

Unit IV: *Chemical Kinetics*

Syllabus:

Rate of a reaction (average and instantaneous), factors affecting rates of reaction: concentration, temperature, catalyst; order and molecularity of a reaction; rate law and specific rate constant, integrated rate equations and half life (only for zero and first order reactions); concept of collision theory (elementary idea, no mathematical treatment).

Objectives

- define the average and instantaneous rate of a reaction;
- express the rate of a reaction in terms of change in concentration of either of the reactants or products with time;
- distinguish between elementary and complex reactions;
- differentiate between the molecularity and order of a reaction;
- define rate constant;

Objectives

- discuss the dependence of rate of reactions on concentration, temperature and catalyst;
- derive integrated rate equations for the zero and first order reactions;
- determine the rate constants for zeroth and first order reactions;
- describe collision theory.

For any chemical reaction, chemists try to find out

- (a) the feasibility of a chemical reaction which can be predicted by thermodynamics (as you know that a reaction with $\Delta G < 0$, at constant temperature and pressure is feasible);
- (b) extent to which a reaction will proceed can be determined from chemical equilibrium;
- (c) speed of a reaction i.e. time taken by a reaction to reach equilibrium.

Chemical kinetics

- *Branch of chemistry, which deals with the study of reaction rates and their mechanisms, called **chemical kinetics**.*
- **The word kinetics is derived from the Greek word ‘kinesis’ meaning movement.**
- **Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of a reaction.**

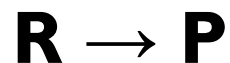
Rate of a Chemical Reaction

The speed of a reaction or the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time.

To be more specific, it can be expressed in terms of:

- (i) the rate of decrease in concentration of any one of the reactants, or
- (ii) the rate of increase in concentration of any one of the products.

Consider a hypothetical reaction, assuming that the volume of the system remains constant.



One mole of the reactant R produces one mole of the product P.

If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2 then,

$$\Delta t = t_2 - t_1$$

$$\Delta[\mathbf{R}] = [\mathbf{R}]_2 - [\mathbf{R}]_1$$

$$\Delta[\mathbf{P}] = [\mathbf{P}]_2 - [\mathbf{P}]_1$$

The square brackets in the above expressions are used to express molar concentration.

Rate of disappearance of R

$$= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta[\mathbf{R}]}{\Delta t}$$

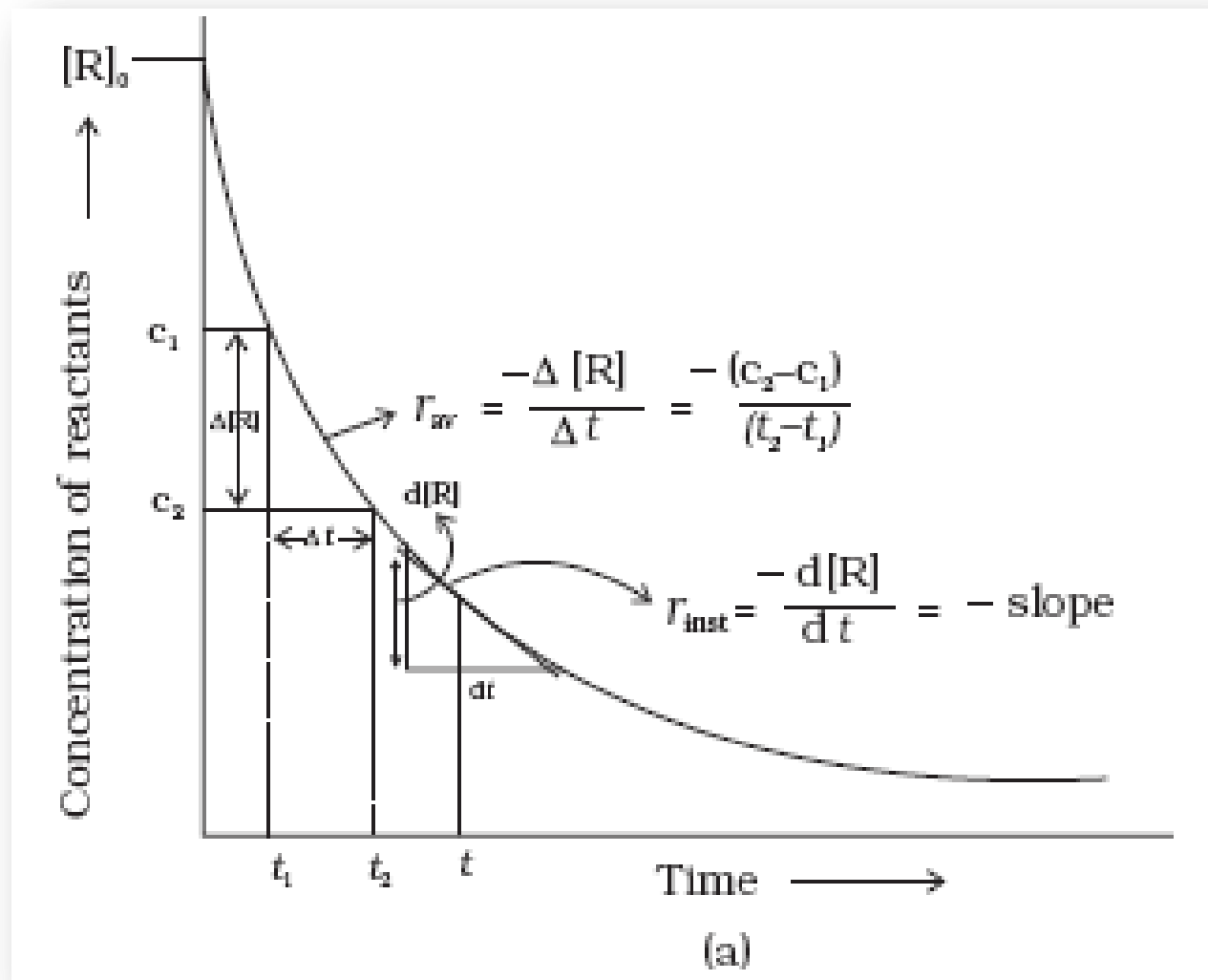
Rate of appearance of P

$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = + \frac{\Delta[\text{P}]}{\Delta t}$$

