a substance other than the reactants is adsorbed on the concerned surface, the inhibition occurs. This is due to the fact that on adsorption of the substance, the effective surface area is reduced and therefore, the rate is also reduced.

Let us consider a unimolecular reaction on the surface. Let that at any time, surface covered by reactant (A) is θ and surface covered by substance (inhibitor) is θ_I. Then

$$\theta = \frac{KP}{1 + KP + K_\text{I}P_\text{I}} \tag{6.61}$$

where P and P_I are partial pressures of the reactant and inhibitor, respectively, and K and K_I represent their adsorption constants.

Since, rate is proportional to θ, we have

$$\text{Rate} = \frac{K'KP}{1 + KP + K_\text{I}P_\text{I}} \tag{6.62}$$

where K' is a proportionality constant.

At low pressure of the reactant, $KP << (1 + K_\text{I}P_\text{I})$, the above equation reduces to

$$\text{Rate} = \frac{K'KP}{1 + K_\text{I}P_\text{I}} \tag{6.63}$$

Further, if inhibitor is strongly adsorbed

$$K_\text{I}P_\text{I} >> 1$$

then

$$\text{Rate} = \frac{K'KP}{K_\text{I}P_\text{I}} = K''\frac{P}{P_\text{I}} \tag{6.64}$$

where $K'' = \frac{K'K}{K_\text{I}}$.

Thus, rate of reaction is directly proportional to reactant pressure and inversely proportional to inhibitor pressure.

Similarly, the inhibition equation can also be derived for a bimolecular surface reaction. Let us consider a reaction between two reactants A and B and inhibition by a inhibitor (I). If P_1, P_2 and P_I are the respective partial pressures of A, B and I, then the fractions of the surface covered by A and B are given as

$$\theta_1 = \frac{K_1P_1}{1 + K_1P_1 + K_2P_2 + K_IP_I}$$

$$\theta_2 = \frac{K_2P_2}{1 + K_1P_1 + K_2P_2 + K_IP_I}$$

Now, the rate of reaction is proportional to $\theta_1\theta_2$, i.e.

$$\text{Rate of reaction} = K\theta_1\theta_2$$

where K is proportionality constant. Thus, rate of reaction is given as

$$\text{Rate} = \frac{KK_1K_2P_1P_2}{(1 + K_1P_1 + K_2P_2 + K_IP_I)^2} \tag{6.65}$$

However, if the inhibitor is a diatomic molecule and adsorbed atomically, the rate becomes

$$\text{Rate} = \frac{KK_1K_2P_1P_2}{(1 + K_1P_1 + K_2P_2 + K_I^{1/2}P_I^{1/2})^2} \tag{6.66}$$

At low pressures of A and B and strong adsorption of inhibitor, i.e. when

$$K_I^{1/2}P_I^{1/2} >> (1 + K_1P_1 + K_2P_2)$$

The rate can be written as

$$\text{Rate} = \frac{KK_1K_2P_1P_2}{K_IP_I} \tag{6.67}$$

Therefore, the rate is inversely proportional to partial presence of inhibitor.

EXERCISES

1. For enzyme catalyzed reaction

$$\text{S} + \text{E} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{X (fast)}$$

$$\text{X} \xrightarrow{k_2} \text{P} + \text{E (slow)}$$

derive the rate law and answer the following:

  - (a) What is meant by Michaelis-Menten constant k_m?
  - (b) Prove that order of reaction in substrate changes from unity to zero at higher [S].
  - (c) What is the rate and value of k_m, if $k_2 >> k_1$.
  - (d) Draw the potential energy diagram for enzyme catalyzed reaction.

2. What is Lineweaver-Burk plot? The intercept and slope of Lineweaver-Burk plot were obtained as 5.0×10^{-3} and 1.5×10^{-5}, respectively. Calculate the value of k_m and maximum rate.
3. Discuss the effect of pH in an enzyme catalyzed reaction.
4. Discuss the acid-base catalysis and suggest an overall rate expression for the acid-base catalysis.

   From the overall rate expression obtain the following:
   - (a) Convert the equation as a function of single variable [H^+] or [OH^-].
   - (b) Discuss Skrabal diagram.
   - (c) What will be the value of rate constant for H^+ catalysis and for OH^- catalysis.
5. Discuss the mechanism of the following:
   - (a) Catalysis by acid.
   - (b) Catalysis by base.
6. Prove that for a unimolecular surface reaction, the order of reaction with respect to reactant decreases from unity to zero as adsorption of the reactant increases from slight adsorption to strong adsorption.
7. Discuss the various steps involved in heterogeneous catalysis. Derive an expression for the rate constant and discuss limiting cases of rate equation.
8. What is meant by CMC of a surfactant? How it can be determined?
9. Discuss the general mechanism of micellar catalyzed reaction and compare it with enzyme catalyzed reactions.
10. What is phase transfer catalysis? How it is useful? Discuss the general mechanism of phase transfer catalysis.
11. Discuss and explain the kinetics of inhibition for the following:
    - (i) Reversible reaction
    - (ii) Surface reaction
    - (iii) Enzyme catalysis
    - (iv) Chain reactions
12. Differentiate between phase transfer catalyst and surfactant.

7
Fast Reactions

7.1 Introduction

One of the important recent developments in chemical kinetics has been a great interest in the study of very fast reactions which complete in less than about 1 sec. With special laser techniques it is now possible to study the reactions occurring in a few pico seconds ($\approx 10^{-12}$sec). The techniques, which have been designed to monitor concentrations and to measure the rate coefficients, include flash photolysis, relaxation methods and flow techniques. The other techniques including shock tubes and molecular beams have been used to explore the dependence of reaction rate on the state of rotational/ vibrational excitation of molecules or on the energy with which molecules colloid and the rate (state-to-state cross sections and rates) at which the energy is changed from one form into another.

Table 7.1 Ranges of rate constants amenable to different techniques

Technique	Range of rate constant
Conventional methods	10^{-7} s^{-1} to 1 s^{-1}; 10^{-7} mol^{-1}dm^{3}s^{-1} to 1mol^{-1}dm^{3}s^{-1}
Rapid reaction methods	1 s^{-1} to 10^{9} s^{-1}; 1 mol^{-1}dm^{3}s^{-1} to 10^{11} mol^{-1}dm^{3}s^{-1}
(i) Flow methods	
Continuous flow method	10^{2}-10^{8} mol^{-1}dm^{3}s^{-1}
Accelerated flow method	10^{2}-10^{7} mol^{-1}dm^{3}s^{-1}
Stopped flow method	10^{2}-10^{8} mol^{-1}dm^{3}s^{-1}
(ii) Relaxation method	
Temperature jump	10^{2}-10^{11} mol^{-1}dm^{3}s^{-1}
Pressure jump	10^{2}-10^{3} mol^{-1}dm^{3}s^{-1}
Electric impulse	10^{2}-10^{11} mol^{-1}dm^{3}s^{-1}
Ultrasonic	10^{4}-10^{11} mol^{-1}dm^{3}s^{-1}
(iii) Initiating of the reaction by radiation flash photolysis	10^{2}-10^{10}
(iv) Magnetic resonance spectroscopy	
Electron spin resonance	10^{5}-10^{11}
Nuclear magnetic resonance	10^{2}-10^{11}

7.2 Flow Techniques

The flow systems are generally of two types, viz. (i) plug flow (Fig. 7.1), in which there is no stirring in the reactor and (ii) stirred flow, in which there is stirring in the reactor to effect complete mixing within the reactor.

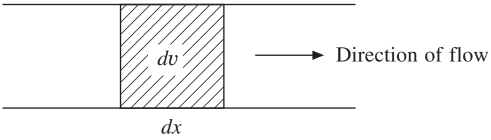


Fig. 7.1 Plug flow.

(a) Plug Flow

This is illustrated schematically as,
Let us consider a reaction of nth order with respect to reactant A as follows:

$$nA \xrightarrow{k} P$$

Then the rate of disappearance of substance is given by

$$\text{Rate of disappearance} = -dc/dt = kc^n \tag{7.1}$$

where c is the concentration of reactant at time t.

Let dv be an element of volume in the reactor. Then,

$$\text{Rate of disappearance of reactant in a volume } dv = kc^n dv$$

After the system operates for a sufficient period of time, a steady state is established and three processes contribute to steady state as follows:

(i) The molecules entering in reactor in time dt, i.e. $ucdt$, where u is the volume of rate of flow of reaction mixture passed through the reactor (liter per sec).
(ii) The molecules leaving the reactor in time dt, i.e. $u(c + dc)dt$.
(iii) The molecules disappearing by chemical reaction in time dt $(-dn)$. Also

$$-dn = kc^n dv\ dt \tag{7.2}$$

The steady-state equation is obtained as follows:

Rate of entry of reactant = Rate of exit of reactant + Amount reacted

i.e
$$ucdt = u(c + dc)dt + kc^n dvdt \tag{7.3}$$

or
$$-\frac{dc}{c^n} = \frac{k}{u}dv \tag{7.4}$$

If c_i and c_f are initial and final concentrations of reactant, then

$$-\int_{c_i}^{c_f} \frac{dc}{c} = \frac{k}{u}\int_0^v dv$$

where v is volume of the reactant.

On integrating the above equation for $n = 1$, we get

$$\ln \frac{c_f}{c_i} = \frac{k}{u} V_0$$

or
$$c_f = c_i\, e^{-kV_0/u} \tag{7.5}$$

This equation may be compared by general first order equation, $C = C_0\, e^{-kt}$ and the quantity V_0/u replaced by time, is known as *contact time for the reaction*. The contact time may be reduced by using high flow rate and small volume. The equation may be tested by varying V_0/u, i.e. either by varying volume of reactor or the flow rate.

Equation (7.5) can be written for nth order as

$$\frac{1}{(n-1)}\left(\frac{1}{c_f^{n-1}} - \frac{1}{c_i^{n-1}}\right) = \frac{kV_0}{u} \tag{7.6}$$

The above equations are valid only when there is no volume change during the course of reaction.

(b) Stirred Flow

The complete mixing in a stirred flow reactor has been discussed by Denbigh. In stirred flow, the composition becomes uniform throughout the entire volume of the reactor as a result of efficient stirring.

Rate of flow of reactants into the reactor = uc_i

Rate of flow of reactants out of the reactor = uc_f

Rate of reaction in the reactor = $uc_i - uc_f$

Also, Rate of reaction in the reactor = $r \cdot V$, where r is the rate per unit volume and V the volume.

Therefore,

$$r \cdot V = uc_i - uc_f$$

or
$$r = u\,(c_i - c_f)/V \tag{7.7}$$

Thus, the measurement of c_i and c_f at a given flow rate u allows the reaction rate to be calculated from equation (7.7). The order of reaction and rate constant can be determined by carrying out experiments at different concentrations of reactants and rates of flow.

7.2.1 Continuous Flow Method

In this method (Fig. 7.2), the reactants are forced into a mixing chamber and allowed to flow through a tube called *observation tube*. The analysis of reaction mixture is made at different points along the observation tube and thus the progress of the reaction at different times can be obtained.

The analysis can be made *in situ* using an optical, thermal, electrical or other method. The average time, during which the reaction proceeds before an element of volume and reaches a distance d along the reaction tube, is d/v, where v is the linear velocity. From the measurements made at various

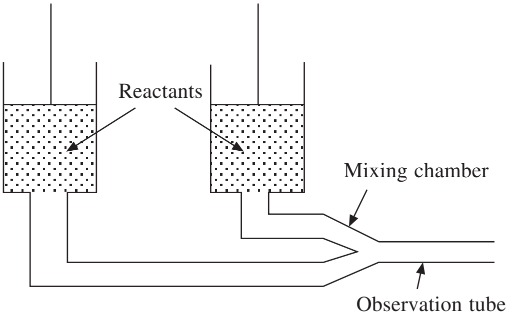


Fig. 7.2 Schematic diagram for continuous flow method.

distances, a concentration time plot can be obtained from which the rate constant can be determined. Since the velocity of flow of the magnitude of 10×10^3 cm $\sec^{-1}$ can be achieved, the shortest time interval for reaction that is accessible is of the order of 10^{-3}sec.

7.2.2 Accelerated Flow Method

This method is similar to continuous flow method except that the rate of flow is continuously varied and the analysis is made at a fixed point along the observation tube. Since the rate of flow changes with time, the reaction mixtures arriving at observation point have different time. In the accelerated flow method the output from a photo electric colorimeter is fed to a cathode-ray oscilloscope, which sweeps out a complete time-concentration record which may be photographed. The method is useful for very rapid enzyme reactions and requires only small quantities of reactants.

7.2.3 Stopped Flow Method

In this method (Fig. 7.3), the rapidly mixed reactants emerge through an

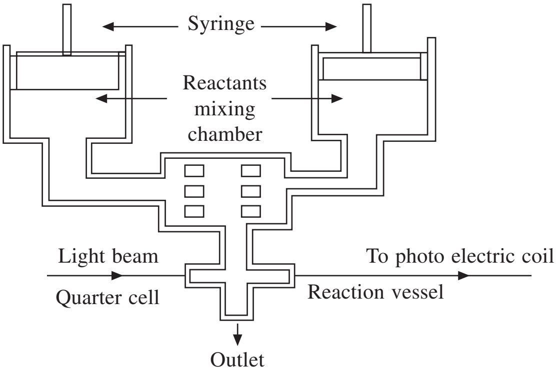


Fig. 7.3 Stopped flow technique.

observation tube as in continuous flow method. But the flow is suddenly stopped and comes to rest within 10^{-3}sec. Progress of reaction is monitored by using a method that has a rapid response. By oscilloscopic methods the concentration can again be studied as a function of time after the flow ceases. As the time progresses, the reaction mixture present at the point of observation continues to react. This method is very economical and takes advantage of rapid mixing of reagents. The stopped flow method has following advantages over continuous flow method:

(i) The method is not affected by rate and character of flow, provided the mixing is proper.
(ii) A permanent record of the progress of reaction covering a wide range can be obtained.
(iii) A very small quantity of the reactants is required.

7.3 Relaxation Method

The flow techniques are not suitable for the study of reactions whose half-lives are smaller than about a few msec. Many reactions occur with higher rates than the time required for mixing of the reactants in flow techniques. One of the techniques used for study of such reaction is relaxation method.

In this method, the reaction is first allowed to attain equilibrium which is then disturbed in some way. The system approaches to attain a new equilibrium. The speed with which the system approaches its new equilibrium is followed using some special techniques. Let us consider a simple system

$$\mathrm{A} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

The reaction is first order in both the directions. Suppose the system is in equilibrium and a is the initial concentration of A and x the concentration of B at any time t. Then

$$\frac{dx}{dt} = k_1(a - x) - k_1'x \tag{7.8}$$

At equilibrium, $dx/dt = 0$ and let $x = x_e$. Therefore,

$$k_1(a - x_e) = k_1' x_e \tag{7.9}$$

Now system is disturbed so that it is no longer at equilibrium.

The deviation from equilibrium, Δx may be considered as

$$\Delta x = x - x_e$$

and its derivative with time is given as

$$\frac{d\Delta x}{dt} = \frac{dx}{dt} = k_1(a - x) - k_1'x$$

$$= k_1 a - (k_1 + k_1')x$$

$$= k_1 a - (k_1 + k_1')(x_e + \Delta x) \tag{7.10}$$

From equations (7.9) and (7.10), $d\Delta x/dt$ may be written as

$$\frac{d\Delta x}{dt} = -(k_1 + k_1')\Delta x \tag{7.11}$$

The quantity Δx thus varies with time in the same manner as does the concentration of a reactant in a first order reaction. Integrating equation (7.11), we get

$$\ln \frac{(\Delta x)_0}{\Delta x} = (k_1 + k_1')t \tag{7.12}$$

where $\Delta x = (\Delta x)_0$.

When $t = 0$ has been taken as boundary conditions, equation (7.12) gives

$$t^* = \frac{1}{(k_1 + k_1')} \text{ when } \frac{(\Delta x)_0}{\Delta x} = e$$

or

$$\ln \frac{(\Delta x)_0}{\Delta x} = 1$$

where t^* is known as *relaxation time* and may be defined as the time at which the distance from equilibrium is $1/e$ of the initial distance. We can determine $(k_1 + k_1')$ knowing t^*. Obtaining the ratio k_1/k_1' from equilibrium constant, the individual rate constants k_1 and k_1' can be calculated.

The relation between relaxation time and rate constants for some simple systems are given in Table 7.2.

Table 7.2 Relationship between relaxation time and rate constant for some simple reactions

Reaction	Relaxation time
$A \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} X$	$1/\{k_1 + k_1'\}$
$2A \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} X$	$1/\{4k_1[A]_e + k_1'\}$
$A + B \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} X$	$1/\{k_1([A]_e + [B]_e) + k_1'\}$
$A \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} X + Y$	$1/\{k_1 + k_1'([x]_e + [y]_e)\}$
$A \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} 2X$	$1/\{\frac{1}{2}k_1 + 2k_1'[x]_e\}$
$A + B \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} X + Y$	$1/\{k_1([A]_e + [B]_e) + k'([x]_e + [y]_e)\}$

In order to use relaxation method, it should be ensured that the perturbation from equilibrium must be accomplished in a time (~10^{-6} to 10^{-7} sec for fastest reactions) that is much less than the relaxation time. The techniques, which are used for perturbation from equilibrium, include pressure jump or temperature jump methods in which pressure or temperature changes are brought about rapidly. For more shorter perturbation times, high electric fields are also used to bring about perturbation. Ultrasonic vibrations can be used to produce oscillating temperatures. Perturbations may be in the form of step functions, highly damped oscillations or continuous oscillations. The spectrophotometric methods have frequently been used for obtaining the relaxation time.

Problem 7.1 Calculate the relaxation time for the reaction

$$A^+_{(aqu)} + B^-_{(aqu)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AB_{(aqu)}$$

for a temperature jump experiment to a final temperature 400 K. The solution was initially prepared by adding 0.02 moles of AB to water maintaining total volume of 1 liter. Both forward and backward reactions are first order, k_1 and k_2 are 8.0×10^{10} and 5.0×10^6 s^{-1} at 400 K, respectively.

Solution

$$\text{Relaxation time} = \frac{1}{k_1([A_e] + [B_e]) + k_2}$$

$$K_c = \frac{k_1}{k_2} = \frac{8.0 \times 10^{10}}{5.0 \times 10^6} = 1.6 \times 10^4$$

Let x be the concentration dissociate. Then

$$K_c = \frac{a - x}{xx} = \frac{0.02 - x}{x^2}$$

$1.6 \times 10^4\, x^2 = 0.02 - x$. Therefore, $x = 7.6 \times 10^{-4}$

Thus $[A_e] = [B_e] = 7.6 \times 10^{-4}$

Hence,

$$\text{Relaxation time} = \frac{1}{(8.0\times10^{10})(2\times7.6\times10^{-4})+5.0\times10^6}$$

$$= \frac{1}{126.6\times10^6} = 8.22 \times 10^{-9} \text{ sec}$$

7.4 Shock Tubes

A number of fast gaseous reactions have been investigated using shock tubes. The reaction system is taken in a long metal tube, through which a shock wave is passed. As the shock wave traverses an element of gas, the temperature of gas rises sharply and reaction occurs in and behind the shock front. The course of reaction and temperature may be determined by various methods. Various designs of shock tubes have been employed and one such is shown schematically in Fig. 7.4.

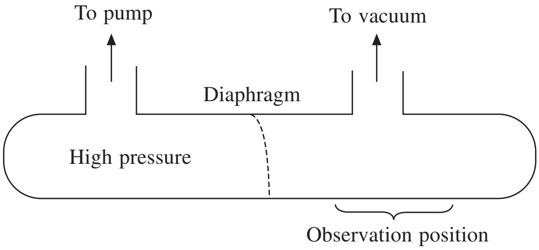


Fig. 7.4 Shock tube.

The tube is divided into two parts, viz. a high pressure and low pressure end, separated by a thin diaphragm made of a metal foil or other material.

The reaction system is kept in the low pressure compartment while the gas is kept in a high pressure compartment. The diaphragm is burst either by mechanical means or by increasing the pressure. When the diaphragm bursts, a plane shock wave moves along the tube. At start, wave is not sharp because of initial turbulence. After traveling a short distance, the wave becomes a true shock wave in which there is a very sharp boundary between high and low-pressure region. As the wave travels, the gas is rapidly raised to a very high temperature and the reaction takes place which can be studied by making rapid observations at various points along the tube. The sharp change in temperature, pressure, density or electrical conductivity etc. may be used as tool for the detection of the arrival of the shock front. In some cases, a time-of-flight mass spectrophotometer has also been used to follow the concentrations of species produced by the shock waves. The shock wave technique has successfully been applied to study the vibrational and rotational energy transfers between gaseous molecules.

7.5 Flash Photolysis

Vary fast reactions, both in gaseous and liquid phases, can be studied by this method. In flash photolysis technique, a light flash of very high intensity and very short duration (~ 10^{-6} sec) is produced in the neighborhood of the reaction vessel. This produces atoms, free radicals and excited species in the reaction system. These species undergo further reactions which can be followed by spectroscopic means. The method is also known as *kinetic spectroscopy*. The first order rate constant as large as 10^5 sec^{-1} and second order rate constants as large as 10^{11} mol^{-1}dm^{3}sec^{-1} can be measured by this technique.

7.6 ESR Spectroscopic Technique

There are large number of fast reactions which proceed by radical mechanism and the radicals formed are very reactive. The radicals of life time of about 0.01 sec have been characterized by electron spin resonance (ESR) studies. Thus, if other parameters are kept constant, the ESR spectroscopy can be used to measure the concentration of the free radical formed. For this, a rapid flow system is usually employed and a special cell is designed to mix the reactants together and subsequently flow through the observation tube. The integrated area of the absorption bands of ESR signals are compared to calculate the concentrations. The progress of reaction can be followed by measuring the areas of absorption bands at different times. The change in shape of the absorption signal with time has been used to investigate the life time of free radicals.

In the reactions which are not extremely fast, rate of reaction can be studied by following the signal intensity of a paramagnetic reactant or product as a function of time. Very rapid electron exchange reaction, for example, exchange of electron between naphthalene and naphthalene radical anion, can also be studied by ESR spectroscopy. When electron exchange occurs, a broadening of the hyperfine component of the ESR spectrum may be observed. The rate constant for electron exchange reaction can be calculated by making use of this broadening as function of time.

7.7 NMR Spectroscopic Techniques

The substance like ^{1}H, ^{14}N, ^{19}F, ^{13}C, ^{17}O, ^{31}P contain nuclei with a spin and thus exhibit nuclear magnetic resonance (NMR) like ESR. In NMR also the shapes of line or signal are used for obtaining the information on kinetics of the reaction.

Let us consider a simple proton exchange reaction

$$AH + BH' \rightleftharpoons AH' + BH$$

when equimolecular mixture of AH and BH′ is taken and if, there is no interaction, the NMR spectrum will show two separate peaks representing the characteristic chemical shifts of two compounds, i.e. AH and BH′. However, if there is a proton exchange, as in the above reaction, and if the rate of this exchange is enhanced by raising temperature, the two lines first broaden and approach to each other and then become a single broad line.

The broadening of each line is due to the shortening of the mean life time of two molecules.

Shortening of the life time due to reaction leads to an increase in line width. The increase in line width will not continue indefinitely. As the rate of exchange of protons rises, two protons in two different environments do not behave as independent and, therefore, the lines broaden and finally merge. If average time spent by a given proton is t_0 and if two lines are separated by $\Delta\nu_{AB,}$ then at the point where the lines coalesce

$$t_0 = \sqrt{2}/(\pi \times \Delta\nu)$$

From this value, and by known concentrations, the rate constant of the process can be evaluated.

EXERCISES

1. Give a brief account of flow methods for studying the fast reactions.
2. What is relaxation time? How it is related with rate constants in the following reactions?

   (i) $A \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} B$

   (ii) $A + B \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} B + C$

   (iii) $A \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} B + C$

   (iv) $A + B \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} C + D$
3. In an experiment for the reaction

   $$A \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} B + C$$

   the relaxation time has been observed as 25 sec. Calculate the values of k_1 and k_1', where the equilibrium constant for reaction is 10^{-14}.
4. How a fast reaction can be initiated and studied by flash photolysis?
5. Describe in brief the techniques which can be used to study the kinetics of fast reactions.

8

Reactions in Solutions

8.1 Introduction

When a reaction follows the same mechanism in solution and in the gaseous state, the kinetics remain same in both. However, because of the increased interactions in condensed media, the mechanism is frequently changed and also the kinetics correspondingly. When a chemical reaction takes place in solution, the solvent is usually in so much excess that its concentration does not change appreciably as the reaction proceeds and is, therefore, not involved in the rate expression. However, if solvent enters into chemical change and does not regenerate at the end of the process, the solvent would be said to exert a chemical effect on the reaction and will thus be involved in the rate expression.

The reaction in solution can be considered to take place in three steps, viz.

(i) Diffusion of reactant molecules towards each other.
(ii) Chemical transformation.
(iii) Diffusion of products away from each other.

The rates of many chemical reactions does not appear to depend on the solvent. This is because the activation energy for the process of diffusion in a liquid is nearly 20 kJ mol^{-1} whereas for chemical reactions it is quite large. Thus, step (i) is usually not rate determining step in reactions in solutions. When the reaction takes place in solution, it is step (ii) that determines the rate of a bimolecular reaction. This conclusion is supported by the fact that the rates of these reactions do not depend upon the viscosity of the solvent. The rate should be effected by the solvent if diffusion of reactant is the rate determining step.

There are some processes occurring in solutions, e.g. quenching of the fluorescence in solution, certain heterogeneous reactions etc., in which the diffusion is the rate controlling. These reactions occur very rapidly, e.g. ionic recombinations.

8.2 Theory of Absolute Reaction Rate

In reactions between gas molecules, the rate constant can be determined in terms of partition functions of reactants and activated complex. The evaluation of partition functions is very difficult due to greater uncertainty about these in solution, and therefore, the rate of reaction in solution is related to that in gas phase by incorporating activity coefficients

Activity = Concentration × Activity coefficient

Activity coefficient $\rightarrow 1$ when solution → ideal solution, i.e. very dilute solution.

Let us consider the reaction

$$\mathrm{A} + \mathrm{B} \overset{K^{\#}}{\rightleftharpoons} X^{\#} \rightarrow \text{Products}$$

Considering the gaseous reactants to be in their standard states, the rate constant k_g in gas phase can be written as

$$(k_g)_0 = \frac{k_b T}{h} K_g^{\#} \tag{8.1}$$

When solution is infinitely dilute, i.e. in the ideal state, rate constant in solution $(k_s)_0$ will be given by

$$(k_s)_0 = \frac{k_b T}{h} K_s^{\#} \tag{8.2}$$

$K^{\#}$ is equilibrium constant. If we consider the reference standard state to be gaseous, $K_g^{\#} = K_s^{\#}$ because the activity and fugacity coefficients are unity in very dilute solution and ideal gas, respectively. Then $(k_g)_0$ and $(k_s)_0$ will be the same.

In a nonideal solution,

$$K_s^{\#} = \frac{a_x^{\#}}{a_A a_B} \tag{8.3}$$

where a's represent respective activities. Or

$$K_s^{\#} = \frac{C_x^{\#} f_x^{\#}}{C_A f_A C_B f_B} = \frac{C_x^{\#}}{C_A C_B} \frac{f_x^{\#}}{f_A f_B}$$

where C is the concentration and f the activity coefficient. Therefore, the rate constant may be written as

$$(k_s) = \frac{k_b T}{h} K_s^{\#} \frac{f_A f_B}{f_x^{\#}}$$

or

$$k_s = k_g \frac{f_A f_B}{f_x^{\#}} \tag{8.4}$$

Equation (8.4) can be used for relating the rate constant in solution with that in gas phase.

If rates in solution and in gas phase are to be equal, the activity coefficient factor, i.e. $f_A f_B / f_x^{\#}$ must be equal to unity. For unimolecular reactions, where the reactant and activated complex have similar structures and f_A and $f_x^{\#}$ do not differ widely, the rate of reaction in solution will be quite similar to that in the gas phase.

8.3 Influence of Internal Pressure

For regular solutions, the influence of the solvent is determined by molar volumes and internal pressure terms. Since the molar volumes do not vary greatly, the internal pressure factor is more important. If the internal pressures of solvent, reactants and activated complex are similar, the solvent will have little effect on the rate of reaction as compared to a solvent in which reaction behaves ideally. If the internal pressure of the solvent is close to that of reactants but appreciably different from that of the activated complex, the rate of reaction in this solvent will be low. On the other hand, if solvent has an internal pressure similar to that of activated complex, but different from one or both the reactants, rate of reaction in this solvent will be high. Since the activated complex has properties which approach the properties of the product, it may be concluded, in general, that the reaction in which the products are of higher internal pressure than the reactants, it is accelerated by solvent of high internal pressure.

8.4 Influence of Solvation

The degree of solvation of the reactants and activated complex affect the rate of reaction. When the activated complex is solvated to a greater extent in comparison to reactants, the rate of reaction will be greater than that in a non solvating solvent. This is because the activity coefficient of the complex is smaller than it is in a solvent that does not solvate it. This lowers the potential energy of activated complex or causes a decrease in the activation energy of the reaction.

On the other hand, if one or both the reactants are solvated, while the activated complex is not, the necessary energy of activation is increased and consequently the rate of reaction is diminished. In case the reactant and activated complex are both solvated, the overall effect on both the activation energy and rate of reaction may be small.

8.5 Reactions between Ions

The reactions between the ions are generally very rapid. In ionic reactions, where two ions simply combine, the rate of reaction is governed by the diffusion of ions towards each other and activation energy for the combination is very small. However, there are many reactions between ions which may be as slow as reactions between neutral molecules. Thus, reactions involve the making and breaking of covalent bonds or electron transfer.

The effect of electrostatic attraction and repulsion are important in ionic reactions. If the ions of opposite signs are involved in the reaction, the frequency of collisions will be increased by attractive forces. The frequency factors for such reactions has been observed to be much higher than normal (~10^{10} lit mol^{-1} sec^{-1}). On the other hand, if the reaction involves ions of same sign, the number of collisions will be smaller and consequently frequency factors will be abnormally low.

A very simple model for reaction between two ions in solution is shown in Fig. 8.1. This model is referred as double sphere model. Z_A and Z_B indicate the number of positive or negative charges on the ions. Initially the ions are at infinite distance from each other and in activated state they are considered to be intact and they are d_{AB} distance apart.

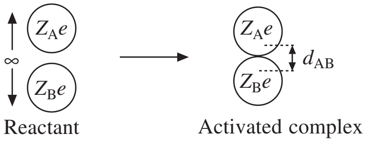


Fig. 8.1 Model for reaction between ions.

When the ions are at distance x apart, the force f acting on them is

$$f = \frac{Z_A Z_B e^2}{Dx^2}$$

where D is dielectric constant of the medium. The work that will be done in moving the ions from an initial distance of infinity to a final distance of d_{AB} is given by

$$W = -\int_{\infty}^{d_{AB}} \frac{Z_A Z_B e^2}{Dx^2}\, dx = \frac{Z_A Z_B e^2}{Dd_{AB}} \tag{8.5}$$

where negative sign shows that x decreases by dx when the ions move to each other by a distance dx. This work is equal to the electrostatic contribution to the free energy increase when the ions are moved up to each other. Therefore, the free energy of activation per molecule may be given as

$$\frac{\Delta G^{\#}}{N} = \frac{\Delta G_0^{\#}}{N} + \frac{Z_A Z_B e^2}{Dd_{AB}}$$

$\Delta G_0^{\#}$ is free energy for non electrostatic term. Therefore, the rate constant for a reaction between ions

$$k = \frac{k_b T}{h} e^{-\Delta G_0^{\#}/RT}\, e^{-\frac{Z_A Z_B e^2}{Dd_{AB} RT}}$$

or

$$\ln k = \ln \frac{k_b T}{h} - \frac{\Delta G_0^{\#}}{RT} - \frac{Z_A Z_B e^2}{Dd_{AB} RT} \tag{8.6}$$

which is again simplified as

$$\ln k = \ln k_0 - \frac{Z_A Z_B e^2}{D d_{AB} RT} \tag{8.7}$$

where k_0 is the rate constant in a medium of infinite dielectric constant, i.e. $k_0 = k$ when there is no electrostatic forces.

According to equation (8.7), ln k of a reaction between ions should vary linearly with $1/D$. This has been tested for various reactions. The slope of the plot of ln k versus $1/D$ gives the value of $Z_A Z_B e^2/d_{AB}RT$ and the value of d_{AB} can be obtained from slope. The equation predicts a linear plot of ln k against $1/D$ with a negative slope if the charges of the ions are same, and a positive slope if the charges are opposite. This treatment has also been extended to give an interpretation of the magnitudes of the frequency factors of reactions.

8.6 Entropy Change

The electrostatic contribution to the free energy of activation per mole is given as

$$\Delta G^{\#}(\text{e.s.}) = \frac{N Z_A Z_B e^2}{D d_{AB}} \tag{8.8}$$

while the entropy S is related with ΔG as

$$S = -\left[\frac{\partial G}{\partial T}\right]_p$$

because only D in equation (8.8) is temperature dependent.

Therefore, electrostatic contribution to the entropy is given by

$$\Delta S^{\#}(\text{e.s.}) = \frac{N Z_A Z_B e^2}{D^2 d_{AB}}\left[\frac{\partial D}{\partial T}\right]_p = \frac{N Z_A Z_B e^2}{D d_{AB}}\left[\frac{\partial \ln D}{\partial T}\right]_p \tag{8.9}$$

In aqueous solution, D is 80 and $(\partial \ln D/\partial T)_p$ remains constant (–0.0046) over a considerable range. If d_{AB} is 2.0×10^{-8} cm, equation (8.9) gives

$$\Delta S^{\#}(\text{e.s.}) = -\,10\, Z_A Z_B \tag{8.10}$$

or

$$\Delta S \approx 40\ Z_A Z_B \text{ JK}^{-1} \text{ mol}^{-1}$$

which indicates that the entropy of activation in aqueous solution should decrease by about 10 units for each unit of $Z_A Z_B$.

Further, since frequency factor is proportional to $e^{\Delta S^{\#}/R}$ or $10^{\Delta S^{\#}}/2.303R$, the frequency factor should decrease by a factor of $10^{10}/4.57$, i.e. by about one hundred fold for each unit of $Z_A Z_B$.

When the ions are of same charge, the activated complex bears more charge, the solvent molecules in the neighborhood of ion are acted upon by strong electrostatic forces, which restrict their freedom of motion. This effect is known as *electrostriction*. There is a consequent loss of entropy. Larger the charge on ion, greater will be the loss in entropy.

On the other hand, when reacting ions are of opposite charge, there will be a loss of charge on activated complex. Consiquently, there is a decrease in electrostriction and an increase in the entropy. This is shown schematically in Fig. 8.2.

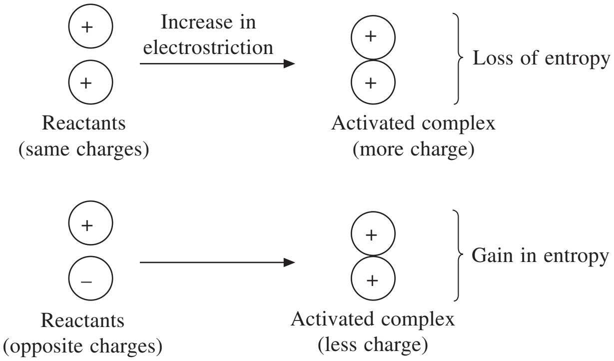


Fig. 8.2 Reaction between ions and entropy change.

8.7 Influence of Ionic Strength (Salt Effect)

It is generally observed that the rate of reaction can be altered by the presence of non-reacting or inert ionic species in the solution. This effect is especially great for reactions between ions, where rate of reaction is effected even at low concentrations. The influence of a charged species on the rate of reaction is known as *salt effect.* The effects are classified as primary and secondary salt effects . The primary salt effect is the influence of electrolyte concentration on the activity coefficient and rate of reaction, whereas the secondary salt effect is the actual change in the concentration of the reacting ions resulting from the addition of electrolytes. Both effects are important in the study of ionic reactions in solutions. The primary salt effect is involved in non-catalytic reactions and has been considered here. The deviation from ideal behaviour can be expressed in terms of Brönsted-Bjerrum equation.

Let us consider a reaction

$$\mathrm{A} + \mathrm{B} \overset{K^{\#}}{\rightleftharpoons} \mathrm{X}^{\#} \xrightarrow{k} \text{Product}$$

where $K^{\#}$ is the equilibrium constant for activation process and is given as

$$K^{\#} = \frac{a^{\#}}{a_\mathrm{A} a_\mathrm{B}} = \frac{[\mathrm{X}^{\#}]}{[\mathrm{A}][\mathrm{B}]} \frac{f^{\#}}{f_\mathrm{A} f_\mathrm{B}} \tag{8.11}$$

or

$$[\mathrm{X}^{\#}] = K^{\#}[\mathrm{A}][\mathrm{B}]\frac{f_\mathrm{A} f_\mathrm{B}}{f^{\#}}$$

The rate of reaction is given by

$$\text{Rate} = [\text{X}^{\#}]\frac{k_b T}{h} \tag{8.12}$$

or
$$\text{Rate} = \frac{k_b T}{h} K^{\#}[\text{A}][\text{B}]\frac{f_A f_B}{f^{\#}} \tag{8.13}$$

Experimentally, the rate of reaction is given as

$$\text{Rate} = k[\text{A}]\ [\text{B}] \tag{8.14}$$

From equations (8.13) and (8.14), the rate constant k for reaction is obtained as

$$k = \frac{k_b T}{h} K^{\#} \frac{f_A f_B}{f^{\#}} \tag{8.15}$$

or
$$k = k_0 \frac{f_A f_B}{f^{\#}} \tag{8.16}$$

where k_0 is the rate constant when all activity coefficient are unity.

Equation (8.16) may be written as

or
$$\log k = \log k_0 + \log f_A + \log f_B - \log f^{\#} \tag{8.17}$$

Activity coefficient vary with the concentration especially in the presence of added electrolyte. Lewis and Randall introduced the quantity called *ionic strength* which is a measure of the intensity of the electric field due to the ions in a solution. It is defined as the sum of the terms obtained by multiplying the molarity (concentration) of each ion present in solution by the square of its valence

$$\mu = \frac{1}{2}\Sigma\, m_i Z_i^2 \quad \text{or} \quad \frac{1}{2}\Sigma C_i Z_i^2$$

According to Deybe-Huckel limiting law, the activity coefficient f of an ion is related to the ionic strength as

$$\log f = -QZ^2\sqrt{\mu}$$

where Q is a constant given by

$$\frac{N^2 e^3 (2\pi)^{1/2}}{2.303(Dk_b T)^{3/2}(1000)^{1/2}}$$

Since the charge on activated complex = $(Z_A + Z_B)$, equation (8.17) can be written as

$$\log_{10} k = \log k_0 - Q\surd[Z_A^2 + Z_B^2 - (Z_A + Z_B)^2]$$
$$= \log k_0 + 2QZ_A Z_B\sqrt{\mu} \tag{8.18}$$

where the value of Q is approximately 0.51 for aqueous solution at 25°C. Equation (8.18), therefore, can be written as

$$\log k = \log k_0 + 1.02\, Z_A Z_B \sqrt{\mu} \qquad (8.19)$$

Equation (8.19) has been tested for a considerable number of times. A plot of log k versus $\sqrt{\mu}$ will give a straight line with slope equal to 1.02 $Z_A Z_B$ (Fig. 8.3) Sign of $Z_A Z_B$ determines the direction of slope. If one of the reactant is a neutral molecule, $Z_A Z_B$ is zero and rate constant is expected to be independent of ionic strength. If the reactions involve similarly charged ions, $Z_A Z_B$ will be positive and slope of straight line will be positive, i.e. rate of reaction will increase on addition of electrolyte. On the other hand, if the reaction involves oppositely charged species in rate determining step, $Z_A Z_B$ will be negative and the rate of reaction will decrease on increasing μ, i.e. on adding salt in reaction mixture.

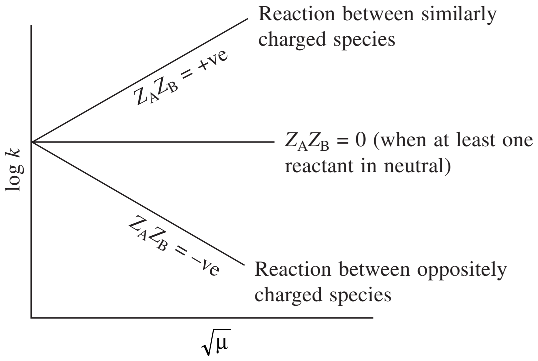


Fig. 8.3 Plot of log k versus $\sqrt{\mu}$.