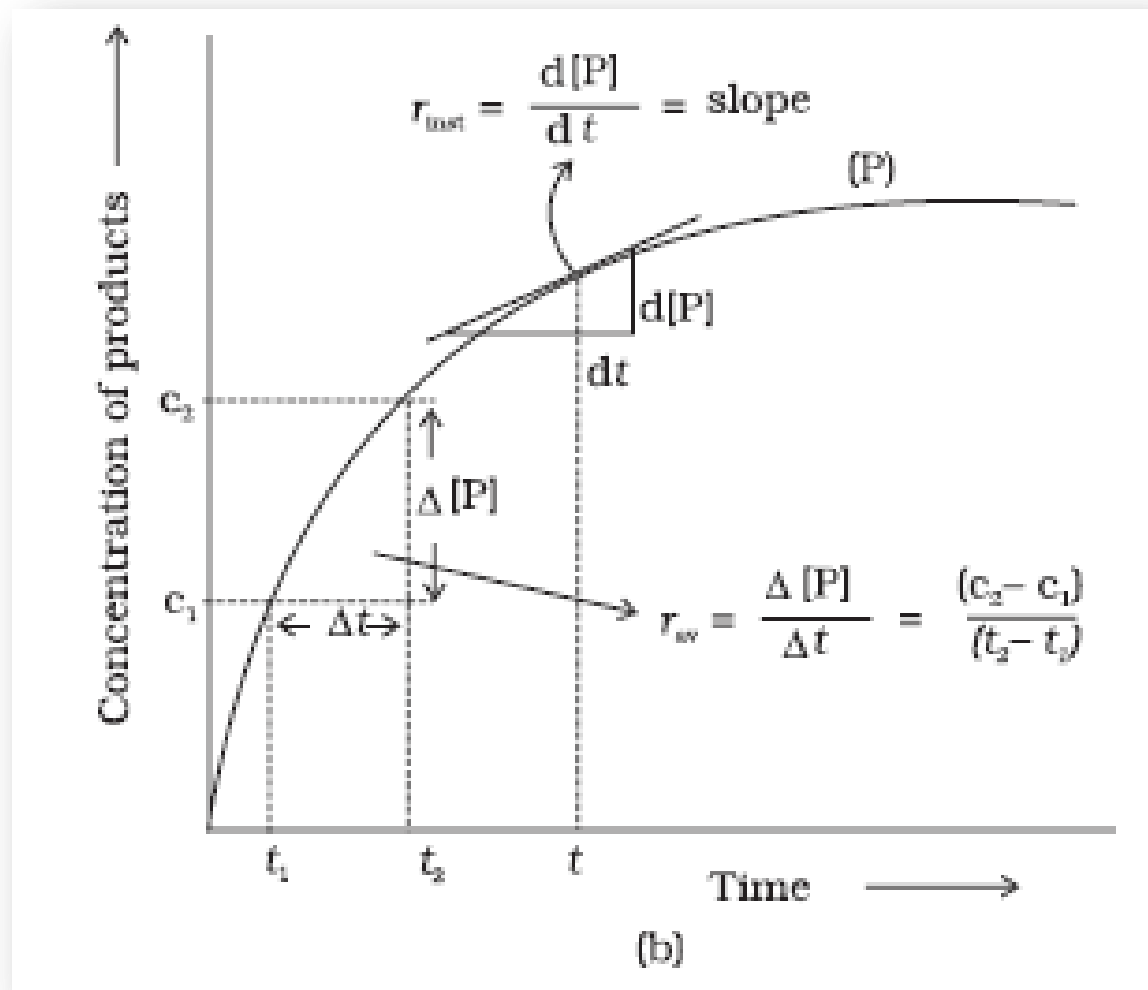
Since, $\Delta[\text{R}]$ is a negative quantity (as concentration of reactants is decreasing), it is multiplied with -1 to make the rate of the reaction a positive quantity. Equations (4.1) and (4.2) given above represent the average rate of a reaction, r_{av} .

Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur

Graph of Conc'n of reactants v/s time



Graph of concn of Products v/s time



Instantaneous rate.

Instantaneous rate may be defined as

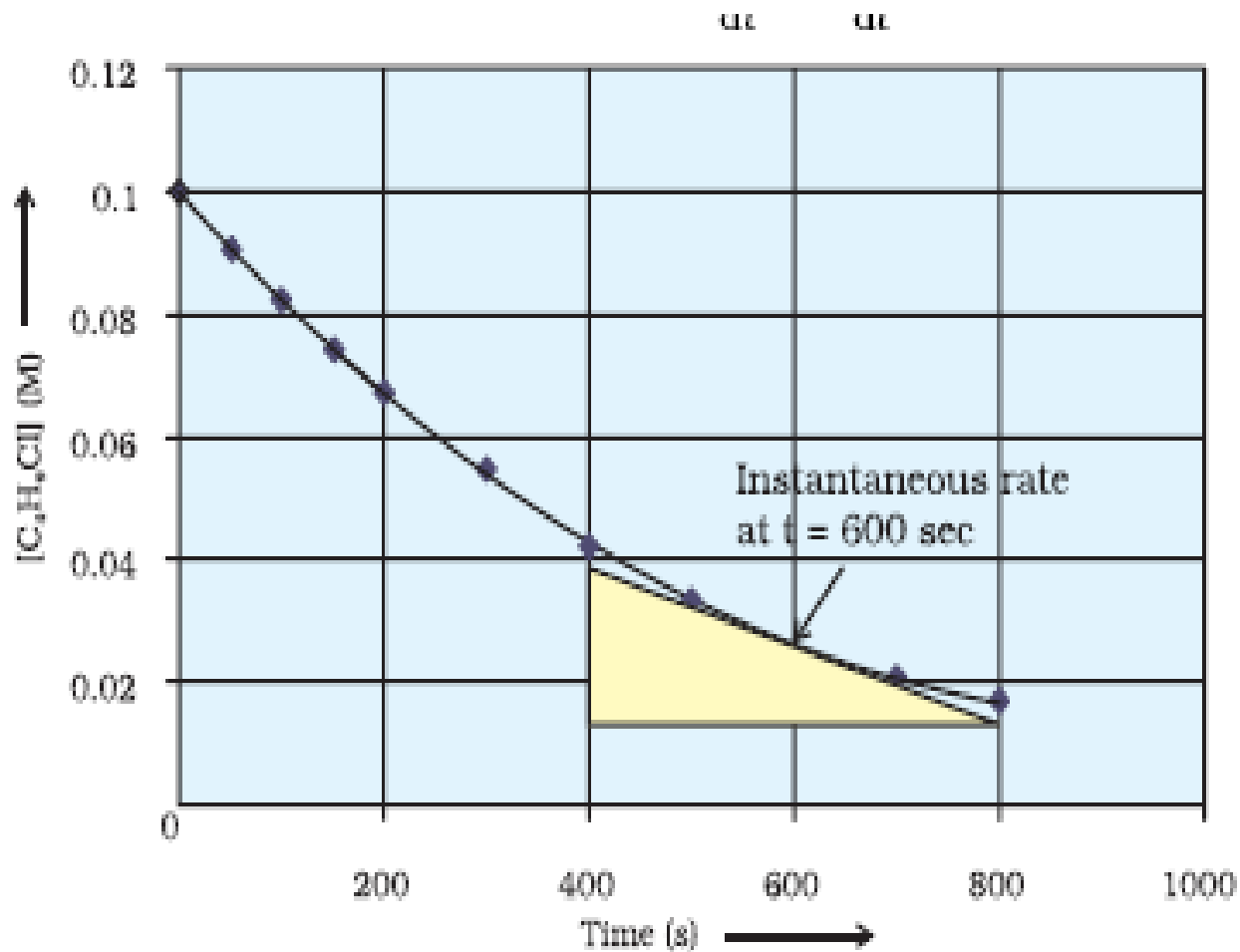
The rate of change of concentration of any one of the species involved in the reaction at particular instant of time.