For reactions

(a) $S_2O_8^{2-} + I^-$; $Z_A Z_B = 2$
(b) $CH_3COOC_2H_5 + OH^-$; $Z_A Z_B = 0$
(c) $CO(NH_3)_5Br^{2+} + OH^-$; $Z_A Z_B = -2$

8.8 Secondary Salt Effect

In primary salt effect, addition of an electrolyte (salt) or variation of ionic strength affects the activity coefficients and hence the rate of reaction. However, in a reaction where H^+ or OH^- ions produced from a weak acid or weak base act as catalyting agent, the addition of salt influences the concentration of H^+ or OH^- ions. Since the rate of reaction depends upon the concentration of H^+ or OH^-, it will be affected by the salt concentration. This phenomenon is known as *secondary salt effect.*

Let us consider a reaction which is catalyzed by H^+ produced by weak acid HA. The dissociation constant of acid is given as

$$HA \rightleftharpoons H^+ + A^-$$

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

or $$[H^+] = K_a \frac{[HA]}{[A^-]} \frac{f_{HA}}{f_{A^-} f_{H^+}} \tag{8.20}$$

or $$[H^+] = K \frac{f_{HA}}{f_{A^-} f_{H^+}} \tag{8.21}$$

where K = Constant = K_a [HA]/[A^-]; because [HA]/[A^-] will remain constant for a given acid salt mixture.

Since the rate depends on [H^+], the rate constant for a given acid salt ratio may be given as

$$k = k_0 \frac{f_{HA}}{f_{H^+} f_{A^-}} \tag{8.22}$$

where k_0 is the rate constant in absence of secondary salt effect and includes the primary salt effect. Equation (8.22) at 25°C, may be given as

$$\log k = \log k_0 + 1.018\sqrt{\mu} \tag{8.23}$$

When μ is increased, the concentration of H^+ increases, and therefore, rate of acid catalysed reaction will also increase. Similar results are obtained for reactions catalysed by hydroxyl ions. The ionic strength must be kept constant when we examine a general acid/base catalysed reaction because, if ionic strength is not kept constant the rate constant will change in accordance with equation (8.18).

The oxidation of ascorbic acid AH_2 by Ag(I) involves the rate determining step as

$$AH^- + Ag^+ \rightarrow AH^0 + Ag$$

This mechanism suggested by Mushran and coworkers is likely to give negative primary and positive secondary salt effect. At low ionic strength, both the salt effects will be a function of charge alone and thus will correspond to no net salt effect. At high ionic strength, the charge independent term involving direct proportionality to ionic strength will become more significant, resulting in negative salt effect. This observation has been found to be in excellent agreement with experimental results.

8.9 Reactions between the Dipoles

A theory for the influence of the dielectric constant of the medium on the free energy of a polar molecule has been given by Kirkwood. According to the theory, the free energy transfer of a polar molecule, having dipole moment μ and radius *r*; from a medium of dielectric constant unity to another (having dielectric constant *D*) is given by

$$\Delta G = -\frac{\mu^2(D-1)}{r^3(2D+1)} \tag{8.24}$$

Applying this theory to the transition state theory for the reaction

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{X}^{\#} \rightarrow \text{Products}$$

where A, B and $\mathrm{X}^{\#}$ are polar species, and taking

$$k = \frac{RT}{Nh} e^{-\Delta G^{\#}/RT}$$

we can derive the rate constant in the form of equation

$$\ln k = \ln k_0 - \frac{N(D-1)}{RT(2D+1)}\left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu^{\#2}}{r^{\#2}}\right) \tag{8.25}$$

where *k* is rate constant in medium of dielectric constant *D*, k_0 is rate constant in a condensed medium of dielectric constant unity when the non-electrostatic forces are the same for activated complex as for the reactants, μ_A, μ_B and $\mu^{\#}$ are dipole moment of A, B and $\mathrm{X}^{\#}$, respectively, and r_A, r_B and $r^{\#}$ are the corresponding radii. If the activated complex is more polar than the reactants, $\mu^{\#} > \mu_A$ or μ_B, a plot of ln *k* versus $(D - 1)/(2D + 1)$ will be linear with a positive slope. In such cases, *k* increases as the dielectric constant of the medium increases. This has been verified by reactions in mixture of two solvents of different dielectric constants in variable proportions so that *D* varies. The equation is not reliable, in general, if the reaction rates in different solvents of various dielectric constants are compared, especially if the activated complex is more polar than the reactants (since $r^{\#}$ varies from one solvent to another). On expending $(D - 1)/(2D + 1)$, we get

$$\frac{D-1}{2D+1} = \frac{1}{2} - \frac{3}{4D} + \frac{3}{8D^2} - \frac{3}{16D^3} + \ldots.$$

Neglecting higher terms, we obtain

$$\frac{D-1}{2D+1} = \frac{1}{2} - \frac{3}{4D} \tag{8.26}$$

and therefore, a plot of ln *k* versus $1/D$ can be plotted in place of ln *k* versus $\{(D - 1)/(2D + 1)\}$.

The influence of the dielectric constant on the rate of reaction does not seems to be very useful in distinguishing the reaction between ion-ion, ion-dipole or dipole-dipole reactions. Generally, if rate constant decreases as the dielectric constant is decreased, an interaction of ion-dipole type reaction is indicated.

8.10 Kinetic Isotope Effect

The bond energy of a compound will be affected by change in masses of atoms that are bonded. When an element in a compound is replaced by an isotope of the element, the rate of reaction of that compound is altered and the extent of alteration depends on the closeness of bond to the reaction taking place. The effect on the rate will be more when the bond involved in the substitution itself is cleaved in the reaction. The extent to which the rate is affected will depend on the extent to which the bond strength is affected and this in turn will depend on the relative differences in masses of the element and its isotope.

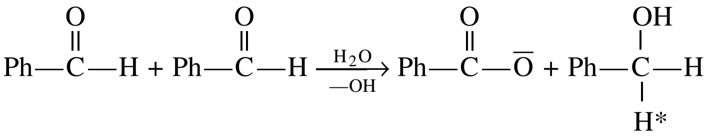
Let us consider that a C—H bond cleavages in the mechanism of reaction. Now, if deuterium is substituted for hydrogen, the rate is reduced.

Further, if tritium is substituted for hydrogen in C—H bond, a more reduction of rate is observed. This is because the mass ratio is highest for hydrogen isotopes. Since the isotope substitution affect the reduced mass and according to collision theory, Z is proportional to $(1/\mu)^{1/2}$, the rate will also be affected. The ratio of rate constants k_H/k_D and k_H/k_T are 7 and 16, respectively, when deuterium and tritium is substituted in place of hydrogen in the bond cleaved in the mechanism. This is called the *primary kinetic isotope effect*. The change in rate constant due to presence of a heavier isotope in a molecule at a position not directly involved in the bond transformation is called *secondary kinetic isotope effect*. However, when molecules are heavy, isotopic substitution will not alter the masses to any considerable extend and hence the isotope effect will be insignificant.

The isotope effect is generally used to:

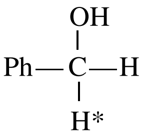
(a) observe that a particular bond is broken in the rate limiting step of a reaction or not. For example, if C—H bond is breaking in the rate determining step, the substitution of deuterium (D) will slow down the rate by about 7 fold.

(b) solve some of the mechanistic problems that are known. For example, let us consider the Cannizzaro reaction



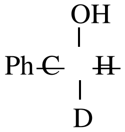
$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}H + Ph{-}\overset{\overset{O}{\|}}{C}{-}H \xrightarrow[\text{—OH}]{H_2O} Ph{-}\overset{\overset{O}{\|}}{C}{-}\overline{O} + Ph{-}\overset{\overset{OH}{|}}{\underset{\underset{H^*}{|}}{C}}{-}H}$$

to observe that in



$$\mathrm{Ph{-}\overset{\overset{OH}{|}}{\underset{\underset{H^*}{|}}{C}}{-}H}$$

H* came from water molecule or from second molecule of benzaldehyde. The reaction when carried out in D_2O medium, no



$$\mathrm{Ph{-}\overset{\displaystyle OH}{\underset{\displaystyle D}{C}}{-}H}$$

was formed. This clearly indicates that H* comes from second molecule of benzaldehyde.

The rate constant k by collision theory is

$$k = pZe^{-E/RT} \tag{a}$$

where p, Z and E are steric factor, collision number and energy of activation, respectively.

Again, Z is proportional to $(1/\mu)^{1/2}$, where μ is the reduced mass. Therefore, when isotope is substituted, the rate constant will change. Let

$$k_\mathrm{I} = pZ_\mathrm{I}\, e^{-E_\mathrm{I}/RT} \tag{b}$$

where k_I, Z_I and E_I are the rate constant, collision number and activation energy, respectively, in case of isotope substitution.

From equations (a) and (b), we get

$$k/k_\mathrm{I} = (Z/Z_\mathrm{I})e^{-\frac{E-E_\mathrm{I}}{RT}} \tag{c}$$

or

$$k/k_\mathrm{I} = \left(\frac{\mu_\mathrm{I}}{\mu}\right)^{1/2} e^{-\frac{E-E_\mathrm{I}}{RT}} \tag{d}$$

where μ_I is the reduced mass of isotope-substituted system.

When molecules are heavy, isotope substitution will not alter the masses to any considerable extent and $(\mu_\mathrm{I}/\mu)^{1/2}$ will tend to unity.

In order to consider the energy factor, let us consider the energy in ground state. The vibrational energy of molecule in ground state is given as

$$E_0 = \frac{1}{2}h\nu_0 \tag{e}$$

where $\nu_0 = \frac{1}{2\pi}\sqrt{k_\mathrm{f}/\mu}$ (k_f being force constant).

For isotopic substitution, the ground state energy and frequency of vibration will be given as

$$E_0^\mathrm{I} = \frac{1}{2}h\nu_0^\mathrm{I} \tag{f}$$

where $\nu_0^\mathrm{I} = \frac{1}{2\pi}\sqrt{k_\mathrm{f}/\mu_\mathrm{I}}$.

From equations (e) and (f), we get

$$\nu_0^\mathrm{I} = \nu_0(\mu/\mu_\mathrm{I})^{1/2}$$

and $$\Delta E = E_0 - E_0^{\mathrm{I}} = \frac{1}{2}h(\nu_0 - \nu_0^{\mathrm{I}})$$

or $$\Delta E_0 = \frac{1}{2}h\{\nu_0 - \nu_0(\mu/\mu_{\mathrm{I}})^{1/2}\}$$

$$= \frac{1}{2}h\nu_0\{1 - (\mu/\mu_{\mathrm{I}})^{1/2}\} = E_0\{1 - (\mu/\mu_{\mathrm{I}})^{1/2}\} \qquad \text{(g)}$$

The replacement of the light element with heavy isotope lowers the energy by ΔE_0, which is given by equation (g). For ground state of hydrogen $\nu_0 = 4405\ \mathrm{cm}^{-1}$ and $(\mu_H/\mu_D)^{1/2} = 0.70$. Thus, the value of ΔE_0 is obtained as $7.74\ \mathrm{kJ\ mol}^{-1}$.

The replacement of light isotope with heavy isotope in activated state also lowers the energy. Let the lowering in energy in activation state be represented as $\Delta E_0^{\#}$. It has been observed that $\Delta E_0^{\#}$ is less than ΔE_0 and, therefore, ratio of $k/k_{\mathrm{I}} > 1$. When the bond involving the isotope element in activated complex is completely broken $\Delta E_0^{\#}$ and k/k_{I} will be maximum. However, when the bonds in activated complex is stronger than in the initial molecule, i.e. $\Delta E_0^{\#} > \Delta E_0$, the value of k/k_{I} will be less than unity. This is called *reverse isotope effect.*

8.11 Solvent Isotope Effect

The rate of a chemical reaction may change on changing the isotopic composition of the solvent, e.g. changing solvent from H_2O to D_2O. If H of water or of an alcoholic solvent is replaced by D, there may be a change in the rate of reaction.

The solvent isotope effect has widely been used in distinguishing between whether proton transfer occurs prior to or in the rate-determining step. When proton transfer is the rate determining step, the rate in D_2O will be less than in H_2O. This is a normal primary kinetic isotope effect. However, if there is a fast reversible proton transfer prior to the rate determining step, the reactions occur more rapidly in D_2O than in H_2O.

Let us consider the reaction

$$\mathrm{S} + \mathrm{H_3O^+} \overset{K}{\rightleftharpoons} \mathrm{SH^+} + \mathrm{H_2O}$$

$$\mathrm{SH^+} \xrightarrow{k} \text{Product} \quad \text{(slow, rate determining)}$$

$$\text{Rate} = \frac{dP}{dt} = k[\mathrm{SH^+}] = kK[\mathrm{S}][\mathrm{H_3O^+}]$$

When H_2O is replaced by D_2O, since D_3O^+ is a stronger acid than H_3O^+, the concentration of SD^+ in D_2O will be greater than that of SH^+ in H_2O and, therefore, the reaction will be faster in D_2O. Similarly, in base catalysed reactions, DO^- being a stronger base than HO^-, an increase in the rate in D_2O compared to that in water is expected.

8.12 Hemmett Equation

The introduction of a substituent in an organic compound may affect its reactivity in a given reaction. A number of quantitative relationships have been suggested in connection with the effect of substituents on the rate constant of the reaction. Such structure-reactivity co-relations are helpful in predicting the reactivity of organic compounds in various reactions and also in verifying the reaction mechanism. One such useful relationship was proposed by Hemmett, which relates the equilibrium and rate constants for the reaction of meta and para substituted benzene derivatives.

$$\log k = \log k_0 + \sigma\rho$$

or

$$\log K = \log K_0 + \sigma\rho \tag{8.27}$$

where k and k_0 are rate constants for substituted and parent compound respectively and K and K_0 are equilibrium constants for reaction in case of substituted and parent compound, respectively. The parameter σ (substituent constant) depends only on the substituent, while ρ is a parameter known as *reaction constant* that varies with the reaction and external conditions.

Reaction constant ρ has been chosen as unity for the ionization equilibrium constant for benzoic acid in aqueous solution and for the substituted benzoic acids defined as

$$\rho = \log\left(\frac{\text{Ionization constant of a substituted benzoic acid}}{\text{Ionization constant of benzoic acid}}\right) \tag{8.28}$$

By determining the ρ, the values of ρ for other reaction can thus be obtained. Hemmett equation has been applied quite accurately to a large number of reactions.

The substituent constant σ is a measure of polar effect (relative to hydrogen of the meta or para position). σ is positive when $K > K_0$. A positive value of σ has been found in electron withdrawing substituents like ~~NO~~ $_2$,~~Cl~~ etc. These electron withdrawing substituents stabilize the anion of the acid and increases the strength of substituted acid. For electron donating substituents, σ is negative. The value of σ lies between 0 and ±1.0. In general, σ is not dependent on solvent and temperature. It has been observed that for substituents which can interact with the solvent, viz. ~~OH~~, the value changes with solvent composition.

The reaction constant ρ depends on nature of reaction, solvent and temperature. It is a measure of the susceptibility of the reaction to polar effect. A positive value of ρ for a reaction shows that the reaction is accelerated by electron withdrawing substituents (σ = + 1.0). Thus a positive value of ρ indicates the reaction center has higher electron density in the transition state than in the starting material. While negative value of ρ indicates that the reaction center has a lower electron density in the transition state than in the starting material and the reaction is accelerated by electron donating substituents. In general, the value of ρ has been found to be between –5 and +5. A small value of ρ has been observed in reaction involving free radical intermediates or a cyclic transition state. The values of σ and ρ for some cases are given in Table 8.1.

Table 8.1 Substituent constants and reaction constants

Substituent constants			Reaction constants	
Group	Meta	Para	Reaction	Value of constants
CH_3	–0.07	–0.17	Benzoic acid ionization in water	1.00
C_2H_5	–0.04	–0.15	Ionization of phenol in water	2.11
OH	0.00	–0.46	Alkaline hydrolysis of methyl benzoate in 60% ethanol	2.46
Cl	0.37	0.23	Acid hydrolysis of ethyl benzoate	0.144
NO_2	0.71	0.75	in 60% ethanol	–

8.13 Linear Free Energy Relationship

There is a linear relationship between the free energies of activation for one homologous series of reactions and those of another. The Hemmett relationship are equivalent to the existence of linear relationship between the free energies for different series. The rate constant of a reaction is related with the free energy of activation by the equation

$$k = \frac{k_b T}{h} e^{-\Delta G^{\#}/RT} \tag{8.29}$$

The logarithm of rate constant is given by

$$\log k = \log \frac{k_b T}{h} - \frac{\Delta G^{\#}}{2.303RT} \tag{8.30}$$

Similarly

$$\log k_0 = \log \frac{k_b T}{h} - \frac{\Delta G_0^{\#}}{2.303RT} \tag{8.31}$$

Substituting the values of log k and log k_0 in the Hemmett equation, i.e. $\log k = \log k_0 + \sigma\rho$, we get

$$\Delta G^{\#} = \Delta G_0^{\#} - 2.303\,RT\,\sigma\rho$$

or

$$\frac{\Delta G^{\#}}{\rho} = \frac{\Delta G_0^{\#}}{\rho} - 2.303\,RT\,\sigma \tag{8.32}$$

This equation, with a particular value of reaction constant ρ may apply to any reaction involving a reactant having a series of substituents. For a second series of homologous reactions having reaction constant ρ′, a similar equation can be written as

$$\Delta G'^{\#} = \Delta G_0'^{\#} - 2.303\, RT\, \sigma\rho'$$

or

$$\frac{\Delta G'^{\#}}{\rho'} = \frac{\Delta G_0'^{\#}}{\rho'} - 2.303\, RT\sigma \tag{8.33}$$

Subtracting equation (8.33) from (8.32), we get

$$\frac{\Delta G^{\#}}{\rho} - \frac{\Delta G'^{\#}}{\rho'} = \frac{\Delta G_0^{\#}}{\rho} - \frac{\Delta G_0'^{\#}}{\rho'} \tag{8.34}$$

Which can also be written as

$$\Delta G^{\#} - \frac{\rho}{\rho'}\Delta G'^{\#} = \text{Constant} \tag{8.35}$$

This is a linear relationship between the free energy of activation for homologous series of reaction. An equivalent relationship

$$\Delta G - \frac{\rho}{\rho'}\Delta G' = \text{Constant} \tag{8.36}$$

applies for free energies of overall reaction.

Thus, a plot of ΔG and $\Delta G'$ is linear as shown in Fig. 8.4.

The linear free energy relationship has been observed in large number of cases. The applicability of the relationship is quite poor for ortho-substituents because these substituents exert not only electron-attracting or electron repelling effect but also a steric effect which usually leads to a decrease in the rate of reaction.

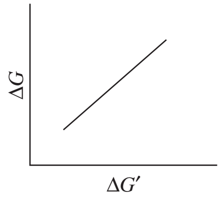


Fig. 8.4 Plot of ΔG and ΔG′.

8.14 The Taft Equation

The Hemmett equation is not applicable well to the reactions of aliphatic compounds partly due to some steric interference between the substituents and reaction site. For aliphatic compounds, Taft has proposed the following equation

$$\log k = \log k_0 + \sigma^*\rho^* \tag{8.37}$$

where k is rate constant for a particular member of reaction series and k_0 the rate constant for the parent compound (usually the methyl compound).

Polar substituent constant σ^* is defined as

$$\sigma^* = \frac{1}{2.5}[\log (k/k_0)_{\text{basic}} - \log(k/k_0)_{\text{acidic}}] \tag{8.38}$$

where k_0 is rate constant for an ester and k the rate constant for ester having the substituent alpha to carbonyl group. The rate constants have been compared for acidic and basic hydrolysis of ester. An arbitrary factor 2.5 has been introduced to bring σ^* values on approximately same scale as the Hemmett σ values. The term $\log (k/k_0)_{\text{acidic}}$ is a measure of the contribution of steric effect to the free energy of activation while $\log (k/k_0)_{\text{basic}}$ is a measure of the contribution of both, i.e. steric effect and inductive effect to the free energy of activation. The difference of the two terms is thus a measure of the inductive effect alone. Thus, the polar substituent constant σ^* is a measure of the electron attracting ability of the substituent. ρ^* is the reaction constant, analogous to Hemmett's equation. A positive ρ^* value indicates that the reaction is facilitated by electron withdrawal as in the Hemmett equation.

In terms of equilibrium constant, the Taft equation is written as

$$\log K = \log K_0 + \sigma^* \rho^* \tag{8.39}$$

Some values of Taft σ^* and ρ^* are given in Table 8.2.

Table 8.2 Values of Taft σ^* and ρ^*

Group	σ^*	Reaction	ρ^*
CH_3	0.00	$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$	1.72
C_2H_5	−0.10	$RCH_2OH + H_2SO_4 \rightleftharpoons RCH_2OSO_3H + H_2O$	4.60
H	0.49		
C_6H_5	0.60	$C_6H_5COCHR_2 + BrOH^- \rightarrow C_6H_5COCR_2Br + Br^-$	
CH_3CO	1.65		
Cl_3C	2.65		

8.15 Compensation Effect

It has frequently been observed that for a given reaction investigated in a series of solvent and also for the homologous reactions in which substituents are introduced into a reactant, a plot of $T\Delta S^\#$ against $\Delta H^\#$ was a straight line with approximately unit slope as shown in Fig. 8.5.

Since $\Delta G^\# = \Delta H^\# - T\Delta S$ and if there is exact relationship between $\Delta H^\#$ and $T\Delta S^\#$ with unit slope, there will be no variation in $\Delta G^\#$.