$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

As $\Delta t \rightarrow 0$ or

$$r_{inst} = \frac{-d[R]}{dt} = \frac{d[P]}{dt}$$

Instantaneous rate.



Units of rate of a reaction

From equations (4.1) and (4.2), it is clear that units of rate are concentration time⁻¹.

For example, if concentration is in mol L⁻¹ and time is in seconds then the units will be mol L⁻¹s⁻¹.

However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be atm s⁻¹.

Now consider a reaction



Where stoichiometric coefficients of the reactants and products are same, then rate of the reaction is given as

$$\text{Rate of reaction} = -\frac{\Delta[\text{Hg}]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = \frac{\Delta[\text{HgCl}_2]}{\Delta t}$$

i.e., rate of disappearance of any of the reactants is same as the rate of appearance of the products.

But in the following reaction, two moles of **HI** decompose to produce one mole each of **H₂** and **I₂**,



- For expressing the rate of such a reaction where stoichiometric coefficients of reactants or products are not equal to one, rate of disappearance of any of the reactants or the rate of appearance of products is divided by their respective stoichiometric coefficients.
- Since rate of consumption of HI is twice the rate of formation of H₂ or I₂, to make them equal, the term Δ[HI] is divided by 2.
- The rate of this reaction is given by

$$\text{Rate of reaction} = -\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t}$$

Similarly, for the reaction



$$\text{Rate} = -\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = -\frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

Factors Influencing Rate of a Reaction

Rate of reaction depends upon the experimental conditions such as

- Concentration of reactants (*pressure in case of gases*),
- Temperature
- and catalyst.

Dependence of Rate on Concentration

- The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products.
- The representation of rate of reaction in terms of concentration of the reactants is known as **rate law**.
- **It is also called as rate equation or rate expression.**

Rate Expression and Rate Constant

- Rate of a reaction decreases with the passage of time as the concentration of reactants decrease.
- Conversely, rates generally increase when reactant concentrations increase.
- So, rate of a reaction depends upon the concentration of reactants

Consider a general reaction



where a, b, c and d are the stoichiometric coefficients of reactants and products.

The rate expression for this reaction is

$$\text{Rate} \propto [A]^x [B]^y \quad (4.4)$$

where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants. Above equation can also be written as

$$\text{Rate} = k [A]^x [B]^y \quad (4.4a)$$

$$-\frac{d[R]}{dt} = k[A]^x [B]^y \quad (4.4b)$$

Rate law

- This form of equation (4.4 b) is known as differential rate equation, where k is a *proportionality constant called **rate constant***.
- *The equation* like (4.4), which relates the rate of a reaction to concentration of reactants is called **rate law** or **rate expression**.
- Thus, **rate law** is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.



Experiment	Initial [NO]/ mol L ⁻¹	Initial [O ₂]/ mol L ⁻¹	Initial rate of formation of NO ₂ / mol L ⁻¹ s ⁻¹
1.	0.30	0.30	0.096
2.	0.60	0.30	0.384
3.	0.30	0.60	0.192
4.	0.60	0.60	0.768

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$

The differential form of this rate expression is given as

$$-\frac{d[\text{R}]}{dt} = k[\text{NO}]^2[\text{O}_2]$$

Now, we observe that for this reaction in the rate equation derived from the experimental data, the exponents of the concentration terms are the same as their stoichiometric coefficients in the balanced chemical equation.

Some other examples are given below:

Reaction	Experimental rate expression
1. $\text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl}$	Rate = $k [\text{CHCl}_3] [\text{Cl}_2]^{1/2}$
2. $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$	Rate = $k [\text{CH}_3\text{COOC}_2\text{H}_5]^1 [\text{H}_2\text{O}]^0$

In these reactions, the exponents of the concentration terms are not the same as their stoichiometric coefficients. Thus, we can say that:

Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e., theoretically but must be determined experimentally.

Order of a Reaction

- Rate = $k [A]^x [B]^y$
- x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of these exponents, i.e., $x + y$ gives the overall order of a reaction whereas x and y represent the order with respect to the reactants A and B respectively.
- **The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.**

❑ Calculate the overall order of a reaction which has the rate expression

$$(a) \text{ Rate} = k [A]^{1/2} [B]^{3/2}$$

$$(b) \text{ Rate} = k [A]^{3/2} [B]^{-1}$$

Solution:(a) $\text{Rate} = k [A]^x [B]^y$

$$\text{order} = x + y$$

(a) So order = $1/2 + 3/2 = 2$, i.e., second order

(b) order = $3/2 + (-1) = 1/2$, i.e., half order.

Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.

Units of rate constant

For a general reaction



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

Where $x + y = n =$ order of the reaction

$$k = \frac{\text{Rate}}{[A]^x [B]^y}$$
$$= \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n}$$

Taking SI units of concentration, mol L^{-1} and time, s, the units of k for different reaction order are listed in Table 4.3

Table 4.3: Units of rate constant

Reaction	Order	Units of rate constant
Zero order reaction	0	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1} \text{s}^{-1}$
First order reaction	1	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^1} = \text{s}^{-1}$
Second order reaction	2	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1} \text{L s}^{-1}$

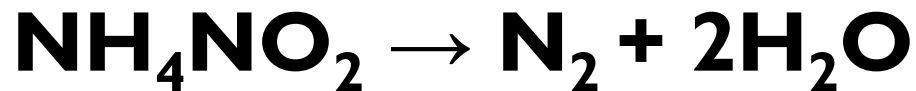
Identify the reaction order from each of the following rate constants.

(i) $k = 2.3 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$

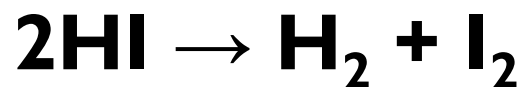
(ii) $k = 3 \times 10^{-4} \text{ s}^{-1}$

Molecularity of a Reaction

- The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.
- The reaction can be unimolecular when one reacting species is involved,
- for example, decomposition of ammonium nitrite



- Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.



- Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example,



- The probability that more than three molecules can collide and react simultaneously is very small. Hence, the molecularity **greater than three** is **not** observed.

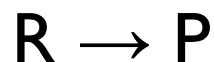
Difference between **Order** & **Molecularity**

- (i) Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.
- (ii) Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning.
- (iii) For complex reaction, order is given by the slowest step and generally, molecularity of the slowest step is same as the order of the overall reaction.