A similar compensation effect has

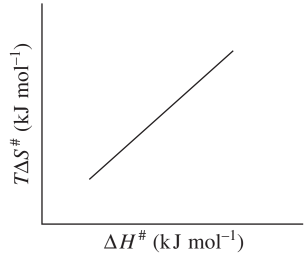


Fig. 8.5 The compensation effect, a plot between $T\Delta S^\#$ against $\Delta H^\#$.

also been observed between ΔH and $T\Delta S$ for overall process in solution. Therefore, the compensation effect between $\Delta H^{\#}$ and $T\Delta S^{\#}$ cannot be explained in terms of purely kinetic effect and it should be explained in terms of solvent-solute interactions. The application of more exact theories which involve the binding between solute-solvent molecules, that might change the freedom of vibration and rotation of solvent molecules etc. can explain the compensation between ΔH and $T\Delta S$.

EXERCISES

1. With the help of transition state theory, compare the rate constant for reaction

$$A + B \rightleftharpoons X^{\#}$$

in gaseous state and solution phase.

2. Describe an equation giving the effect of dielectric constant of the medium on rate constant and discuss the salient features of the equation.
3. Entropy decreases when reacting ions are of opposite sign, while it increases when reacting ions are of same sign. Explain?
4. What is primary salt effect? What will be the effect of ionic strength on the rate of reaction if

   (a) rate determining step involves similar charged species.
   (b) rate determining step involves oppositely charged species.

5. Predict the effect of: (a) increasing dielectric constant and (b) increasing ionic strength on the rates of following reactions:

   (i) $S_2O_8^{-2} + 2I^- \rightarrow 2SO_4^{2-} + I_2$
   (ii) $Br^- + (CH_3)C^+ \rightarrow (CH_3)_3CBr$
   (iii) $CH_3Br + 2H_2O \rightarrow CH_3OH + H_3O^+ + Br^-$
   (iv) $[CO(NH_3)_5Br]^{2+} + Hg^{z+} \rightarrow$ Products

6. Describe briefly the following:

   (a) Kinetic isotope effect
   (b) Hammet equation
   (c) Taft equation
   (d) Linear free energy reactions

7. The rate constant for the hydrolysis of a m-chloro substituted and p-methoxy substituted organic substance are 0.50 and 0.015 at 25 °C, respectively. The σ values of m-Cl and p-OMe are +0.37 and −0.27, respectively. Calculate the reaction constant ρ and rate constant for hydrolysis of unsubsituted substance and p-nitro ($\sigma = +0.75$) substituted substance.
8. Following observations were made on the effect of ionic strength μ on the rate constant k of the reaction A + B→ Product (rds):

$\mu \times 10^3$ (mol dm^{-3})	$10 \times k$ (mol^{-3} dm^3 m^{-1})
2.4	6.30
3.6	6.72
4.4	6.96
6.4	7.08
8.4	7.56

Find the value of $Z_A Z_B$. If charge on A is –1, what will be charge on B?

9

Reaction Dynamics

9.1 Molecular Reaction Dynamics

Reaction dynamics deals with the intra- and intermolecular motions that characterize the elementary act of a chemical reaction. It also deals with the quantum states of the reactants and product. Since the dynamic study is concerned with the microscopic level and dynamic behaviour of reacting molecules, therefore, the term molecular dynamics is employed.

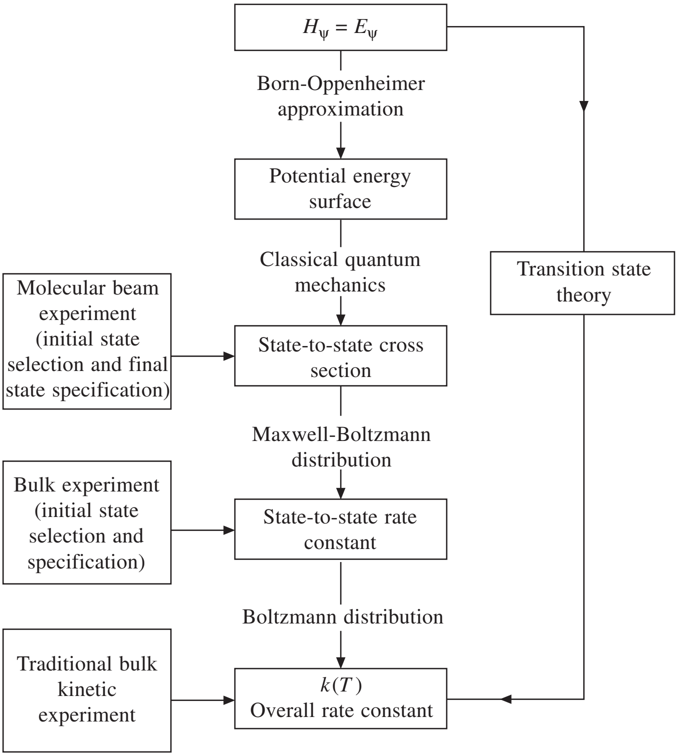
From a study of overall rate constant $k(T)$ for a reaction in the bulk and its dependence on concentrations of reactants, catalyst/inhibitor, temperature etc., the kinetics come up with a mechanism by putting together a lot of direct and indirect evidences. The determination of the overall rate constant $k(T)$ using transition state theory was a more sophisticated approach. But the macroscopic theories such as transition state theory in different versions are split to some extent in some cases, e.g. for very fast reactions. The experimental and theoretical studies in reaction dynamics have given the indications under which it becomes less satisfactory and further work in this direction may contribute much more to solve this problem.

It is now possible to design the experiments using molecular beams and laser techniques such that the initial vibrational, rotational, translational or electronic states of the reagent are selected or final states of products are specified. In contrast to the measurement of overall rate constants in a bulk kinetics experiment, state-to-state differential and integral cross sections can be measured for different initial states of reactants and final states of products in these sophisticated experiments. Molecular beam studies have become more common, lasers have been used to excite the reagent molecules and it has become possible to detect the product molecules by ŀaser-induced fluorescence'. These experimental studies have put forward a dramatic change in experimental study of chemical reactions at the molecular level and has culminated in what is now called *state-to-state chemistry*.

Another development in molecular reaction dynamics or state-to-state chemistry is the theory, which has developed the same way. With the help of electronic computers, it has been possible to study theoretically the molecular collisions underlying the abovementioned experiments and obtain a detailed understanding of the molecular interactions. Corresponding theoretical studies are leading to a better understanding of molecular dynamic behavior of reacting systems.

9.2 Microscopic-Macroscopic Relation

A connection between microscopic quantities such as state-to-state cross sections, state-to-state rate constant and macroscopic quantities such as overall rate constant $k(T)$ is summarized in Flow Chart 1.



Various states in computing overall rate constant $k(T)$, starting from the Schrödinger equation for the system

Flow Chart 1

A simplified approach is statistical rate theory (transition state theory) with the help of which the overall rate constant $k(T)$ may be obtained from potential energy surface (PES) in a single jump averaging out all of the intermediate details. It is generally not possible to extract microscopic details such as energy-dependent cross sections from conventional kinetics experiments. The preferable approach is to calculate microscopic quantities from some model and then perform the downward averaging for comparison with measured quantities.

A knowledge of interaction potential is essential for the study of molecular collision. Therefore, to obtain a potential energy surface (PES) is the first step for any calculation of cross sections and reaction probabilities. The adiabatic PES of reacting system is obtained by solving the time-independent Schrödinger equation within the Born-Oppenheimer approximation. The nuclear motion of PES is followed by using either classical or quantum mechanics. In classical mechanics, the classical equations of motion on PES are solved using Newtonian mechanics and a classical trajectory describing the motion of constituent atoms in space is obtained. A diagram or mathematical description that describes the motion of reaction system over a potential energy surface is known as a trajectory. These trajectories can then be analyzed to determine the likelihood of a reactive encounter, which transforms reactants into products. In quantum mechanics, the phenomenon at atomic level are recognized as intrinsically quantum-mechanical. The time dependent Schrödinger equation is solved using the PES as the potential function in the Hamiltonian operator and probability of product molecules appearing in the collision is determined. In either case, the objective is same, i.e. to establish connections between the microscopic properties and macroscopic phenomena which is also one of the basic goals of chemical kinetics and dynamics.

The state-to-state differential and integral cross sections, rate constant data and the effect of reagent vibration, rotation and translation thereupon, are becoming available for large number of reactive and nonreactive systems. With the current state of art in experimental techniques, e.g. using combinations of molecular-beam and laser techniques, the measurements of state-to-state rate coefficients and of angle- and velocity-dependent cross sections are possible. The measurements of reactive velocity, scattering angles and product and reactant states may all be simultaneously determined with the help of these experimental techniques.

The studies of molecular dynamics is now not only limited to the systems of atom and small molecules in dilute gas phase, the intense current interest is occurring in the condensed phase, i.e. in liquid solutions and in the solid state.

When the molecular collisions occur, we may expect the following elementary processes:

$$\mathrm{A + BC} \rightarrow \begin{cases} \mathrm{A + BC} & \text{Elastic scattering (no transfer of energy among different degrees of freedom)} \\ \left.\begin{array}{l}\mathrm{A + BC}(i) \\ \text{or} \\ \mathrm{A + BC}(j,v)\end{array}\right\} & \text{Inelastic scattering (there is transfer of energy among degrees of freedom but no chemical reaction)} \\ \left.\begin{array}{l}\mathrm{AB + C} \\ \text{or} \\ \mathrm{AC + B}\end{array}\right\} & \text{Reactive scattering (there is a chemical change)} \\ \mathrm{A + B + C} & \text{Collision induced dissociation} \end{cases}$$

9.3 Reaction Rate and Rate Constant

Let us consider a simple bimolecular collision

$$\mathrm{A}(i) + \mathrm{B}(j) \rightarrow \mathrm{C}(l) + \mathrm{D}(n)$$

where i, j, l and n are internal states (collectively electronic, vibrational and rotational states) of the reactants, (A, B) and products (C, D), respectively. Let reactants approach each other with velocity $\vec{v}_\mathrm{A}$ and $\vec{v}_\mathrm{B}$. Now a beam of A(i) with a relative velocity $v\ |\vec{v}_\mathrm{A} - \vec{v}_\mathrm{B}|$ is allowed to interact with molecule B(j) in scattering zone of volume V and the product C(l) is detected at a solid angle with respect to incoming A(i) as shown in Fig. 9.1.

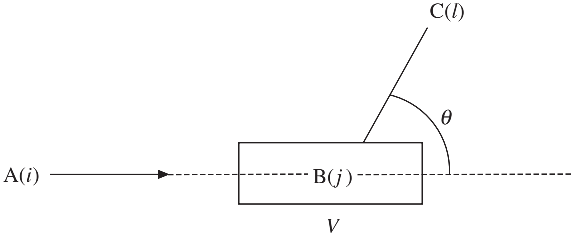


Fig. 9.1

Then rate of reaction may be defined as

$$\frac{dNC_{(l)}(\theta)}{dt}inj,v = \begin{pmatrix}\text{No. of molcules of A arriving at}\\ \text{the scattering zone per unit time}\\ \text{per unit area}\end{pmatrix}$$

$$\times\ (\text{No. of molcules of B in scattering zone of volume } V)$$

$$\times \begin{pmatrix}\text{Probability of reaction producing}\\ \text{product } C_{(l)} \text{ at an angle in the range}\\ \theta \text{ to } \theta + d\theta\text{, while } D(n) \text{ in produced}\\ \text{simultaneously}\end{pmatrix}$$

$$= \{\eta_{\mathrm{A}(i)}v\}\{\eta_{\mathrm{B}(j)}V\}\sigma(ln/ij, v, \theta)d\theta \tag{9.1}$$

where $\eta_\mathrm{A}(i)$ and $\eta_\mathrm{B}(j)$ are number of molecules per unit volume of A and B respectively. σ is a measure of reaction probability and called state-to-state differential cross section. When the measurements are averaged over all the angles, $\sigma(ln/ij, v, \theta)d\theta$ can be integrated over θ

$$\sigma(ln/ij, v) = \int \sigma(ln/ij, v, \theta)d\theta$$

$\sigma(ln/ij, v)$ is called state-to-state integral cross section with units of area. Equation (9.1), therefore, becomes

$$\frac{dN_{C(l)}}{dt}ijn,v = n_{\mathrm{A}(i)}v_{\mathrm{B}(j)}V\cdot\ \sigma(ln/ij, v) \tag{9.2}$$

When velocity is not selected, an average over the relative velocity yields

$$\frac{dN_{\mathrm{C}(l)}}{dt} ijn = f(v) n_{\mathrm{A}(i)} v n_{\mathrm{B}(j)} V \sigma (ln/ij; v) dv \tag{9.3}$$

where $f(v)$ is the fraction of molecular pairs having relative velocity in the range v and $v + dv$. At thermal equilibrium, $f(v)$ corresponds to Maxwell-Boltzmann distribution. Equation (9.3) can be rearranged as

$$\frac{1}{V} \frac{dN_{\mathrm{C}(l)}}{dt} ijn = \left(\int f(v) v \sigma (ln/ij; v) dv \right) n_{\mathrm{A}(i)} n_{\mathrm{B}(j)} \tag{9.4}$$

Equation (9.4) in terms of rate constant can be written as

$$k_{ij}^{ln}(T) = \left(\int f(v) v \sigma (ln/ij,\, v) dv \right) \tag{9.5}$$

where $k_{ij}^{ln}(T)$ is called state-to-state rate constant and equation (9.5) resembles with traditional rate equation.

In traditional bulk kinetic experiments, the internal states are also not selected and we measure the overall rate. The overall rate constant may be written as

$$\frac{1}{V} \frac{dNc}{dt} = \sum_{ijln} \frac{1}{V} \frac{dN_{\mathrm{C}(l)}}{dt} ijn = \sum_{ijln} k_{ij}^{ln}(T) n_{\mathrm{A}(i)} n_{\mathrm{B}(j)} = k(T) n_{\mathrm{A}} n_{\mathrm{B}} \tag{9.6}$$

and

$$k(T) = \sum_{ijln} k_{ij}^{ln}(T) X_{\mathrm{A}(i)} X_{\mathrm{B}(j)} \tag{9.7}$$

where $X_{\mathrm{A}(i)} = \dfrac{n_{\mathrm{A}(i)}}{n_{\mathrm{A}}}$ and $X_{\mathrm{B}(j)} = \dfrac{n_{\mathrm{B}(j)}}{n_{\mathrm{B}}}$.

At thermal equilibrium

$$X_{\mathrm{A}(i)} = g_i e^{-E_i/k_{\mathrm{B}}T} / Q_{\mathrm{A}}$$

where g_i is the degeneracy of i th internal state and Q_{A} is the partition function for A. Similar expression holds for B(j) also.

Thus, we see that overall rate constant that is determined from traditional bulk kinetics experiments for an elementary reaction is an average of microscopic observables, which are dependent on internal states of the reactants and products, the relative translational energy of reactants and the product scattering angle. Their relation may be summarised as follows:

$$\mathrm{A}(i) + \mathrm{B}(j) \rightarrow \mathrm{C}(l) + \mathrm{D}(n)$$

$$\begin{tikzcd}
\sigma(ln/ij,\, v\theta) \arrow[d, "\int d\theta"] & \text{State-to-state differential reaction cross section} \arrow[d] \\
\sigma(ln/ij,\, v) & \text{State-to-state integral cross section}
\end{tikzcd}$$

$$\begin{tikzcd} {} \arrow[d, "\int vf(v)d\theta"] & {} \arrow[d] \\ k_{ij}^{ln}(T) \arrow[d, "\sum_{ijln}"] & \text{State-to-state rate constant} \arrow[d] \\ k(T) & \text{Overall rate constant} \end{tikzcd}$$

9.4 Distribution of Velocities of Molecules

Under ordinary conditions, the molecules of a gas have speed which are not uniform but distributed over a range. In general, the distribution of velocities of molecules A and B, by Maxwell law is given as

$$f(v_i)dv_i = \left(\frac{2}{\pi}\right)^{1/2}\left(\frac{m_i}{k_B T}\right)^{3/2} v_i^2 e^{-\frac{m_i v_i^2}{2k_B T}} dv_i \tag{9.8}$$

where $f(v_i)dv_i$ at given temperature T is the fraction of the molecules of type i which have velocity in the range v_i to $v_i + dv_i$, m_i is the mass of molecule and k_B the Boltzmann constant.

When we consider the collision between the molecules, each pair of colliding molecules may be described either by the positions (r_A, r_B) and velocities (v_A, v_B) of the two particles or by the position r_G and velocity v_G of centre of mass of two particles together with the position r and velocity v of the particles relative to the other.

The fraction of the number of A, B pairs whose relative speed is in the range $v + dv$ is given by

$$f(v)dv = 4\pi\left(\frac{\mu}{2\pi k_B T}\right)^{3/2} e^{-\frac{\mu v^2}{2k_B T}} v^2 dv \tag{9.9}$$

where μ is the reduced mass, i.e. $\mu = \frac{m_A m_B}{m_A + m_B}$. Now $f(v)dv$ represents fraction of pair of particles A and B rather than of individual particle.

9.5 Rate of Reaction for Collisions with a Distribution of Relative Speeds

If we consider only the chemical identity and kinemetic velocity of each species without considering the internal states, the overall rate constant from equation (9.5) may be written as

$$k(T) = \int f(v)v\sigma(v)dv \tag{9.10}$$

Using the Maxwell-Boltzmann distribution, i.e. equation (9.9), we get

$$k(T) = \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \int_0^\infty v\sigma(v)e^{-\frac{\mu v^2}{2k_B T}} 4\pi v^2 dv \tag{9.11}$$

Again, we can replace the velocity v, by the relative kinetic energy using the relation $E = \frac{1}{2}\mu v^2$. Substituting the relation in equation (9.11), we get

$$k(T) = \frac{1}{k_B T}\left(\frac{8}{\pi\mu k_B T}\right)^{1/2}\int_0^D E\sigma(E)e^{-\frac{E}{k_B T}}dE \qquad (9.12)$$

9.6 Collision Cross Sections

A cross section for any specific event, such as a chemical reaction, is a proportionality factor which measures the likelihood of the event when reactants approach in a specified way.

9.6.1 Cross Section for Hard Sphere Model

Let us consider b as the impact parameter, i.e. distance between the centre mass of B and relative velocity vector as shown in Fig. 9.2. The contribution of impact parameter from b to $b + db$ to the collision cross section is

$$d\sigma(v) = 2\pi bP(b)db$$

The total collision cross section, therefore, is

$$\sigma(v) = \int_0^{b_{\max}} 2\pi bP(b)db \quad (9.13)$$

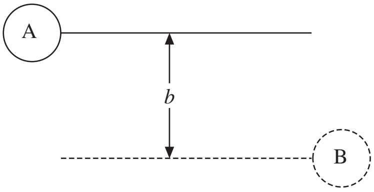


Fig. 9.2

where $b_{\max}$ corresponds to θ (scattering angle) = 0, ($b_{\min}$) to $\theta = \pi$ and $b_{\min} = 0$ (because hard spheres on collision produce a 180° deflection).

In hard sphere model, $b_{\max}$ is equal to collision diameter d and is the sum of the radii of A and B, i.e. $b_{\max} = r_A + r_B$.

The collision cross section σ becomes equal to $\pi(r_A + r_B)^2$ if every collision (defined by physical contact of the spheres A and B) leads to reaction, that is

$$P(b) = 1,\ 0 \le b \le b_{\max}$$

$$P(b) = 0,\ b > b_{\max}$$

Now, for hard sphere model the rate constant is given by

$$k = \sigma\int f(v)v\,dv = \pi(r_A + r_B)^2\left\{\frac{8k_B T}{\pi\mu}\right\}^{1/2} = \left\{\frac{8\pi k_B T}{\mu}\right\}^{1/2} d^2 \qquad (9.14)$$

where k_B is Boltzmann's constant and μ is reduced mass of A and B, i.e. $\mu = \frac{m_A m_B}{m_A + m_B}$. Thus, the rate constant is equal to the collision frequency for two hard spheres A and B. The energy dependence of cross section for hard sphere model is shown in Fig. 9.3.

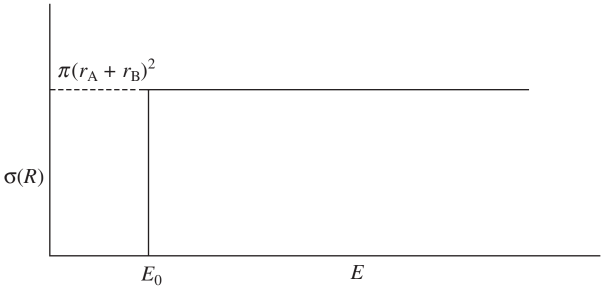


Fig. 9.3

9.6.2 Collision between Reactive Hard Spheres

Let us consider a collision between hard sphere molecules A and B with relative velocity v and kinetic energy $E\left(=\frac{1}{2}\mu v^2\right)$ in centre of mass coordinate system. The minimum approach distance between two hard spheres $d = \frac{r_A + r_B}{2}$. The impact parameter b is given by the perpendicular distance between parallel lines drawn in the direction of v through the centers of molecules A and B.