Integrated Rate Equations

Zero Order Reactions

Consider the reaction,



$$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0$$

As any quantity raised to power zero is unity

$$\text{Rate} = -\frac{d[R]}{dt} = k \times 1$$

$$d[R] = -k dt$$

Integrating both sides

$$[R] = -k t + I \tag{4.5}$$

where, I is the constant of integration.

At $t = 0$, the concentration of the reactant $R = [R]_0$, where $[R]_0$ is initial concentration of the reactant.

Substituting in equation (4.5)

$$[R]_0 = -k \times 0 + I$$

$$[R]_0 = I$$

Substituting the value of I in the equation (4.5)

$$[R] = -kt + [R]_0 \quad (4.6)$$

Comparing (4.6) with equation of a straight line, $y = mx + c$, if we plot $[R]$ against t , we get a straight line (Fig. 4.3) with slope = $-k$ and intercept equal to $[R]_0$.

Further simplifying equation (4.6), we get the rate constant, k as

$$k = \frac{[R]_0 - [R]}{t} \quad (4.7)$$

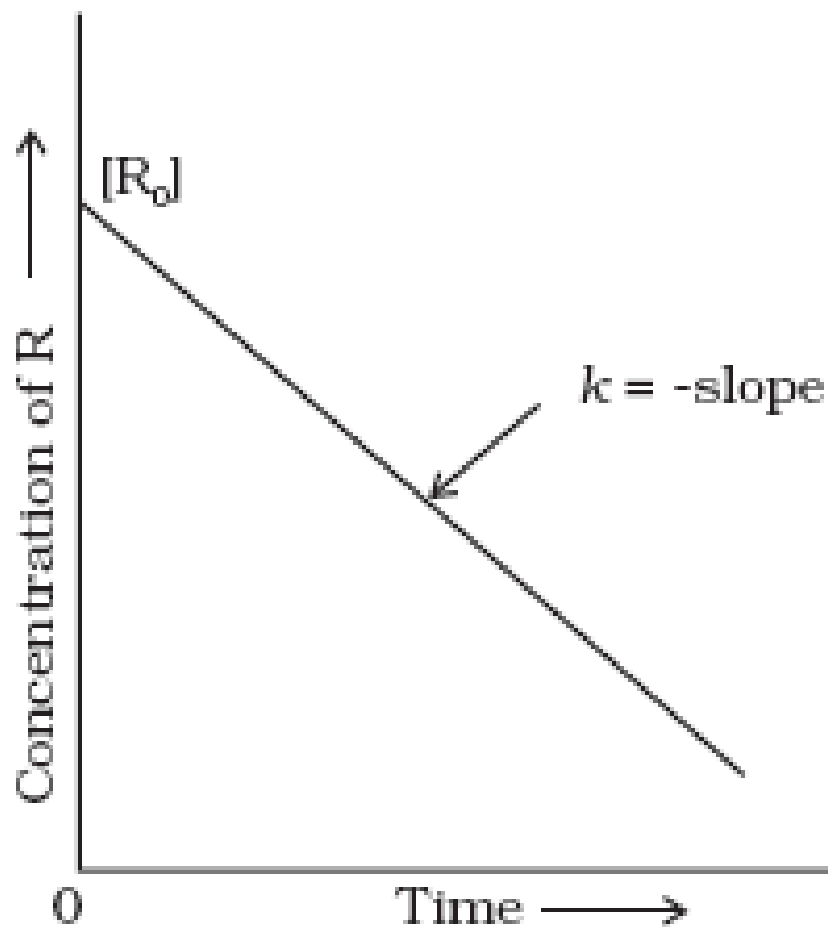


Fig. 4.3: *Variation in the concentration vs time plot for a zero order reaction*

Examples of Zero Order Reactions

❑ The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.



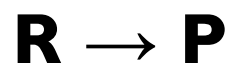
$$\text{Rate} = k [\text{NH}_3]^0 = k$$

❑ In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration.

❑ **The thermal decomposition of HI on gold surface is another example of zero order reaction.**

First Order Reactions

Consider the reaction,



$$\text{Rate} = -\frac{d[\mathbf{R}]}{dt} = k[\mathbf{R}]$$

$$\text{or } \frac{d[\mathbf{R}]}{[\mathbf{R}]} = -kdt$$

Integrating this equation, we get

$$\ln [\mathbf{R}] = -kt + I \tag{4.8}$$

Again, I is the constant of integration and its value can be determined easily.

When $t = 0$, $R = [R]_0$, where $[R]_0$ is the initial concentration of the reactant.

Therefore, equation (4.8) can be written as

$$\ln [R]_0 = -k \times 0 + I$$

$$\ln [R]_0 = I$$

Substituting the value of I in equation (4.8)

$$\ln[R] = -kt + \ln[R]_0 \quad (4.9)$$

Rearranging this equation

$$\ln \frac{[R]}{[R]_0} = -kt$$

$$\text{or } k = \frac{1}{t} \ln \frac{[R]_0}{[R]} \quad (4.10)$$

At time t_1 from equation (4.8)

$$*\ln[R]_1 = -kt_1 + *\ln[R]_0 \quad (4.11)$$

At time t_2

$$\ln[R]_2 = -kt_2 + \ln[R]_0 \quad (4.12)$$

where, $[R]_1$ and $[R]_2$ are the concentrations of the reactants at time t_1 and t_2 respectively.

Subtracting (4.12) from (4.11)

$$\ln[R]_1 - \ln[R]_2 = -kt_1 - (-kt_2)$$

$$\ln \frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

$$k = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2} \quad (4.13)$$

Equation (4.9) can also be written as

$$\ln \frac{[R]}{[R]_0} = -kt$$

Taking antilog of both sides

$$[R] = [R]_0 e^{-kt} \quad (4.14)$$

Comparing equation (4.9) with $y = mx + c$, if we plot $\ln [R]$ against t (Fig. 4.4) we get a straight line with slope = $-k$ and intercept equal to $\ln [R]_0$

$$\ln[R] = -kt + \ln[R]_0$$

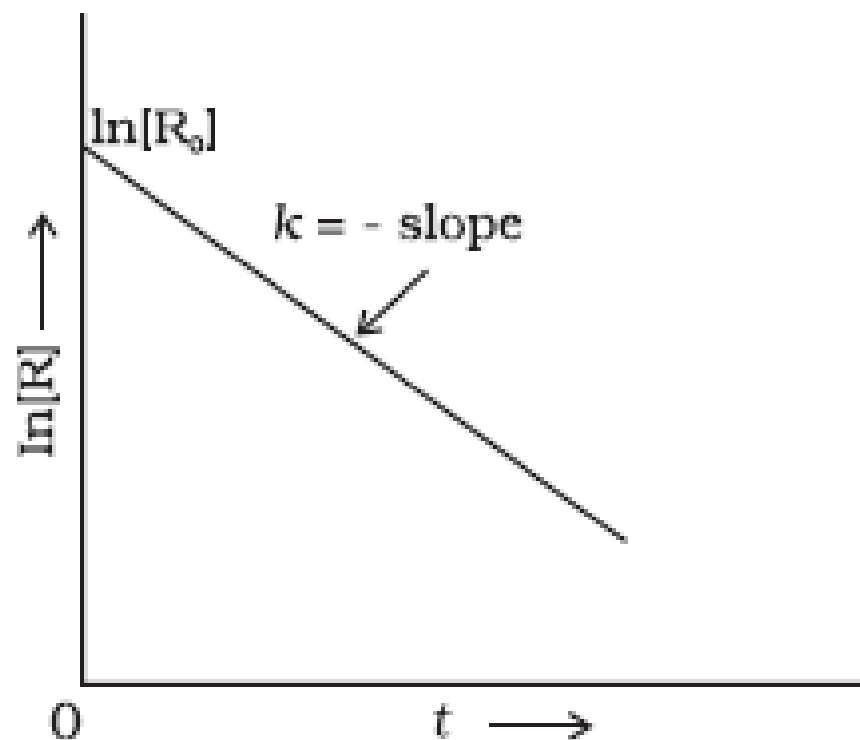


Fig. 4.4: A plot between $\ln[R]$ and t for a first order reaction

The first order rate equation (4.10) can also be written in the form

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad (4.15)$$

$$* \log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

If we plot a graph between $\log [R]_0/[R]$ vs t ,
the slope = $k/2.303$

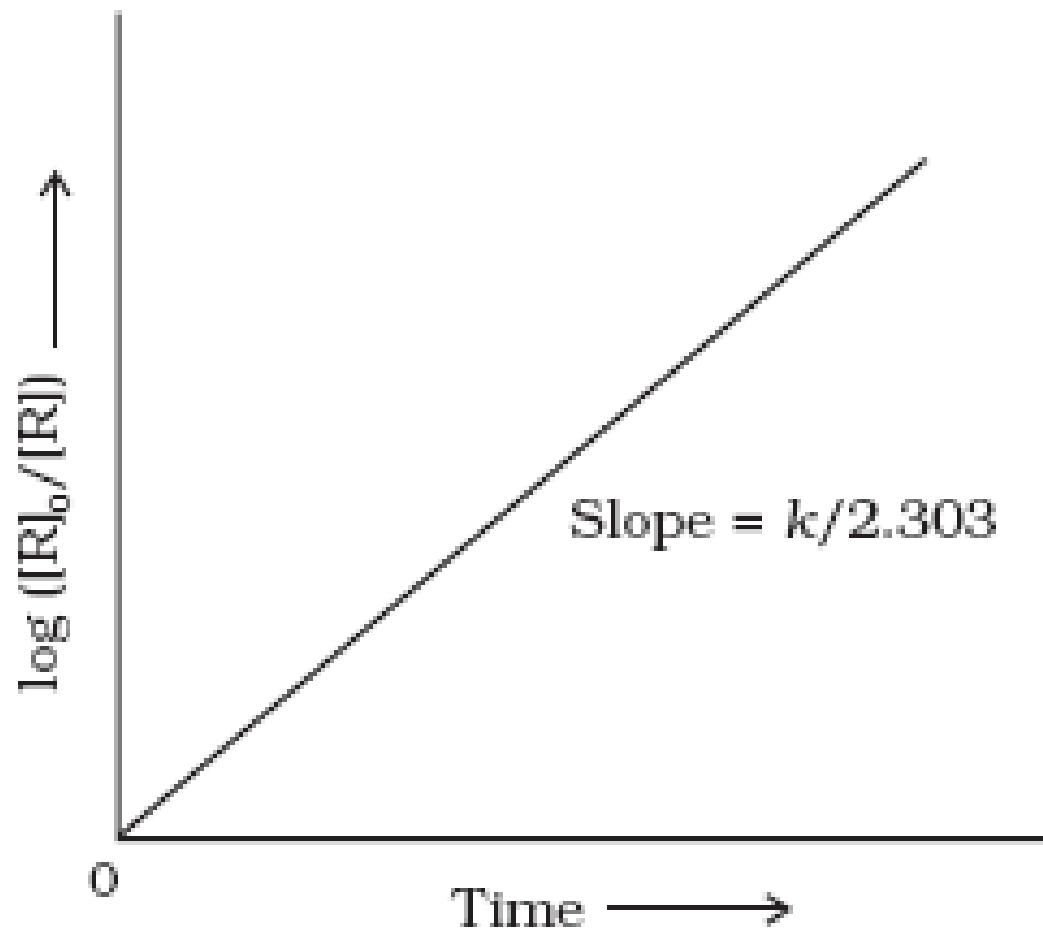


Fig. 4.5: Plot of $\log [R]_0/[R]$ vs time for a first order reaction

Examples of first order reaction

- Hydrogenation of ethene is an example of first order reaction.



$$\text{Rate} = k [\text{C}_2\text{H}_4]$$

- All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.



$$\text{Rate} = k [\text{Ra}]$$

- Decomposition of N_2O_5 and N_2O are some more examples of first order reactions.

Half-Life of a Reaction

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.

For a zero order reaction, rate constant is given by equation

$$k = \frac{[R]_0 - [R]}{t}$$

$$\text{At } t = t_{1/2}, [R] = \frac{1}{2}[R]_0$$

The rate constant at $t_{1/2}$ becomes

$$k = \frac{[R]_0 - 1/2[R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

For the first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad (4.15)$$

$$\text{at } t_{1/2} \quad [R] = \frac{[R]_0}{2} \quad (4.16)$$

So, the above equation becomes

$$k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]/2}$$

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

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

$$t_{1/2} = \frac{0.693}{k}$$

○It can be seen that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species.

○The half-life of a first order equation is readily calculated from the rate constant and vice versa.

For zero order reaction $t_{1/2} \propto [R]_0$. For first order reaction $t_{1/2}$ is independent of $[R]_0$.

I. A first order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14} \text{ s}^{-1}$. Find the half-life of the reaction.