The relative velocity v can be resolved into v_1 and v_2, i.e. along the lines of centers and its perpendicular as shown in Fig. 9.4. The kinetic energy E may be given as

$$E = \frac{1}{2}\mu v_1^2 + \frac{1}{2}\mu v_2^2 \tag{9.15}$$

where $\frac{1}{2}\mu v_1^2$ represents energy which is tangential to the surfaces of the interacting spheres and $\frac{1}{2}\mu v_2^2$, denoted by E_c, represents the energy directed along the lines of centers E_c and effective in bringing out the reaction.

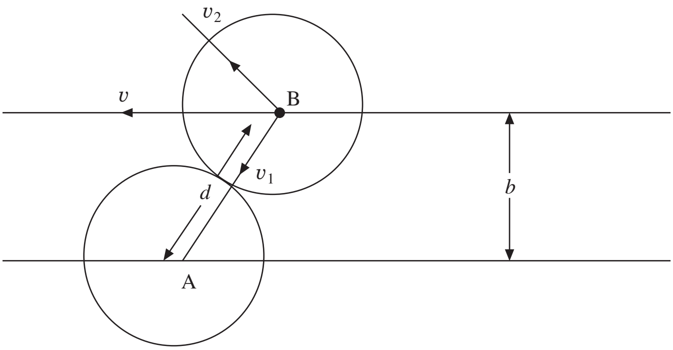


Fig. 9.4

The energy along the line of center may be given as

$$\frac{E_c}{E} = 1 - \frac{b^2}{(r_A + r_B)^2} \text{ when } b \leq (r_A + r_B) \text{ or } E_c = E\left[1 - \frac{b^2}{(r_A + r_B)^2}\right]$$

and $\frac{E_c}{E} = 0$ when $b > (r_A + r_B)$.

The energy dependent reaction probability

$$P(E_c) = 0 \qquad \text{when } E_c < E^*$$

$$P(E_c) = 1 \qquad \text{when } E_c \geq E^*$$

where E^* is minimum energy threshold for the reaction to occur.

The reaction cross section is given as

$$\sigma(E) = \int_0^\infty P(E) 2\pi b db$$

Therefore, the expression for reaction cross section is obtained as

$$\sigma(E) = \int_0^\infty P(E,b) 2\pi b\, db = \left\{\begin{array}{l} 0 \quad \text{when } E < E^* \\ \left\{\pi(r_A + r_B)^2 \left\{1 - \frac{E^*}{E_c}\right\}\right\} \end{array}\right. \tag{9.16}$$

The energy dependence of cross section for reactive hard sphere model is shown in Fig. 9.5.

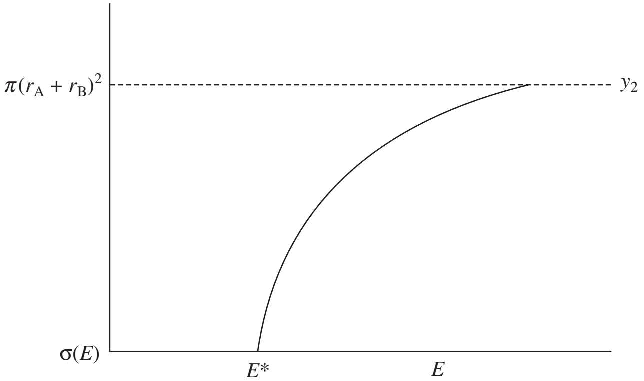


Fig. 9.5 Energy dependence of reactive cross section for reactive hard sphere model.

Now the thermal rate coefficient is given by

$$k(T) = \frac{1}{k_B T}\left(\frac{8}{\pi\mu k_B T}\right)^{1/2} \int_0^\infty E\sigma(E) e^{-\frac{E}{k_B T}} dE \tag{9.17}$$

Using equation (9.16), equation (9.17) can be written as

$$k(T) = \frac{1}{k_B T}\left(\frac{8}{\pi\mu k_B T}\right)^{1/2}\int_0^\infty \pi(r_A + r_B)^2 (E - E^*)e^{-\frac{E}{k_B T}} dE$$

$$= \pi(r_A + r_B)^2\left(\frac{8k_B T}{\pi\mu}\right)^{1/2} e^{-\frac{E^*}{k_B T}} \qquad (9.18)$$

Thus, $k(T)$ involving these factors, becomes

$$\underset{\text{(Hard sphere cross section)}}{k(T) = \{\pi(r_A + r_B)^2\}} \times \underset{\text{(Mean velocity)}}{\left\{\frac{8k_B T}{\pi\mu}\right\}^{1/2}} \times \underset{\text{(Arrhenius factor)}}{e^{-\frac{E^*}{k_B T}}} \qquad (9.19)$$

9.7 Activation Energy

Considering the Arrhenius equation

$$k = Ae^{-E_{act}/RT}$$

or

$$\ln(k) = \ln A - \frac{E_{act}}{RT} \qquad (9.20)$$

The activation energy E_{act} is determined by plotting ln (k) versus $1/T$ and computing the slope of the resultant straight line. Conventionally, the E_{act} has been considered equal to classical barrier height E_c or adiabatic transition state barrier height E_0 or reaction threshold energy E_0 shown in Fig. 9.6. However, there are instances where a plot of ln k versus $1/T$ is not a simple straight line. A negative energy of activation is also reported in some cases. In such cases the conventional interpretation of E_{act} loses its meaning.

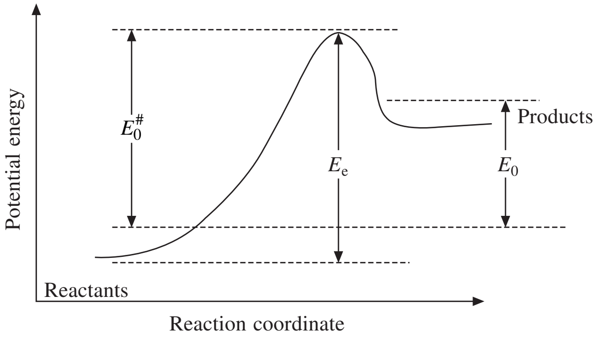


Fig. 9.6 Energy reaction coordinate diagram.

The unambiguous way to define E_{act} is to rewrite the Arrhenius equation as

$$E_{act} = RT^2 \frac{d(\ln k)}{dT} \qquad (9.21)$$

A generalized relationship between the activation energy and the energy of colliding systems can be obtained from the derivative of ln k with respect to T.

Again, we have

$$k(T) = \sum_{ijln} k_{ij}^{ln}(T) X_{\mathrm{A(i)}} X_{\mathrm{B}(j)} \tag{9.22}$$

where

$$X_{\mathrm{A}(i)} = g_i e^{-E_i/k_{\mathrm{B}}T}/\mathrm{QA}$$

$$X_{\mathrm{B}(i)} = g_i e^{-E_i/k_{\mathrm{B}}T}/\mathrm{QB}$$

and

$$k_{ij}^{ln}(T) = \int f(v)\sigma(ln/ij; v)dv$$

Therefore,

$$\frac{d(\ln k)}{dT} = \frac{d}{dT}\left[\ln \sum \frac{g_i g_j}{\mathrm{Q_A Q_B}} e^{-E_{ij}/k_{\mathrm{B}}T}\right]\int f(v)v\sigma(ln/ij; v)dv \tag{9.23}$$

On solving the above equations, we get

$$\frac{d(\ln k)}{dT} = \frac{\{(\langle E_{\mathrm{tran}} + E_{\mathrm{int}}\rangle)_{\text{reactive collision}} - (\langle E_{\mathrm{tran}} + E_{\mathrm{int}}\rangle_{\text{all collision}}\}}{k_{\mathrm{B}}T^2} \tag{9.24}$$

where E_{trans} and E_{int} refer to the relative translational and internal energies of (A, B) pair and $\langle\ \rangle$ shows the appropriate averages. Such an interpretation allows for variation of E_{act} with temperature and therefore a plot of ln k versus $1/T$ shows a curvature.

For the hard sphere model, when energy collision leads to reaction, the rate constant is given by

$$k = \pi d^2 \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{1/2} \tag{9.25}$$

Therefore, $E_{\mathrm{act}} = \frac{1}{2}RT$, which shows that even when threshold energy E_0 is zero, the E_{act} has a non-zero value. In case of line of center model, a collision is reactive only if the component of the relative translational energy along the line joining the centre of mass of the two molecules exceeds E_0. In case of line of centers of model, the rate constant is given by

$$k = \pi d^2 \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{1/2} e^{-E_0/k_{\mathrm{B}}T} \tag{9.26}$$

Hence,

$$E_{\mathrm{act}} = E_0 + \frac{1}{2}k_{\mathrm{B}}T \tag{9.27}$$

In general, the activation energy for a given elementary reaction is different from the threshold energy. Experimentally it has also been verified in some reactions, e.g. E_0 and E_{act} for the reaction $NO + O_3 \rightarrow NO_2 + O_2$ have been obtained as 3.0 ± 0.45 kcals mol^{-1} and 4.2 ± 0.3 kcals mol^{-1}, respectively.

Molecular beam experiments and also computed dynamical theories for some reactions have shown that cross section σ varies with E_{trans} as shown in Fig. 9.7.

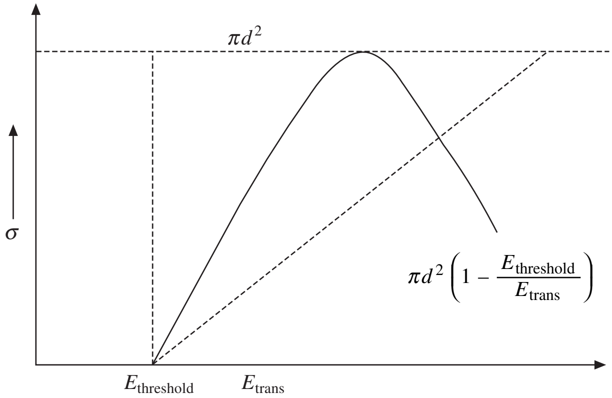


Fig. 9.7 Variation of σ with E_{trans} for a bimolecular exchange.

The variation of σ with E_{trans} is known as excitation function. It is zero for $E_{trans} < E_{threshold}$, then rises to a maximum and then decreases. At room temperature (Fig. 9.8) it is the rising portion of the excitation function that is sampled and, therefore, $\langle E_{trans} \rangle_{reactive}$ is greater than $\langle E_{trans} \rangle_{all\ collision}$ and thus the positive E_{act} is obtained. At very high temperature it is possible that high energy tail of the Maxwell Boltzmann distribution contributes less resulting in the less average energy for reactive collisions than the overall average energy. Under such conditions, a simple bimolecular exchange reaction will have a negative activation energy.

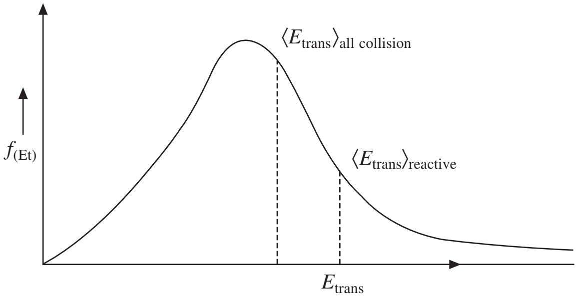


Fig. 9.8 The positive E_{act} energy.

It is also clear that E_{act} can be a function of temperature and can be different for different initial states of the reactants.

9.8 Potential Energy Surface

A dynamical study of molecular collisions requires construction of the Hamiltonian $H = T + V$, where T and V are kinetic energy (KE) and potential energy (PE), respectively. A knowledge of the interaction potential, therefore, is essential for the study of molecular dynamics.

The potential energy of a diatomic molecule depends on only the distance between two bonded atoms. The potential energy of a diatomic molecule can be plotted in two dimensions by plotting PE as a function of the bond length. The curve is known as *potential energy curve* (Fig. 9.9).

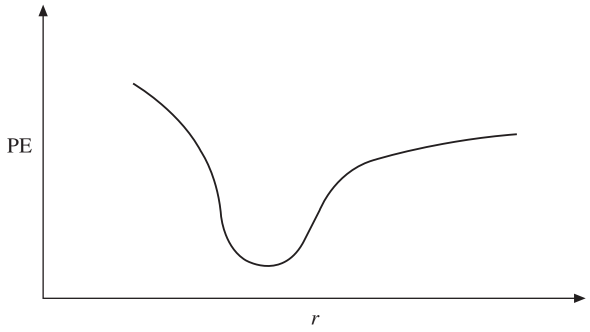


Fig. 9.9 Potential energy curve for a diatomic molecule.

When potential energy depends on more than one geometric parameter, i.e. internuclear distances, the word surface is used in place of curve, and the plot is known as *potential energy surface* (PES).

For a nonlinear molecule consisting of N atoms, the potential energy surface depends on $3N - 6$ independent coordinates and depicts how the PE changes as relative coordinates of the atomic nuclei involved in the chemical reaction are varied. For example, consider the water molecule (Fig. 9.10).

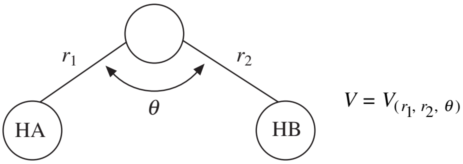


Fig. 9.10

The potential energy of water molecule is a function of three parameters, i.e. r_1, r_2 and angle θ. A plot of the complete potential energy surface of a water molecule, therefore, will be four dimensional. Since we are limited to three dimensions for plotting functions, we cannot draw the entire potential energy surface of a water molecule in a single plot. However, we can draw parts of PES. Let if one geometric parameter, say θ, has been fixed, then potential energy will be a function of r_1 and r_2 at constant θ, and the plot will be a three dimensional. Such a plot is a cross sectional cut of the full potential surface. A cross sectional plot shows how the PE of molecule changes on variation of the some geometric variables while holding the other constant.

Potential energy surface for a chemical reaction can be obtained using electronic structure techniques or by solving Schrödinger equation within Born-Oppenheimer approximation. For each geometry, there is a PE value of the system.

Let us take a simple exchange reaction

$$\underset{\text{(Atom)}}{\text{A}} + \underset{\substack{\text{(Diatomic}\\\text{molecule)}}}{\text{BC}} \rightarrow \underset{\substack{\text{(Diatomic}\\\text{molecule)}}}{\text{AB}} + \underset{\text{(Atom)}}{\text{C}}$$

There are three internuclear distances r_{AB}, r_{BC} and r_{AC} and a plot of the PE as a function of three independent variables requires four dimensional space. Therefore, we can consider that three atoms lie along a straight line. A plot of PE as a function or r_{AB} and r_{BC} results in a PES as shown in Fig. 9.11.

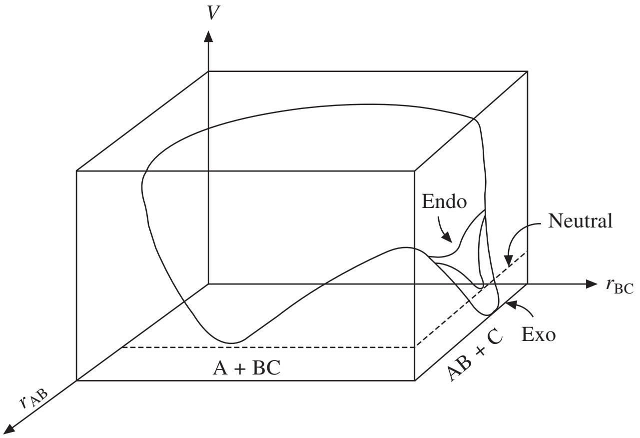


Fig. 9.11 PES for a collinear system A + BC → AB + C.

As $r_{AB} \rightarrow \infty$, A is separated from BC and $V = V_{BC}$. As $r_{BC} \rightarrow \infty$, C is separated from AB and $V = V_{BC}$. As the reaction proceeds, the potential energy changes from BC to AB. As the reactants approach each other, there is some repulsion leading to a maximum barrier when the three atoms are simultaneously closed to each other. Subsequently, there is a drop in the potential leading to the separation of the products. The maximum point is called the *saddle point*.

For an easier understanding, we can plot the PE contours in r_{AB} and r_{BC}

space as shown in Fig. 9.12. The distance r_{BC} (as $r_{AB} \to \infty$) is minimum along r_{BC} and similarly r_{AB} is the minimum along r_{AB} (as $r_{BC} \to \infty$). If we follow from one minimum various stages along the reaction, and mark all the minimum, we obtain the minimum energy path. The dashed line in Fig. 9.12 represents the minimum energy path. When we plot the PE values along the minimum energy path (MEP) against the distance along the MEP, we obtain the plot shown in Fig. 9.13. This is called the *potential energy profile*.

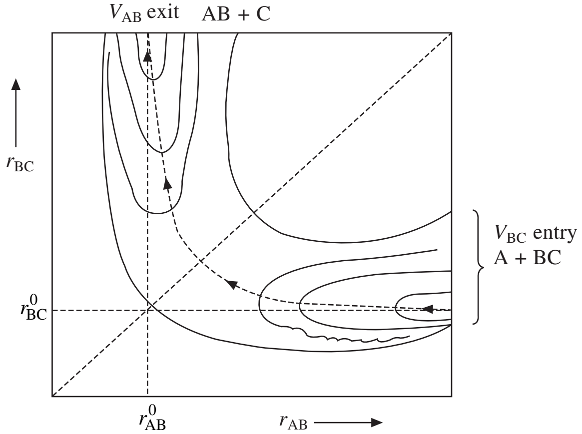


Fig. 9.12 PE contours for A + BC → AB + C reaction.

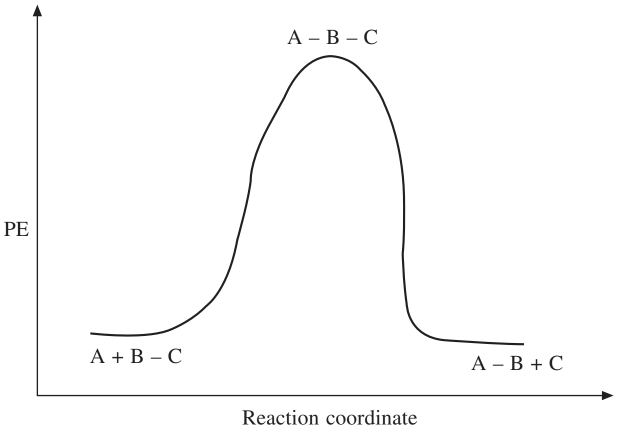


Fig. 9.13 PE profile.

The top of the profile is maximum (saddle point) and is referred as the transition state in the conventional transition state theory. It is called a saddle point because it is maximum along the orthogonal direction (MEP) while it is minimum along diagonal direction of Fig. 9.12. The minimum energy path can be located by starting at the saddle point and mapping out the path of the deepest descent towards the reactants and products. This is called the *reaction path* or *intrinsic reaction coordinate*.

Other type of potential energy surface has a potential energy well (minimum). Fig. 9.14 shows the contour map for this type of potential energy surface. The corresponding potential energy profile is given in Fig. 9.15. Some special reactions may have both, minimum and potential energy barrier, i.e. saddle point.

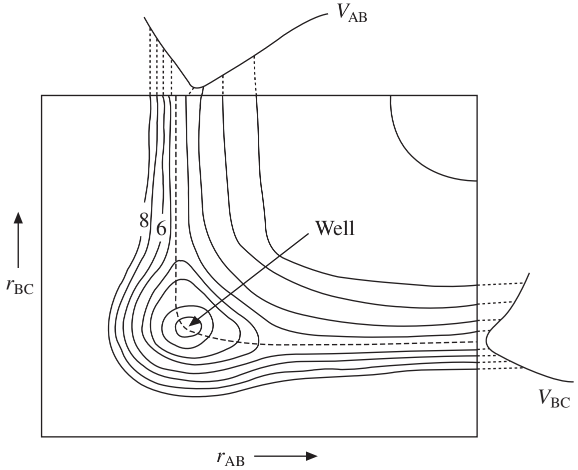


Fig. 9.14 PE contours for a reaction having PE well.

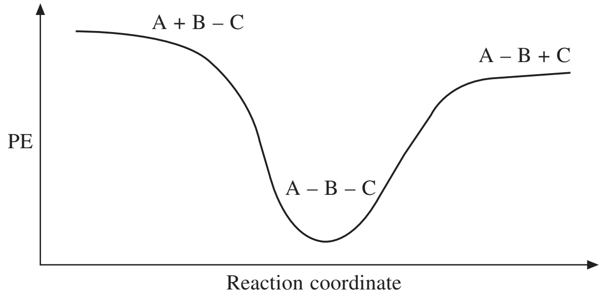


Fig. 9.15 Potential energy profile for PES shown in Fig. 14.