Half-life for a first order reaction is

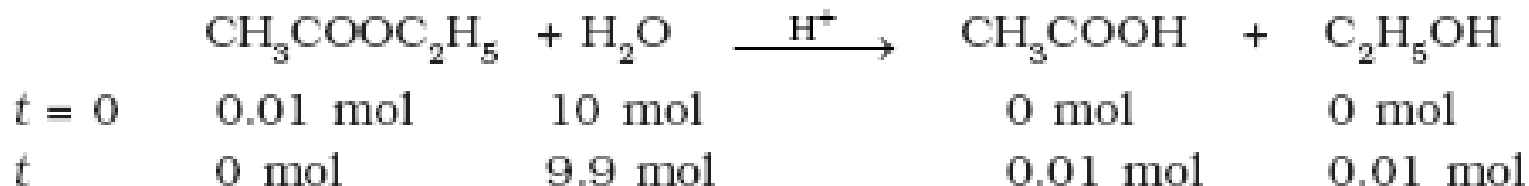
$$t_{1/2} = \frac{0.693}{k}$$

$$t_{1/2} = \frac{0.693}{5.5 \times 10^{-14} \text{ s}^{-1}} = 1.26 \times 10^{14} \text{ s}$$

Table 4.4: Integrated Rate Laws for the Reactions of Zero and First Order

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of k
0	$R \rightarrow P$	$d[R]/dt = -k$	$kt = [R]_0 - [R]$	$[R]$ vs t	$[R]_0/2k$	conc time ⁻¹ or mol L ⁻¹ s ⁻¹
1	$R \rightarrow P$	$d[R]/dt = -k[R]$	$[R] = [R]_0 e^{-kt}$ or $kt = \ln\{[R]_0/[R]\}$	$\ln[R]$ vs t	$\ln 2/k$	time ⁻¹ or s ⁻¹

Pseudo First Order Reaction



The concentration of water does not get altered much during the course of the reaction. So, in the rate equation

$$\text{Rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

the term $[\text{H}_2\text{O}]$ can be taken as constant. The equation, thus, becomes

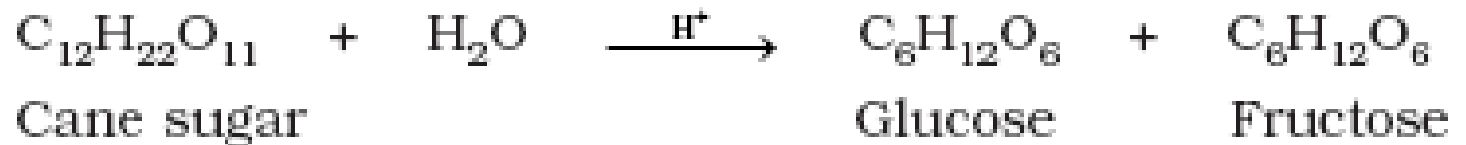
$$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5]$$

$$\text{where } k = k' [\text{H}_2\text{O}]$$

and the reaction behaves as first order reaction. Such reactions are called pseudo first order reactions.

example

Inversion of cane sugar is another pseudo first order reaction.



$$\text{Rate} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

Temperature Dependence of the Rate of a Reaction

□ It has been found that for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.

The temperature dependence of the rate of a chemical reaction can be accurately explained by

Arrhenius equation .

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

where A is *the Arrhenius factor* or the *frequency factor*. It is also called *pre-exponential factor*. It is a constant specific to a particular reaction. R is *gas constant* and E_a is *activation energy measured in joules/mole (J mol⁻¹)*.



According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate (Fig. 4.6).

It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.



Fig. 4.6: *Formation of HI through the intermediate*

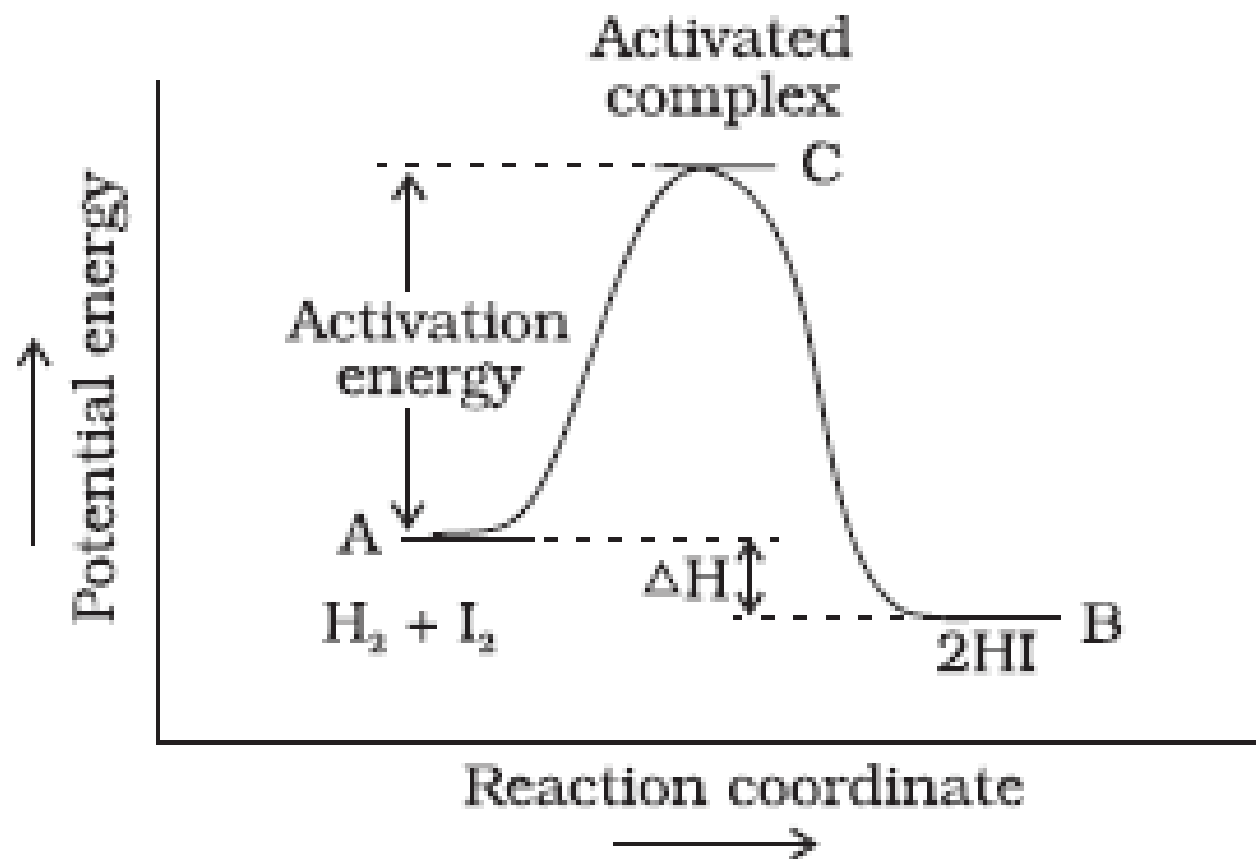


Fig. 4.7: Diagram showing plot of potential energy vs reaction coordinate.