9.8.1 Features of Potential Energy Surface

The potential energy profile and also the location of saddle point appears different for exo- and endothermic reactions. In general, the saddle point is located in the entry channel for an exothermic reaction as shown in Fig. 9.16. For example, reaction F + $H_2 \rightarrow$ FH + H. The shift in location of the saddle point from symmetric position has also been related to the magnitude of the exo (endo) thermicity.

In an exothermic reaction there are two possibilities of releasing the energy. In one, the energy is released as the reagents approach and in other, it is released as the products separate. In the former case, the potential energy

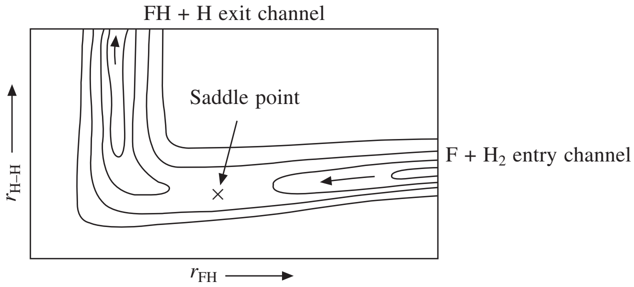


Fig. 9.16 PE contours for an exothermic reaction.

surface is called *attractive* or *early down hill surface* while in latter it is called *repulsive* or *late-down hill surface*. The potential energy profiles for an attractive and repulsive surface of an exothermic reaction are shown in Fig. 9.17.

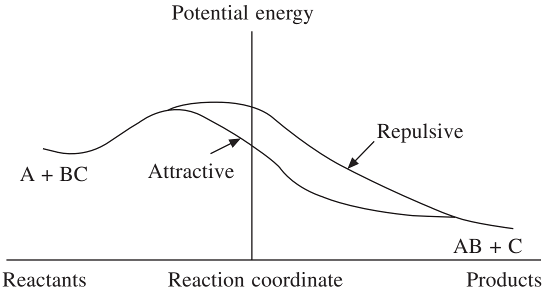


Fig. 9.17 PE profiles for attractive and repulsive surfaces of an exothermic reaction.

In attractive PES, the barrier occurs in the early state of the reaction path, i.e. activated state is reached before there is much extension of BC bond. After the activated state is reached, the system proceeds down the exit valley, with the liberation of energy. In repulsive or late-down hill surface, the energy is released when there is increasing separation of the products. Thus, in attractive surface the energy is released as the reagent approaches while in repulsive surface the energy is released as the product separates. It can also be seen that a considerable amount of released energy passes into vibration energy of the product, i.e. AB–in case of attractive surface. In repulsive surface, most of the energy released goes into translational energy of the products (Fig. 9.18). However, dynamical calculations have shown that for some mass combinations a substantial amount of energy may also go into product vibration.

Similarly, for an endothermic reaction, in which saddle point lies in exit channel, we can envisage two different PES known as *sudden surface* and *gradual surface* shown in Fig. 9.19. On the sudden surface, the rise in potential is sudden while on the gradual surface, it is gradual. The corresponding

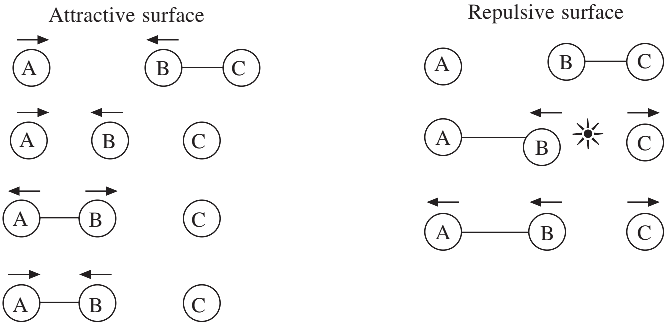


Fig. 9.18 Release of energy in exothermic reaction.

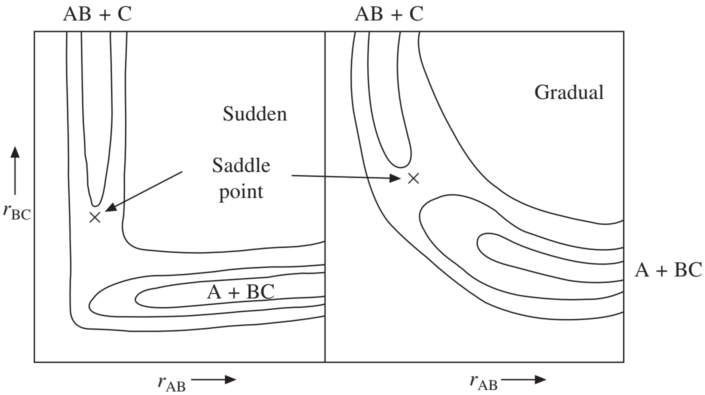


Fig. 9.19 PE contours for sudden and gradual surfaces.

potential energy profile for these surfaces is shown in Fig. 9.20. These surfaces would be complementary to the attractive and repulsive surfaces in the exothermic reaction.

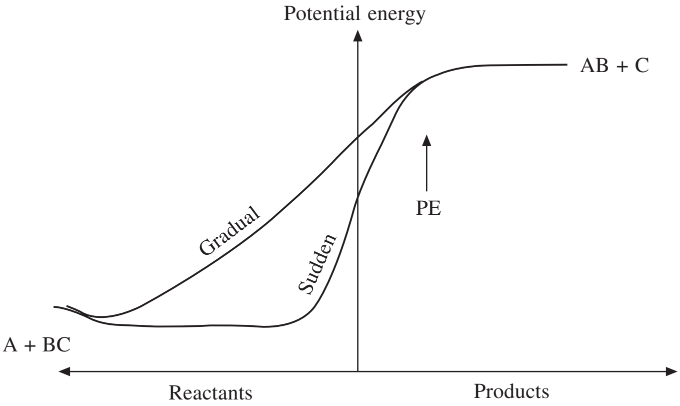


Fig. 9.20 PE profiles for gradual and sudden surfaces.

9.8.2 *Ab initio* Calculation of Potential Energy Surface

Taking the Born-Oppenheimer approximation into consideration, the molecular wave function may be written as

$$\psi = \psi_e(r, R)\, \psi_n(r, R) \tag{9.28}$$

where ψ_e is the electronic wave function that depends on electron coordinate r and nuclear coordinate R and ψ_n is the nuclear wave function. The electronic Schrödinger equation for the molecule is written as

$$(T + V_R + V_A)\psi_e = E_e(R)\psi \tag{9.29}$$

where T is the electron kinetic energy, V_R the electron-electron repulsion energy, V_A electron-nuclear attraction energy. The solution of above equation at a particular nuclear configuration R gives the electronic energy E_e for configuration. The sum of E_e and nuclear-nuclear repulsion energy V_R, i.e. $E_e + V_R$, is the total energy in which the nuclei move with kinetic energy T. Thus, at different nuclear configurations, the total energy can be determined and complete potential energy surface may be obtained.

(a) London-Heitler Method

London (1928) was first to apply this idea to a chemical reaction. London and Heitler developed a simple quantum mechanical treatment of hydrogen molecule, according to which, the allowed energies for H_2 molecules are the sum and differences of two integrals as

$$E = A \pm \alpha \tag{9.30}$$

where integral A is coulombic energy and integral α represents the exchange energy. The coulombic energy is roughly equivalent to the classical energy of the system. The exchange energy appears in quantum mechanics and represents the energy due to exchange of electrons. A and α are negative at ordinary internuclear distances and E represent the energy relative to separated atoms. The lowest energy of most stable state is, therefore, obtained when the positive sign is taken. For a triatomic system (X-Y-Z), which might be involved in a simple displacement reaction, viz.

$$X + YZ \rightarrow XY + Z$$

The energy E is obtained as

$$E = A + B + C - \left[\frac{1}{2}\left\{(\alpha-\beta)^2 + (\beta-\gamma)^2 + (\gamma-\alpha)^2\right\}\right]^{1/2} \tag{9.31}$$

where A, B and C are coulombic energies and α, β and γ are èxchange' energies as shown in Fig. 9.21.

Equation (9.31) is known as London equation and has been used by Eyring and Polanyi (1931) in their semiempirical calculation of a PES for H-H-H system and then used by many workers for a variety of reactions. The

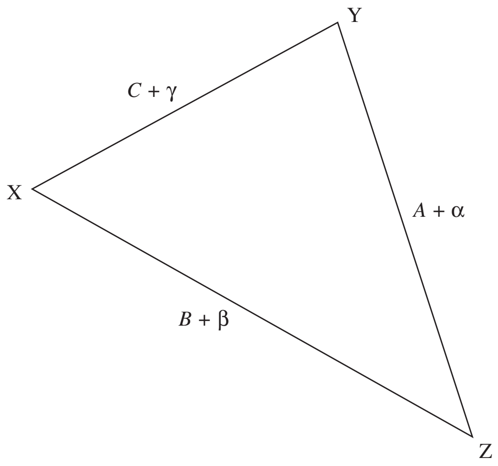


Fig. 9.21 A triatomic complex XYZ. Energy of diatomic molecule YZ with X is involved in $A + \alpha$, where A is coulombic energy and α the exchange energy. The energy of other diatomic molecules may be represented accordingly.

semiempirical treatments, although based on quantum mechanical theory, make use of experimental results and adjustments have been made to obtain more satisfactory results.

(b) London-Eyring-Polanyi (LEP) Method

On the basis of London equation (9.31), Eyring and Polanyi calculated the potential energy surface, which is known as London-Eyring-Polanyi (LEP) surface. In this treatment, the coulombic energy A and exchange energy α for a diatomic molecule have been assumed to be the constant fractions of the total energy E for all internuclear distances. The Morse equation (9.32) used in relating the potential energy to the inter-nuclear distance r is

$$E = D[e^{-2\beta(r-r_0)} - 2e^{-\beta(r-r_0)}] \tag{9.32}$$

where r_0 is the equilibrium internuclear distance, D the classical dissociation energy and β a constant.

The total energy E, thus, can be obtained readily as a function of internuclear distance r from analysis of spectroscopic data and Morse equation. Eyring and Polanyi concluded that the fraction $P\left(\text{where } P = \dfrac{A}{A+\alpha}\right)$ is roughly constant at 10-15% over a range of interatomic distance. Therefore, for any triatomic configuration it is possible to evaluate the coulombic and exchange energies for each pair of atoms on the basis of spectroscopic value of total energy. Thus, the values of A, B, C, α, β and γ can be determined and putting these values in London equation, the required energy of triatomic species may be evaluated.

(c) London-Eyring-Polanyi-Sato Method

Some unsatisfactory feature, viz. potential energy basins appeared when the assumption of constant coulombic and exchange fractions, was made by Erying and Polanyi. Sato proposed an alternative method by considering ρ (fraction constant) as a function of internuclear distance *r*. He also modified the Morse equation by changing the sign between two exponential terms from minus to plus and dividing the expression by two and used the following relations:

$$E_R = A - \alpha \tag{9.33}$$

where E_R is energy for repulsive state of diatomic molecule BC and modified Morse equation

$$E_R = \frac{D}{2}[e^{-2\beta(r-r_0)} + 2e^{-\beta(r-r_0)}] \tag{9.34}$$

Thus, the energy value obtained by equation (9.34) can be set equal to $A - \alpha$. In ground state the energy obtained by equation (9.34) is equal to $A + \alpha$. Therefore, the values of *A* and α can be evaluated for various internuclear separations without assuming a constant ratio ρ. For the triatomic system A-B-C, Sato used the following equation:

$$E = \frac{1}{1+S^2}\left(\mathrm{A+B+C} \pm \left\{\frac{1}{2}[(\alpha-\beta)^2 + (\beta-\gamma)^2 + (\gamma-\alpha)^2]\right\}^{1/2}\right) \tag{9.35}$$

where *S* is an overlap integral.

For different systems, various values of *S* have been used by Sato. The Sato method leads to surfaces free from basins and preferable to LEP method.

(d) Bond-Energy-Bond-Order (BEBO) Method

Johnson and Parr proposed a bond-energy-bond-order approach for determining the PES for hydrogen transfer reactions. The method is based on the assumptions that: (a) the amount of chemical bonding, as reflected in the individual bond orders n_b and n_f (where n_b and n_f are the order of the bonds being broken and formed), is a constant, e.g. $n_b + n_f = 1$ along the reaction coordinates, (b) the total interaction potential can be expressed as a sum of three diatomic potential and (c) empirical relations like Pauling's rule and Badger's rule can be used to calculate bond energies etc. from structural and spectral data.

One such relation given by Pauling is

$$R = R_0 - 0.26 \ln n \tag{9.36}$$

where R_0 is single bond length for a bond connecting two particular atoms. Bond *D* can be related to single bond energy D_0 as

$$D = S_0 n^{\rho} \tag{9.37}$$

where ρ is a constant and is known as bond index.

9.8.3 Fitting of *ab initio* Potential Energy Surfaces

A dynamical study of molecular collision requires a detailed knowledge of the interaction potential as an input. *Ab initio* potential energy (PE) values for a chemical reaction for different geometries are usually reported in the form of table of numbers resulting from sophisticated electronic structure calculations. However, for use in dynamical calculations, the PES must be known in some convenient analytical or numerically interpolated form, which is capable of generating potential and its derivatives accurately and efficiently at any arbitrary geometry.

The various analytic functions and numerical interpolations depending on number of independent variables have been used for fitting the potential energy surfaces.

In earlier years, the simple empirical functions with a minimum number of parameters were used to represent PE curves. Some of the simple functions are follows.

(a) Lennard-Jones Function

In this function

$$V = 4D\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{9.38}$$

where D is the well depth and σ the value of r at which potential energy V becomes zero. However, in this function there are not enough parameters to adequately reproduce an exact potential. Also there is not much flexibility in the function form except to treat power (12 and 6) as variable parameter done by Varshni as

$$v = D\left[\left(\frac{r_e}{r}\right)^{2m} - 2\left(\frac{r_e}{r}\right)^{m}\right] \tag{9.39}$$

(b) Buckingham Function

In Buckingham function

$$V = Ae^{-\alpha r} - Br^{-n} \tag{9.40}$$

where commonly $n = 6$.

At short range, a plot of ln V versus r will be a straight line with a slope (equal to α) and an intercept (equal to A) and thus the value of A and α for Buckingham potential can be determined. The point where the potential V becomes zero would fix the value of B (when $n = 6$ or any other fixed value). The function can be made more flexible by modifying as

$$V = Ae^{-\alpha r} - Br^{-6} - Cr^{-8} - Dr^{-10} \tag{9.41}$$

The different r^{-n} terms in the modified function are not linearly independent and, therefore, inclusion of additional terms does not guarantee the improvement in the fit. Buckingham function also suffers from the fact that as $r \to 0$,

$V \to -\infty$. This is clearly unphysical except in the united atom limit. However, generally it does not affect the result of interest to the chemists.

(c) Morse Function

In this function, we have

$$V = D[e^{-2\beta(r-r_e)} - 2e^{-\beta(r-r_e)}] \tag{9.42}$$

The three parameters in the Morse function D, B, r_e are positive and are usually chosen to fit the bond dissociation energy, the harmonic vibrational frequency and the equilibrium bond length. At $r = r_e$, the Morse function $V = 0$. As $r \to D$, V approaches D. For $r << r_e$, V is large and positive, corresponding to short range repulsion. Although the Morse function has been used extensively, its representation of the potential away from r_e is not satisfactory. Several modifications have been proposed in Morse function.

(d) Extended Rydberg (ER) Function

Murrell and Sorbie have proposed an extended Rydberg function as

$$V = -D[1 + \alpha_1\rho + \alpha_2\rho^2 + \ldots]e^{-(\alpha_1\rho)} \tag{9.43}$$

where $\rho = r - r_e$.

It is better than Morse function, because multiplying the exponential term, bypolynomial convergence can be checked by adding more terms by polynomial. This function can be linearised. A plot of ln V versus r will give the value of D and α_1.

Various other PE functions have been proposed. However, they are more complicated and require large amount of *ab intio* data. Most of the functions are not easily extendable to higher dimensions.

9.8.4 Potential Energy Surfaces for Triatomic Systems

Although *ab initio* PESs are available for a few exchange reactions of type A + BC → AB + C, surfaces at different levels of accuracy have been reported for a variety of systems. Some of the functional forms are discussed as follows.

(a) London-Eyring-Polanyi-Sato (LEPS)

The PE function was proposed by London for $H + H_2 \to H_2 + H$, collinear system and subsequently was modified by Eyring, Polanyi and Sato. One widely used form of the LEPS function is given by

$$(Vr_{AB}, r_{AC}, r_{BC}) = \frac{Q_{AB}}{1 + S_{AB}} + \frac{Q_{BC}}{1 + S_{BC}} + \frac{Q_{AC}}{1 + S_{AC}}$$

$$-\left\{ \frac{1}{2}\left[\left(\frac{J_{AB}}{1 + S_{AB}} - \frac{J_{BC}}{1 + S_{AB}}\right)^2 + \left(\frac{J_{BC}}{1 + S_{BC}} - \frac{J_{AC}}{1 + S_{AC}}\right)^2\right.\right.$$

$$+\left(\frac{J_{\mathrm{AC}}}{1+S_{\mathrm{AC}}}-\frac{J_{\mathrm{AB}}}{1+S_{\mathrm{AB}}}\right)^2\Bigg]\Bigg\}^{1/2} \tag{9.44}$$

where Q, J and S are referred to as coulomb, exchange and overlap integrals, Q and J are determined from Morse and anti-Morse function, respectively, as follows:

$$Q_{\mathrm{i}} + J_{\mathrm{i}} = D_{\mathrm{i}}\{e^{-2\beta_{\mathrm{i}}(r_{\mathrm{i}}-r_{\mathrm{i}}^{e})} - 2e^{-\beta_{\mathrm{i}}(r_{\mathrm{i}}-r_{\mathrm{i}}^{e})}\} \tag{9.45a}$$

$$Q_{\mathrm{i}} - J_{\mathrm{i}} = \frac{1}{2}D_{\mathrm{i}}\{e^{-2\beta_{\mathrm{i}}(r_{\mathrm{i}}-r_{\mathrm{i}}^{e})} + 2e^{-\beta i(r_{\mathrm{i}}-r_{\mathrm{i}}^{e})}\} \tag{9.45b}$$

The original LEPS forms of Sato has $S_{\mathrm{AB}} = S_{\mathrm{BC}} = S_{\mathrm{AC}}$. In this extended form these S parameters are allowed to differ to give more flexibility in the function. It was also observed that changing the sign between two exponential terms of the Morse potential equation (9.45b) from minus to plus and dividing the resulting expression by 2, gives a function which reasonably fits the repulsive potential curve of the first excited state of $\mathrm{H_2}$. The LEPS equation has been applied to a large number of systems for which spectroscopic data are available. It has limited flexibility and does not correctly represent surfaces for a number of AB+C reactions.

(b) DIM (Diatomic-in-Molecules) Approach

A function, which is similar to the London equation and based on the diatomic-in-molecules approach was first used by Kuntz to fit the *ab initio* surface for collinear reaction

$$\mathrm{He + H_2^+ \rightarrow HeH^+ + H}$$

and is expressed as

$$V_{(r_1,r_2,r_3)} = Q_1 + Q_2 + Q_3 - [(J_1 - J_3)^2 + J_2^2]^{1/2}$$

$$Q_{\mathrm{i}}(r_{\mathrm{i}}) = \tfrac{1}{2}[{}^1E(r_{\mathrm{i}}) - {}^2E(r_{\mathrm{i}})] \tag{9.46}$$

$$J_{\mathrm{i}}(r_{\mathrm{i}}) = \tfrac{1}{2}[{}^1E(r_{\mathrm{i}}) + {}^2E(r_{\mathrm{i}})]$$

$$E(r) = pD[e^{-\beta(r-r_0)}\{2 + pe^{-\beta(r-r_0)}\}]$$

where $p = \pm 1$ for repulsive and attractive interactions, respectively.

The DIM function has the advantage that it provides reasonable PE values at geometries for which there are no *ab initio* data available. The DIM function has also a provision for describing the nonlinear geometries even when no *ab initio* input was available for such configurations.