Maxwell and Boltzmann distribution of k.e

- All the molecules in the reacting species do not have the same kinetic energy.
- Since it is difficult to predict the behaviour of any one molecule with precision, **Ludwig Boltzmann** and **James Clark Maxwell** used statistics to predict the behaviour of large number of molecules.
- According to them, the distribution of kinetic energy may be described by plotting the **fraction of molecules** (NE/NT) with a given kinetic energy (E) vs **kinetic energy** (Fig. 4.8).
- Here, NE is the number of molecules with energy E and NT is total number of molecules.

Maxwell Boltzmann distribution curve

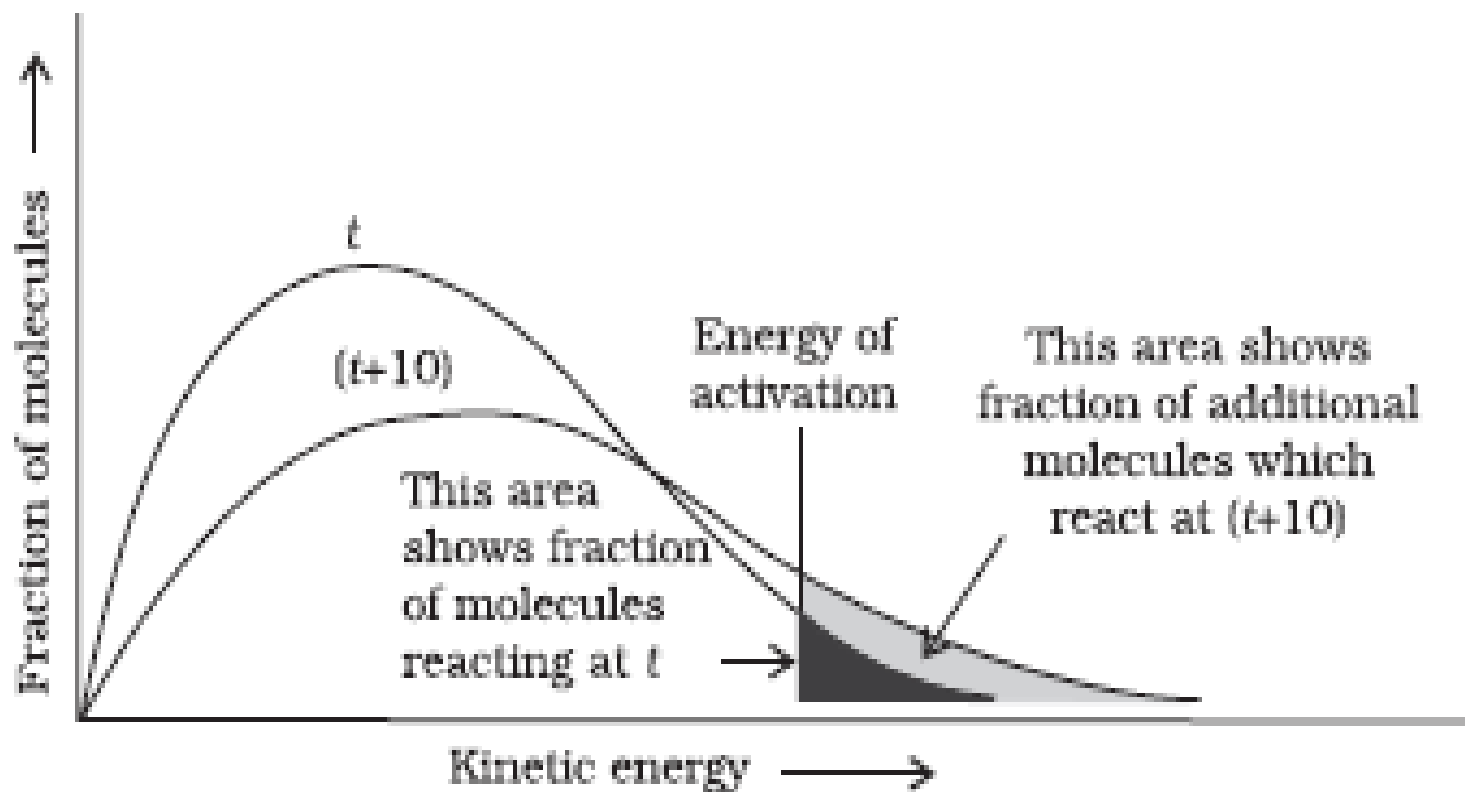


Fig. 4.9: Distribution curve showing temperature dependence of rate of a reaction

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

In the Arrhenius equation (4.18) the factor $e^{-E_a / RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a . Taking natural logarithm of both sides of equation (4.18)

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (4.19)$$

The plot of **ln k** vs **1/T** gives a straight line according to the equation (4.19) as shown in the next slide.

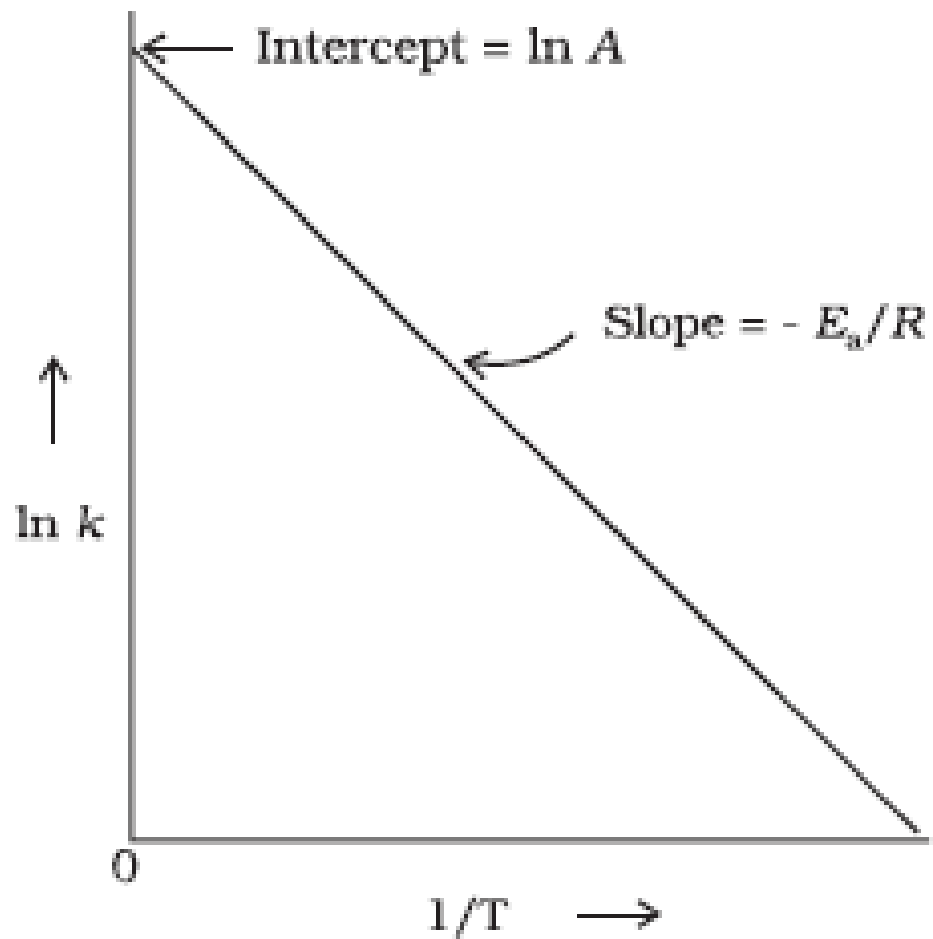


Fig. 4.10: A plot between $\ln k$ and $1/T$

In Fig. 4.10, slope = $-\frac{E_a}{R}$ and intercept = $\ln A$. So we can calculate E_a and A using these values.