(c) Sorbie-Murrell (SM) Function

Sorbie and Murrell have developed a function for triatomic systems based on a many body expansion of PE. It has been applied to repulsive potentials as well and has become an attractive option for fitting *ab initio* PES. It has sufficient flexibility and extendable to higher polyatomic systems and to two-valued surfaces. The potential for triatomic system is decomposed into one-, two- and three-body terms. The potential is given as

$$\begin{aligned} V(r_1, r_2, r_3) = V_A + V_B + V_C + V_{AB}(r_1) + V_{BC}(r_2) \\ + V_{CA}(r_3) + V_{ABC}(r_1, r_2, r_3) \end{aligned} \tag{9.47}$$

The monoatomic terms are constant and can be taken as zero in their ground states. For diatomic terms extended Rydberg (ER) can be used. The three-body term is expressed as a polynomial multiplied by a product of switching functions

$$V_{ABC}(r_1, r_2, r_3) = \rho(s_1, s_2, s_3) \prod_{i=1}^{3} \left(1 - \tanh \frac{1}{2} \gamma_i S_i\right) \tag{9.48}$$

where $S_i = r_i - r_i^0$ is the displacement in bond length from a reference configuration, ρ a polynomial usually contains up to quartic terms in $S_1^i S_2^j S_3^k$, $(i + j + k \leq u)$ $\left(1 - \tanh \frac{\gamma_i S_i}{2}\right)$ is switching function goes to zero for large S_i and γ_i is the coefficient in the polynomial P to be determined. The switching function has the advantage that for large negative S, it remains finite while for large positive, it becomes zero and proper diatomic limits of the potential are obtained.

(d) Blais and Bunker Function

Blais and Bunker developed an analytic function for A + BC → AB + C reactions by using Morse function and a switching function.

$$\begin{aligned} V = D_{AB}\{1 - e^{-\beta_{AB}(r_{AB} - r_{AB}^0)}\}^2 + D_{BC}\{1 - e^{-\beta_{BC}(r_{BC} - r_{BC}^0}\}^2 \\ + D_{BC}[1 - \tanh(a r_{AB+C})] e^{-\beta_{BC}(r_{BC} - r_{BC}^0)} + D_{AB} e^{-\beta_{AC}(r_{AC} - r_{AC}^0)} \end{aligned} \tag{9.49}$$

The first two terms are Morse potentials for A-B and B-C bonds. The third term attenuates the alteration between B and C as A approaches by means of switching function. The last term supplies a repulsive interaction between A and C. The switching function tends from 0 to unity as r_{AB} varies from large to smaller value.

A number of other analytic potential functions such as Rotated-Morse-Curve-Spline (RMCS), Bond-Energy-Bond-Order (BEBO) have been used for fitting of *ab initio* surfaces.

(e) Numerical Functions

It has been observed that a numerical function seems to be better than various analytic functions because the former can be applied to almost any system as long as the dimensionality of the PES is accounted for the dimensionality of the function or of the interpolation technique. Further, if more *ab initio* data becomes available, for the same system, the numerical interpolation can be revised readily while in case of an analytic function, the parameters have to be determined all over again. The parameters determined already do not necessarily lead to a quick convergence with the addition of more *ab initio* PE values and, therefore, sometimes the topological features may change. A numerical function has been better suited in all such cases. The methods for interpolation data can be global or local. In global methods the value of interpolation function depends on all the data while in local method the value of interpolating function depends only on the data at nearly points. Commonly used numerical interpolation scheme is the ‘cubic spline’ provided by McLaughlin and Thompson who used spline functions to represent the potential of $HeH^+ + H_2 \rightarrow He + H_3^+$.

The utility of spline functions to molecular dynamic studies has been tested by Sathyamurthy and Raff by carrying out quassiclassical trajectory and quantum mechanical calculations for various surfaces. However, the accuracy of spline interpolation deteriorated with an increase in dimension from 1 to 2 to 3. Various other numerical interpolation methods, such as Akima’s interpolation in filling *ab initio* PES for reactive systems, have been used.

9.9 Classical Trajectory Calculations

The evaluation of the reaction cross sections as a function of the initial state of the reactants and final state of the products has been described by Karplus, Porter and Sharma (1965), and Greene and Kuppermann (1968) using classical equations of motions for interacting species. For a given potential $V(r_1, r_2, r_3)$, a set of initial coordinates and momenta for the particles determine uniquely the collision trajectory and the occurrence of reaction. The method is described as follows.

For a three-body system such as A + BC → AB + C, there are $3 \times 3 = 9$ degrees of freedom in the problem. However, three degrees of freedom can be eliminated by considering the centre of mass coordinates. If we consider

(a) (q_1, q_2, q_3)	the cartesian coordinates of particle C with respect to B as origin.
(b) (q_4, q_5, q_6)	the cartesian coordinates of particle A with respect to centre of mass of the pair (B, C) as origin.
(c) (q_7, q_8, q_9)	the cartesian coordinates of centre of mass of the entire three particle system.
(d) $(p_1, p_2, \ldots, p_9)$	momenta conjugate to the coordinates $(q_1, q_2, \ldots q_9)$.

The full Hamiltonian for three body problem is given as

$$H = \frac{1}{2\mu_{BC}}[p_1^2 + p_2^2 + p_3^2] + \frac{1}{2\mu_{A,BC}}[p_4^2 + p_5^2 + p_6^2] + V(q_1 q_2 ,. . . q_6) \tag{9.50}$$

where $\frac{1}{\mu_{BC}} = \frac{1}{m_B} + \frac{1}{m_C}$ and $\frac{1}{\mu_{A,BC}} = \frac{1}{m_A} + \frac{1}{m_C}$

Although the derivative of the potential energy with respect to q_i ($i = 1, 2, ,.6$) are required in equation (9.50), the potential energy as an explicit function of internuclear distances, i.e. $V(r_{AB}, r_{BC},, r_{AC})$, where r_{AB}, r_{BC} and r_{AC} are A-B, B-C and A-C internuclear distances, respectively, can be used by introducing the relations between r_{AB}, r_{BC}, r_{AC} and q_i ($i = 1, 2, . . . , 6$).

The potential energy functions are expressed in terms of q_i ($i = 1, 2, ,.6$), which explicitly exhibits its independence of the coordinates of the center of mass. Again, since the momenta conjugate to coordinates (q_7, q_8, q_9), i.e. p_7, p_8 and p_9 remains constants of motion during the entire collision, the term containing them in the Hamiltonian has been subtracted.

The Hamilton's equations for three-body system described by the general dynamical coordinates $q_i p_i$ are

$$\frac{dq_i}{dt} = q_i = \frac{\partial H}{\partial p_i}; \frac{dp_i}{dt} = p_i = -\frac{\partial H}{\partial q_i} = -\frac{\partial v}{\partial q_i} \tag{9.51}$$

Thus, for determination of time variation of q_i and p_i, the integration of 12 simultaneous differential equations are required. Further, reduction in number of dynamical equations by use of conservation of energy or total angular momentum is not worthwhile since the remaining equations become more complicated to solve.

9.9.1 Initial State Properties

To specify and define the initial state of collision, z-axis may be selected as the direction of the initial asymptotic relative velocity vector v_R as shown in Fig. 9.22.

The coordinate system may be oriented so that the atom A and centre of mass BC lie in the Y-Z plane. This gives the simple forms

$$\begin{aligned} p_4^0 &= 0 & q_4^0 &= 0 \\ p_5^0 &= 0 & q_5^0 &= 0 \\ p_6^0 &= \mu_{A,BC} v_R & q_6^0 &= -(r^2 - b^2)^{1/2} \end{aligned} \tag{9.52}$$

where r is initial distance between A and center of mass BC, b is impact parameter, r should be greater than or equal to r_0, i.e. reaction shell radius r_0

should be chosen so that the interaction potential between A and BC is initially zero and trajectory in integrated forward unit $r(t)$ is sufficiently large so that the interaction potential is once again zero.

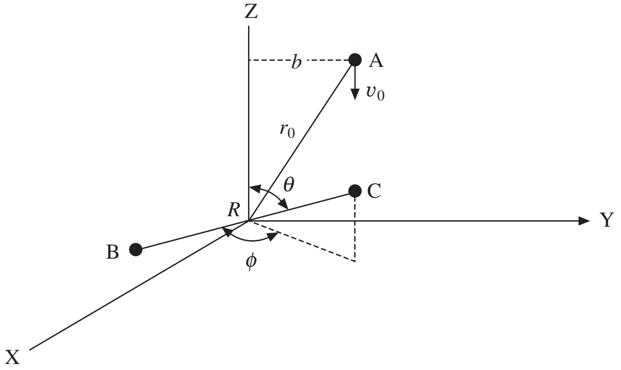


Fig. 9.22

For the determination of the initial state of the molecule, the values of six variables q_i, p_i (i = 1, 2, 3) have to be selected. These can be written by considering the orientation of the molecule BC and specifying by the polar coordinates R, θ and ϕ. Thus

$$\begin{aligned} q_1^0 &= R \sin\theta \cos\phi & p_1^0 &= -\rho (\sin\phi \cos\eta + \cos\phi \cos\theta \sin\eta) \\ q_2^0 &= R \sin\theta \cos\phi & p_2^0 &= \rho(\cos\phi \sin\eta - \sin\phi \cos\theta \sin\eta) \quad (9.53) \\ q_3^0 &= R \cos\theta & p_3^0 &= \rho \sin\theta \sin\eta \end{aligned}$$

where R is initial BC distance, $\rho^2 = \dfrac{J(1+1)h^2}{R^2}$ is proportional to square of rotational angular momentum of BC and η is the angle between the vector $(R_{BC} \times Z)$ and the rotational angular of BC.

The reactant molecule BC is specified to be in an initial vibrational v and rotational state J, which determines ρ and allows R to be set to the maximum bond extension compatible with total vibrational energy. The initial relative velocity v_R may be varied systematically or it may be chosen at random from Boltzmann distribution function. The orientation angle, which specify rotational phase and impact parameter b are selected at random.

The vibrational phase v is characterised by selecting r_0 at random from the interval between r_0 and $r_0 + v_R^0 \tau$, where τ is the vibrational period of BC.

Thus, the initial trajectory is determined by variables v_R, b, r (or q_6), v, J, R, θ, ϕ and η. Depending upon the reaction attributed under consideration, different procedures may be used for specifying the initial variables.

Monte-Carlo method has widely been used for random sampling for many of the initial conditions in these calculations.

9.9.2 Final State Properties

After defining the initial values of the dynamical variables, we can define the final state of collision trajectory as the state in which system leaves the reaction shell, i.e. by inspecting when the distance between any one of the atoms and center of mass of the other two atoms is equal to r_0. This will reflect which atom is bound to which other atom.

When the reaction is complete, let the final molecule be AB. The final energies, the components of velocity of atom C relative to that of the molecule AB, final angular momentum of AB etc. can be determined by calculating classical expectation values over a few cycles of motion. If molecule AC is formed in the reaction, the corresponding expressions can be desired.

9.9.3 Calculation of Reaction Cross Section

Let us consider a collinear reaction

$$\mathrm{A + BC \rightarrow AB + C}$$

Let r_{AB}, r_{BC} and r_{AC} be the internuclear distances for the pairs AB, BC and AC, respectively. As the reaction proceeds, these distances change with time. Before the reactants have approached each other, r_{AB} and r_{AC} are large compared to r_{BC}. After the collision, if collision is non-reactive, r_{AB} and r_{AC} again become large compared to r_{BC} as the collision partners move away from each other. However, if the collision is reactive, initially r_{AB} and r_{AC} are large compared to r_{BC} and after the collision, when the products move away from each other, r_{AC} and r_{BC} are large compared to r_{AB}, as shown in Figs. 9.23 and 9.24. Thus, by knowing r_{AB}, r_{BC} and r_{AC} as functions of time, we can know whether the reaction is reactive or non-reactive.

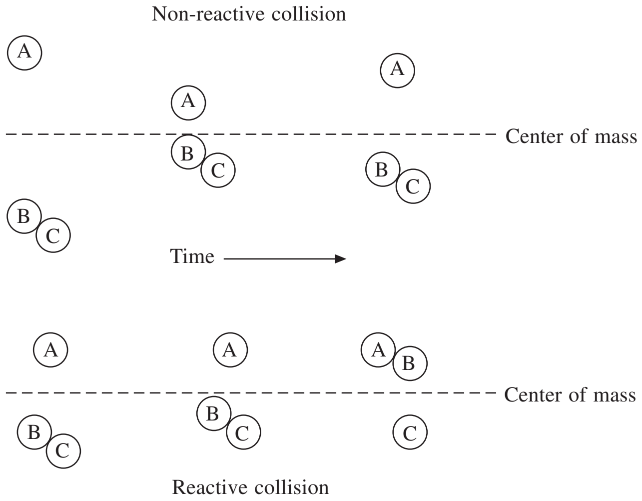


Fig. 9.23 Schematic diagram showing a collinear reaction A + BC → AB + C.

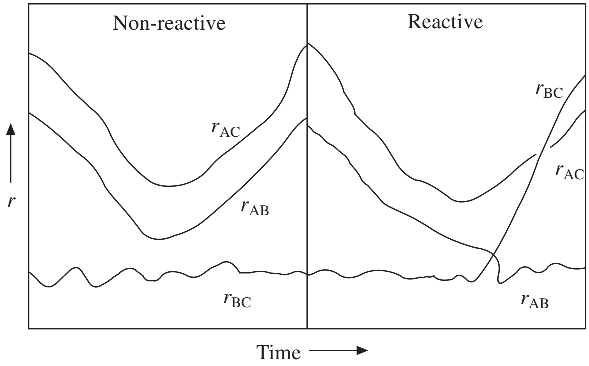


Fig. 9.24 Variation of the internuclear distances for non-reactive and reactive system.

For determination of reaction probability and reaction cross section, a large number of collision trajectories have to be considered and appropriate averages over the initial conditions performed. The reaction probability is calculated for a specified initial relative velocity v_R (i.e. initial relative kinetic energy), rotational state *J*, and impact parameter *b*. The reaction probability is the ratio of number of reactive trajectories to the total number trajectories, i.e.

$$P_r(v_R, J, b) = \lim_{N\to\infty} \frac{N_R(v_R, J, b)}{N(v_R, J, b)} \tag{9.54}$$

The choice of other variables *R*, *r*, *h*, θ, ϕ and η appropriate for Monte-Carlo averaging is made by pseudo random numbers generated on computer. The reactive cross section can be found by averaging the reaction probability over the impact parameter and rotational state

$$\sigma(v_R^0, J) = 2\pi \int_0^{b_{\max}} P_R(v_R^0, J, b)\, b\, db \tag{9.55}$$

$$\sigma(v_R^0, J) = \sum_{J=0}^{J_{\max}} \sigma(v_R^0, J) f(J, T) \tag{9.56}$$

The thermally averaged rate constant is the velocity averaged and can be determined by averaging the velocity

$$k(T) = \int_0^D dv_A \int_0^D dv_{BC} f_A(v_A) f_{BC}(v_{BC}) v_R^0 \sigma(v_R^0) \tag{9.57}$$

It is observed that most reactive collisions tend to occur at small *b* and large v_R^0 so that sampling at random from distribution *f*(*b*) = 2π*b* and $f(v) = 4\pi v^2 e^{-\frac{\mu v^2}{2k_B T}}$ would tend to give a preponderance of non-reactive trajectories. Therefore, it is more efficient to sample from a random distribution of impact parameters and initial relative velocities and then account of ensemble averages by weighting with proper distribution function.

9.10 Potential Energy Surface and Classical Dynamics

The classical description is quite different from the quantum. In classical dynamics we describe the coordinates and momenta simultaneously as a function of time and can follow the path of the system as it goes from reactants to products during the collision. These paths, called *trajectories*, provide a motion picture' of collision process. The results of any real collision can be represented by computing a large number of trajectories to obtain distribution of post-collisions properties of interest (e.g. energy or angular distribution). In fact, the trajectory calculation means the transformation of one distribution function (reagent distribution, pre-collision) into another (product distribution, post-collision), which is determined by PE function.

If we want to study the implications of various features of potential energy surface to dynamical results we have to carry out the dynamics. From a practical point of view, we can use classical mechanics. One numerically solves Hamilton's equations

$$p_i = -\frac{\partial H}{\partial q_i}; \quad q_i = \frac{\partial \mu}{\partial p_i}, \quad i = 1, \ldots, 3N \tag{9.58}$$

$$A = \sum_i \frac{p_i^2}{2m_i} + V(q_1, \ldots, 3N)$$

At given V and a set of $\{p_i, q_i\}$, the time evolution of the system can be followed:

$$q_{i+1} = q_i + \Delta_\mathrm{t} \frac{\partial H}{\partial p_i} \tag{9.59}$$

$$q_{i+1} = q_i - \Delta_\mathrm{t} \frac{\partial H}{\partial p_i}$$

The motion on the PES corresponds to an interchange of potential and kinetic energies and asymptotically rearrangement of particles in a reactive collision. For a given $\{p_i\}$ we can plot the time variation of the coordinates on the top of the PE contours as shown in Fig. 9.25. These are called the trajectories and their behavior would tell as about molecular collisions.

Eyring and Polanyi, and Eyring and Hershfeld tried to calculate the representative trajectories on PES for the $H + H_2 \rightarrow H_2 + H$ reaction but could not succeed due to lack of computational facility at that time. In the early sixties, three different research groups led by Bunker, Karplus and Polanyi developed the quassi-classical trajectory (QCT) approach, which has been proven successful except under circumstances where the quantum mechanical effects like tunneling and resonance are important.

Consider a model PES for a collinear reaction, A + BC → AB + C, on which a typical reactive trajectory has been shown (Fig. 9.25). The motion along r_{AB} would correspond to reactant translation/product vibrational and similarly motion along r_{BC} would correspond to reactant vibration/product translation.

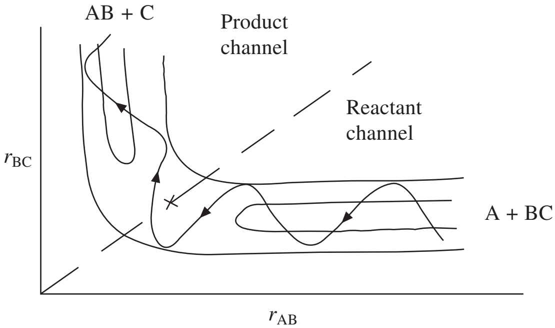


Fig. 9.25 A typical reactive trajectory.

Consider that the saddle point is located in the entry channel (early barrier), e.g. an exothermic reaction (Fig. 9.26). Translation motion along r_{AB} helps the reactants in overcoming the barrier and product molecule is vibrationally excited. Providing vibrational energy in reactant is putting energy in a direction orthogonal to the reaction path and hence does not help the reaction. Again, the trajectory that leads to the reaction has momentum component parallel to r_{AB} and, therefore, the reaction energy is present largely in the product vibration, i.e. reactant translation is helpful for an exothermic reaction and most of the exothermicity would end up as product vibration. This is called *specific energy disposal* arising from an attractive energy release.

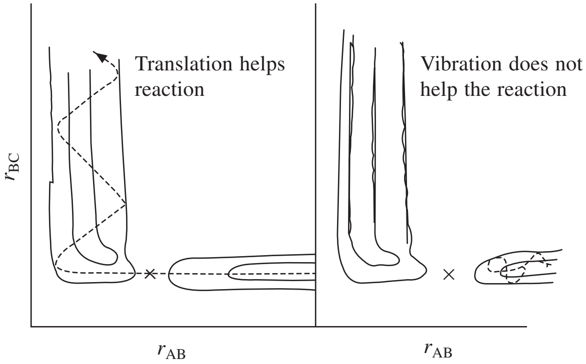


Fig. 9.26 Effect of reactant translation and vibration on collisions, when saddle point (×) is in the entry channel.

In contrast, for an endothermic reaction for which the saddle point lies in the exit channel (late energy barrier), the reactant vibration enhances the reaction probability while translation does not help (Fig. 9.27). Again, the trajectory that leads to reaction has momentum along the product channel and it leads to largely product translation. Thus, in an endothermic reaction, vibrational energy is particularly helpful for reaction and energy passes mainly into translational energy of the product. This is not unexpected, as an endothermic reaction is the reverse of the corresponding exothermic reaction.

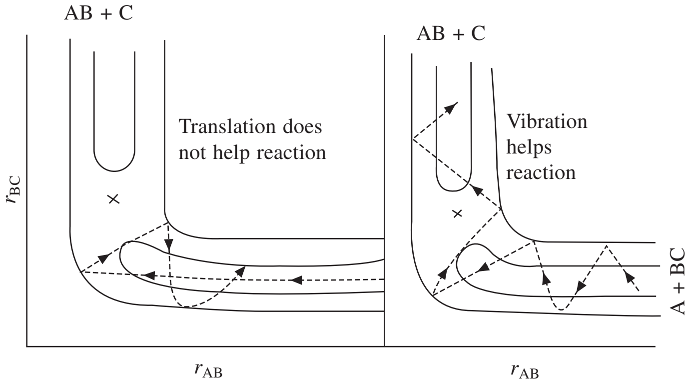


Fig. 9.27 Effect of translation and vibration on collisions, when saddle point (×) is in the exit channel.

If the product molecules are vibrationally excited in an exothermic reaction, it follows from the principle of microscopic reversibility that for the reverse endothermic reaction, vibrational energy should be helpful for the reaction. A state-to-state study by Brooks and co-workers of a slightly endothermic reaction

$$K + ClH \rightarrow KCl + H$$

has shown that vibration in HCl is most effective in leading of reaction HCl ($v = 1$) which is 100 times more reactive than HCl ($v = 0$), vibrational energy has also been found to be most effective for substantially endothermic reactions

$$Br + HCl \rightarrow HBr + Cl$$

$$H + HF \rightarrow H_2 + F$$

The thermoneutral reactions mostly follow the same behaviour as with the endothermic reactions. If there are late barriers, vibrational energy is most effective, otherwise the translational energy is relatively more important.

The shape of the inner repulsive wall is also an important feature, which can be used to classify a PES. In potential energy surface having late barrier there can be two types of behaviour, i.e. sudden and gradual. On gradual surface, a certain amount of translational energy is required in addition to vibrational energy in crossing the barrier while on the sudden surface, very little translational energy is required to cross the barrier (Fig. 9.28). In fact, on a sudden surface, the requirement for reactant vibration is so stringent that a vibrational threshold is expected. If we observe a vibrational threshold for an endothermic reaction which is a good indication that PES for reaction belongs to the sudden category.

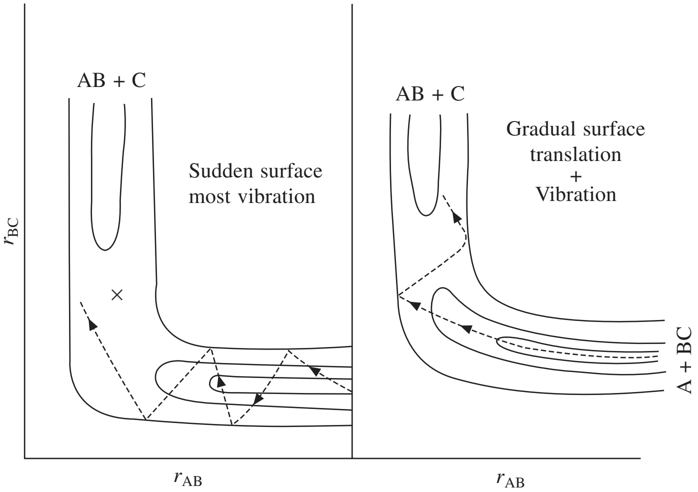


Fig. 9.28 Effect of vibration and translation on sudden and gradual surfaces.

The fraction of released energy that passes into translational and vibrational energies of product depends to a quite significant extent on the mass combination of reactant atoms. This mass effect is referred as kinematic effect. In order to understand mass effect, at least for a collinear reaction, we can transform the motion of the three particles on PES to that of a single particle of a fictitious mass $\mu = \dfrac{m_A(m_B + m_C)}{m_A + m_B + m_C}$ moving on the PES plotted in the coordinates called *scaled* and *skewed coordinates*.

The transformations used are

$$x = r_{AB} + y \tan \theta$$

$$y = (r_{BC/C}) \cos \theta \tag{9.60}$$

where $\mu = \left[\dfrac{m_A(m_B + m_C)}{m_C(m_A + m_B}\right]^{1/2}$ is called the *sealing factor* and $\theta = \sin^{-1}\left[\dfrac{m_A m_C}{(m_A + m_B)(m_B + m_C)}\right]$ the *skewing angle*. The transformed coordinates are shown in Fig. 9.29.

For a collinear reaction

$$A + BC \rightarrow AB + C$$

the system kinetic energy is diagonalized in *x* and *y*. If we use these transformations and, therefore, instead of solving for the motion of a three particle system governed by a potential, we should solve the motion of a

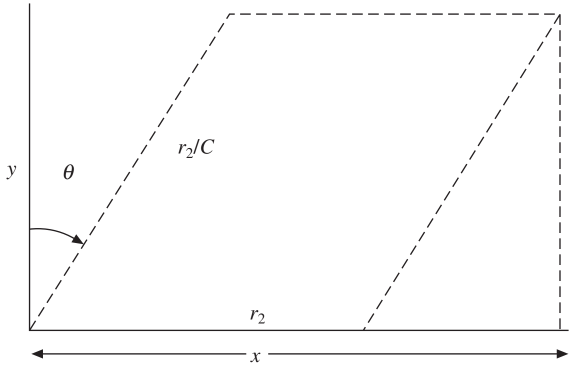


Fig. 9.29 Scaled and skewed coordinates.

single particle of a mass μ in (x, y) coordinates. Depending on the masses of A, B and C the scaling factor and skewing angle change. Without doing any calculations, we can see the effect of different mass combination by examining the PE contours. The PE contours in scaled and skewed coordinates for $H + H_2 \rightarrow H_2 + H$ reaction are shown in Fig. 9.30.

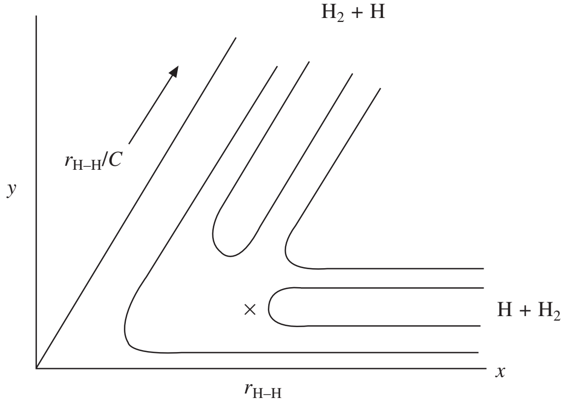


Fig. 9.30 PE contour diagram for $H + H_2 \rightarrow H_2 + H$ in scaled and skewed coordinates.

The PE contours for various mass combinations are shown in Fig. 9.31. For reaction, heavy + heavy-light → heavy-heavy + light, the reactant channel is very narrow and product channel very broad (Fig. 9.31a) and therefore almost every collision leads to product (e.g. Na + ClH → NaCl + H). For reaction, light + heavy-heavy → light-heavy + heavy (e.g. $H + Cl_2 \rightarrow HCl + Cl_2$), the entry channel is much wider than exit channel (Fig. 9.31b) and therefore most of the trajectories get reflected back into entry channel and reaction probability is small. For the mass combination, heavy + light-heavy → heavy-light + heavy (e.g. Cl + HO → ClH + O), the skewing angle is so large that the product channel is bent over the reactant channel (Fig. 9.31c) and every collision leading to the product has a good chance of returning to reactants and vice-versa. Therefore, the atom and the diatom collide with each other repeatedly with a nearly statistical outcome for the reaction.

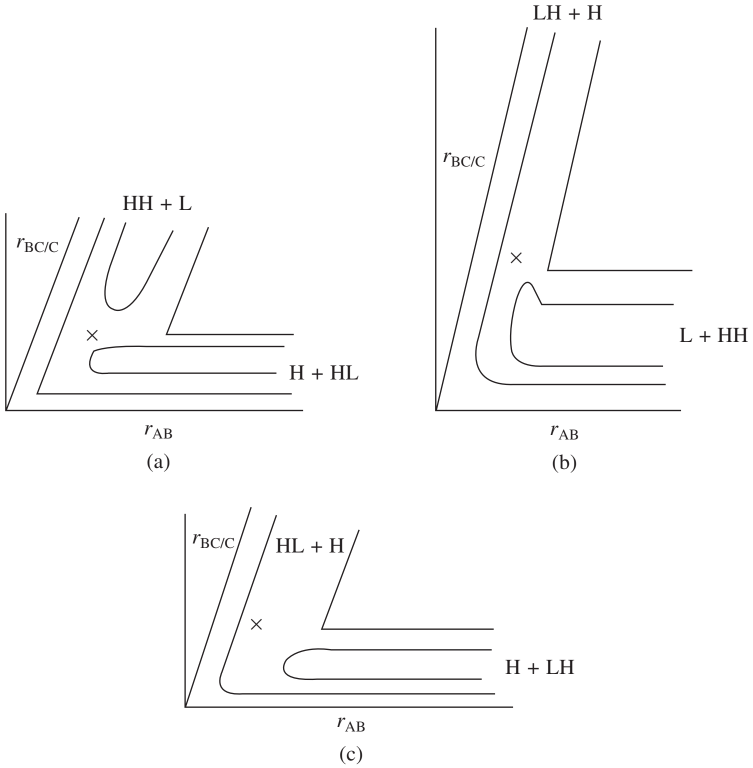


Fig. 9.31 PE contours scaled and skewed coordinates for three different mass combinations. L: light atom; H: heavy atom.

The mass effect can also explain the reactivity of two ends of molecule in its reaction. For example, in reaction

$$\mathrm{F} + \mathrm{HD} \rightarrow \mathrm{FH} + \mathrm{D} \qquad \text{(a)}$$

$$\mathrm{F} + \mathrm{HD} \rightarrow \mathrm{FD} + \mathrm{H} \qquad \text{(b)}$$

It has been found that under identical conditions, FD formation is favoured. This has been observed that the PES plot on scale and skewed axis gave wider product channel in case of reaction (b), which explained the preference of formation of FD when compared to FH.

9.11 Disposal of Excess Energy

The matter of special interest that arises, especially in relation to state-to-state studies, is 'What happens to energy that is in excess of that required to cross the barrier?'

It appears, for all types of reactions, that there is a tendency for excess of translational energy to appear as translational energy in the product and for excess of vibrational energy to appear as vibrational energy in the products. This effect has been referred to as *adiabaticity*. Such a vibrational adiabaticity can be understood in terms of collinear model. Increasing vibrational energy in reactant results in the trajectory traversing through additional regions of the PES and in particular 'cutting the corner' and thereby increasing vibrational energy in the product. The excess energy causes the trajectory in region of the activated state to correspond to a more extended ABC configuration that would otherwise be the case. The system thus 'cut the corner' on PES as illustrated in Fig. 9.32.

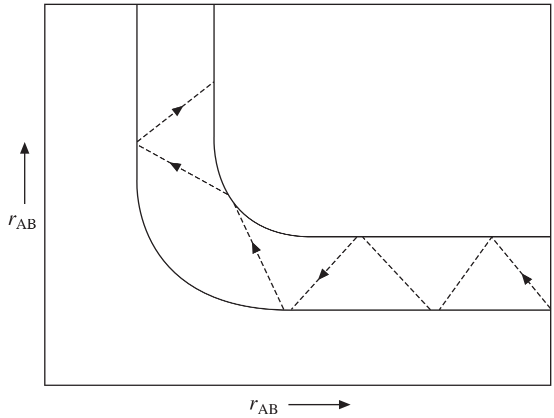


Fig. 9.32 A trajectory showing cutting the corner.

9.12 Influence of Rotational Energy

The rotational energy is expected to play a less important role in chemical reactions due to the following two factors:

(i) The amount of rotational energy residing in a molecule in usually much less compared with the vibrational and transactional energy.
(ii) The rotation in a molecule is dissipated so rapidly that it is not easy to maintain the molecule in a specified rotational state.

However, the experimental studies for some reactions have shown that reactant rotation is also crucial in deciding the collisional outcome. For example, for reaction

$$K + ClH \rightarrow KCl + H$$

an increase in rotational quantum number (j from 1 to 4) at a fixed vibrational quantum number ($v = 1$) resulted in a steady decrease in the reaction rate.

For higher j, rate of reaction increases with further increase in j. The initial decline in the rate has been explained on the basis that as the rotational speed increases, the preferred orientation of the reaction decreases causing a decrease in reaction probability. A subsequent increase in rotation results in preferred orientations again during the approach of the reactants and this can give rise to enhanced rates at higher j. The influence of reactant rotation on various reaction attributes has been reviewed by Sathyamurthy.

9.13 Experimental Chemical Dynamics

9.13.1 Molecular Beam Technique

One of the first approaches to study the microscopic kinetics i.e. state-to-state cross sections and reaction probabilities of a chemical reaction was the crossed molecular beam experiments. The principle of the method consists of intersecting two beams of the reactant molecules in a well-defined scattering volume and catching the product molecules in a suitable detector (Fig. 9.33).

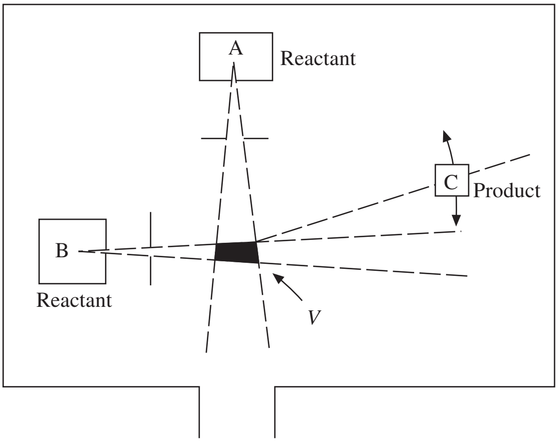


Fig. 9.33 Molecular beam-scattering apparatus.

The beams of reactant molecules A and B intersect in a small scattering volume V. The product molecule C is collected in the detector. The detector can be rotated around the scattering centre. Various devices may be inserted in the beam path, i.e. between reactants and scattering volume and between scattering volume and product species to measure velocity or other properties. The angular distribution of the scattered product can be measured by rotating the detector in the plane defined by two molecular beams. The mass spectrophotometer can also be set to measure a specific molecular mass so that the individual product molecules are detected.

Supersonic molecular beams are used to produce velocities of the molecules in the reactant beams. For generating the supersonic molecular beam, the dilute mixture of reactant molecule with an inert gas (commonly He and Ne) is taken at high pressure. The mixture is allowed to pass through a small nozzle into vacuum chamber. A skimmer (a small pinhole) is used so that a collimated beam of reactant molecule is directed towards the collision region as shown in Fig. 9.34.

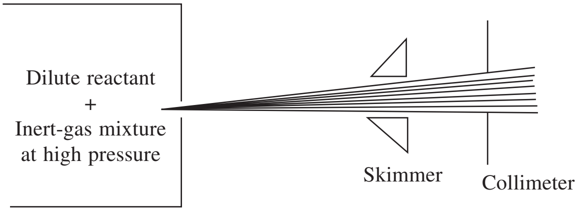


Fig. 9.34

The supersonic molecular beam generates a collection of molecules with a high translational energy but a very small spread (a narrow, non-equilibrium velocity distribution). In addition to this, the molecules can be prepared with low rotational and vibrational energies. The reactive velocity of reactants is specified in crossed molecular beam experiments. The relative velocity or collision energy of the reactants may be changed by varying the conditions under which the molecular beams are generated. By measuring the product as a function of collision energy, the energy dependent reaction cross section, i.e. $\sigma(E)$ can be determined. The product molecules formed moves away from collision region. The motion of product is determined by following the laws of conservation of mass, linear momentum and energy.

Counting the number of molecules of a particular product arriving at the detector as a function of time after collision, the velocity distribution of the product molecules can be resolved. and by knowing the total number of product molecules as a function of the scattering angles, angular distribution of the product molecule can be determined. Measuring the velocity distribution or angular distribution of the product molecules many of the molecular details of gas-phase reactive collision can be determined.

For measuring inelastic quantum transition in scattering between the reactants, the state change method may also be applied in which the molecules are prepared in a definite state before scattering and are then analysed for their final quantum state after scattering by an appropriate state filter which permit only molecules at the desired state to arrive at the detector. The resolving power is usually very high and largely independent to beam velocities.

The first bimolecular reaction studied in crossed molecular beams was between Cs and CCl_4, which was studied by Bull and Moon in 1954. Taylor and Datz and later Greene, Robert and Ross investigated

$$K + MBr \rightarrow KBr + H$$

reaction in detail and obtained information about collision yield and activation energy. Thereafter, a large number of reactions have been studied using crossed molecular beams and results are contributed greatly in understanding elementary chemical reactions.

Sometimes the atoms (or molecules) in molecular beams are put into selected electronic, vibrational and rotational states. The initial state selection can be made with lasers. A laser beam of appropriate frequency is shined onto a molecular beam and the molecule goes onto an appropriate excited state. The efficiency of selection depends upon the absorption coefficient. We can attain sufficient absorption to get highly vibrationally excited molecule with the laser. A spin forbidden transition can also be achieved by using a laser.

9.13.2 Stripping and Rebound Mechanisms

The reactions of the alkali-metal atoms with halogens such as

$$K + Br_2 \rightarrow KBr + Br$$

$$Cs + I_2 \rightarrow CsI + I$$

were found to have very high cross sections of over 100 Å^2 and occur when the reactants are fairly apart (~5 Å)Molecular beam experimental studies of these reactions showed that the products in these reactions, are scattered forward with respect to centre of mass of the system as shown in Fig. 9.35.

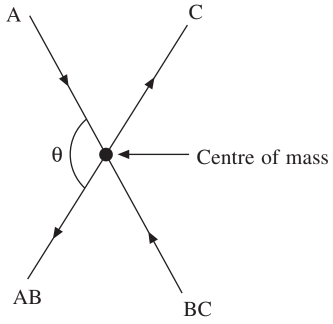


Fig. 9.35 Direction of motion of reactants and products relative to centre of mass (stripping mechanism).

A and BC approach to the centre of mass, A strips off B and then A and C continue to move almost undisturbed in their original direction. These type of reactions are said to occur by a stripping mechanism when PES are attractive.

In contrast, certain reaction such as

$$K + CH_3I \rightarrow KI + CH_3$$

have lower cross section (~10 Å^2) exhibit backward scattering as shown in Fig. 3.6.

A and BC approach to centre of mass, A strips off B and then AB and C return roughly in the direction from which they came. These reactions are said to occur by a rebound mechanism and generally occur when the surface are repulsive. In such reactions the life-time of activated complex, i.e. (ABC) must be short and reaction is said to be direct or impulsive. If life-time is much, rotation may occur and the products may separate in random directions. For many such reactions, the life-time of complexes has been observed less then 5×10^{-13}sec. J.C. Polanyi discussed the relationship of these reactions with shapes of PES with special attention to mass effects.

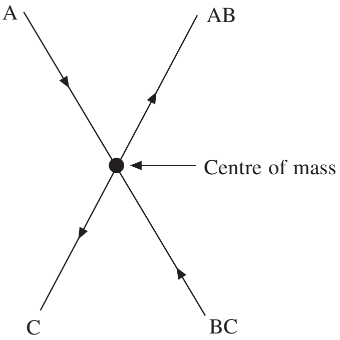


Fig. 9.36 Direction of motion of reactants and products relative to centre of mass (rebound mechanism).

9.13.3 State-to-State Kinetics

Various reactions in which the reactants are in particular vibrational and rotational states have been investigated and state-to-state kinetics have been studied. Two procedures have been used in these investigations. Brooks and coworkers first employed the molecular beam method for studying the state-to-state kinetics. The reactants molecules are put into desired vibrational and rotational states by laser excitation and identified the states by their fluorescence. In molecular beam experiments, it is possible to control the translational energy and mutual orientation of the reactants and to determine the degree of polarization of the rotational angular momentum of the product.

Polanyi and co-workers used the technique, which involved the experiments in bulk. The reactants are put into desired vibrational and rotational states by producing them in an exothermic pre-reaction. For example, OH radical in vibrational excited states can be formed by the reactions

$$H + NO_2 \rightarrow OH\ (v = 1 \text{ to } 3) + NO$$

$$H + O_3 \rightarrow OH\ (v = 6 \text{ to } 9) + O_2$$

The course of reactions was followed either by determining product concentrations by monitoring their infrared chemiluminescence or by luminescence, i.e. by following the decrease in the luminescence of the reactant molecules, which had been excited vibrationally and rotationally.

The molecular beam method has an advantage as compared to bulk method because translational energy can be controlled in the molecular beam method. However, in bulk method the reactant molecules can be formed in much wider range of vibrational and rotational states.

Brook and co-workers were able to excite the HCl molecules to $v = 1$ state using a chemical laser and showed that HCl ($v = 1$) was 100 times more reactive than HCl ($v = 0$) on collision with K atom. In a velocity selected beam experiment it was also observed that for the same amount of energy reagent, vibration was ten times more effective than translational in bringing out the reaction

$$\mathrm{K + ClH \rightarrow KCl + H}$$

Dispert and coworkers were able to prepare HCl molecules in not only a specific vibrational state ($v = 1$) but also in a specific rotational state ($j = 1, 2, 3, 4$) and showed that the rotational excitation was hindering the reaction. Polanyi and co-workers studied the endothermic reaction

$$\mathrm{Br + HCl}(v) \rightarrow \mathrm{HBr + Cl}$$

by preparing HCl molecules into various vibrational states ($v = 1, 2, 3, 4$) and determined the rate constants by the use of luminescence depletion method. It is observed that excitation to the $v = 1$ and $v = 2$ states gives considerable increased rate as compared with $v = 0$. At $v = 2$, the reaction becomes exothermic and further excitation has a smaller effect.

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