At temperature T_1 , equation (4.19) is

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad (4.20)$$

At temperature T_2 , equation (4.19) is

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \quad (4.21)$$

(since A is constant for a given reaction)

k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively.

Subtracting equation (4.20) from (4.21), we obtain

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (4.22)$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

- I. The rate constants of a reaction at 500K and 700K are 0.02s^{-1} and 0.07s^{-1} respectively. Calculate the values of E_a and A .

• **Solution**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{0.07}{0.02} = \left(\frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \right) \left[\frac{700 - 500}{700 \times 500} \right]$$

$$0.544 = E_a \times 5.714 \times 10^{-4} / 19.15$$

$$E_a = 0.544 \times 19.15 / 5.714 \times 10^{-4} = 18230.8 \text{ J}$$

Since $k = Ae^{-E_a/RT}$

$$0.02 = Ae^{-18230.8/8.314 \times 500}$$

$$A = 0.02/0.012 = 1.61$$

problem

The first order rate constant for the decomposition of ethyl iodide by the reaction



at 600K is $1.60 \times 10^{-5} \text{ s}^{-1}$. Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700K.

Solution We know that

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

$$\log k_2 = \log k_1 + \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$= \log(1.60 \times 10^{-5}) + \frac{209000 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left[\frac{1}{600 \text{ K}} - \frac{1}{700 \text{ K}} \right]$$

$$\log k_2 = -4.796 + 2.599 = -2.197$$

$$k_2 = 6.36 \times 10^{-3} \text{ s}^{-1}$$

Effect of Catalyst

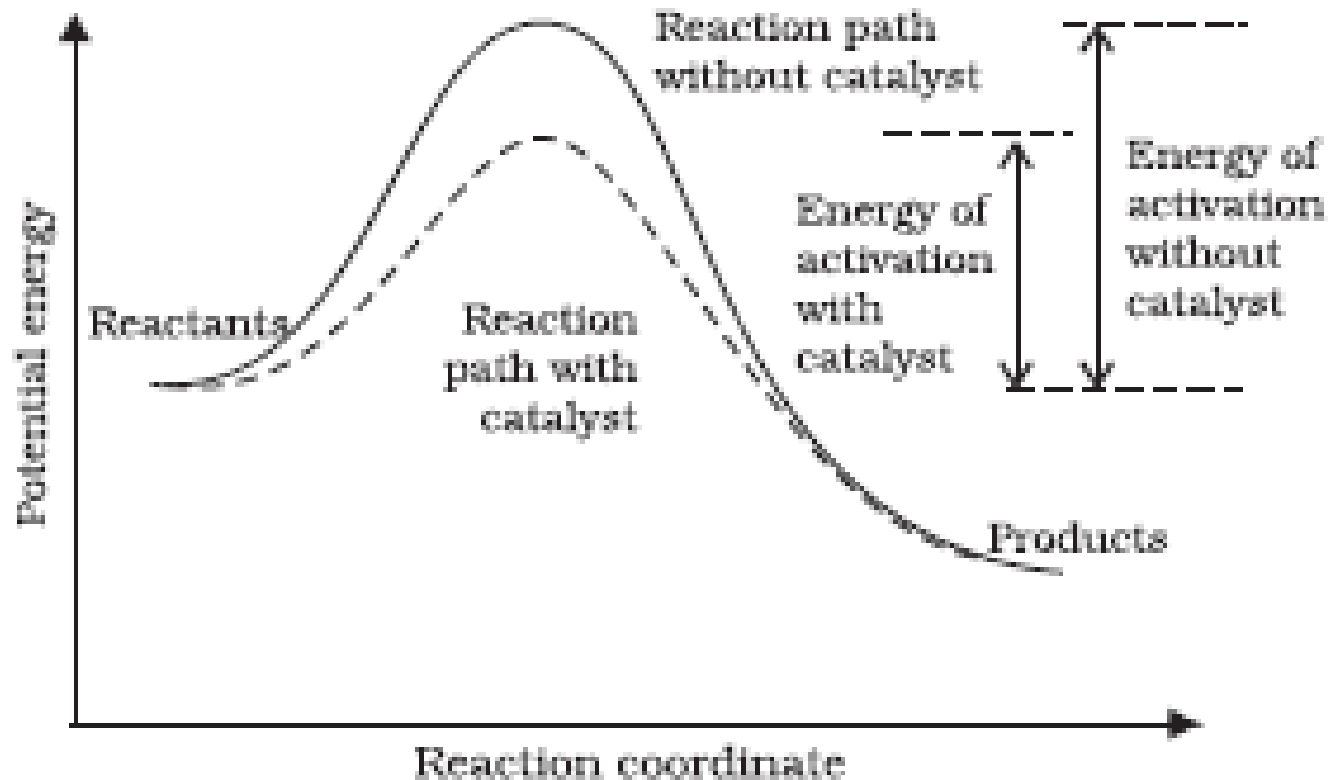


Fig. 4.11: *Effect of catalyst on activation energy*

Effect of Catalyst

- Catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change.
- The action of the catalyst can be explained by intermediate complex theory.
- According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.
- It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier

Effect of Catalyst

- A small amount of the catalyst can catalyse a large amount of reactants.
- A catalyst does not alter Gibbs energy, ΔG of a reaction.
- It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.
- It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, that is, it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

Collision Theory of Chemical Reactions

- Collision theory, which was developed by Max Trautz and William Lewis in 1916 -18,
- It is based on kinetic theory of gases.
- According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other.
- **The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).**

- For a bimolecular elementary reaction



rate of reaction can be expressed as

$$\text{Rate} = Z_{AB} e^{-E_a/RT} \quad (4.23)$$

where Z_{AB} represents the collision frequency of reactants, A and B and $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a . Comparing (4.23) with Arrhenius equation, we can say that A is related to collision frequency.

Effective collisions

- The collisions in which molecules collide with sufficient kinetic energy (called threshold energy^{*}) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as **effective collisions**.

Proper orientation

- formation of methanol from bromoethane depends upon the orientation of reactant molecules.
- *The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed*

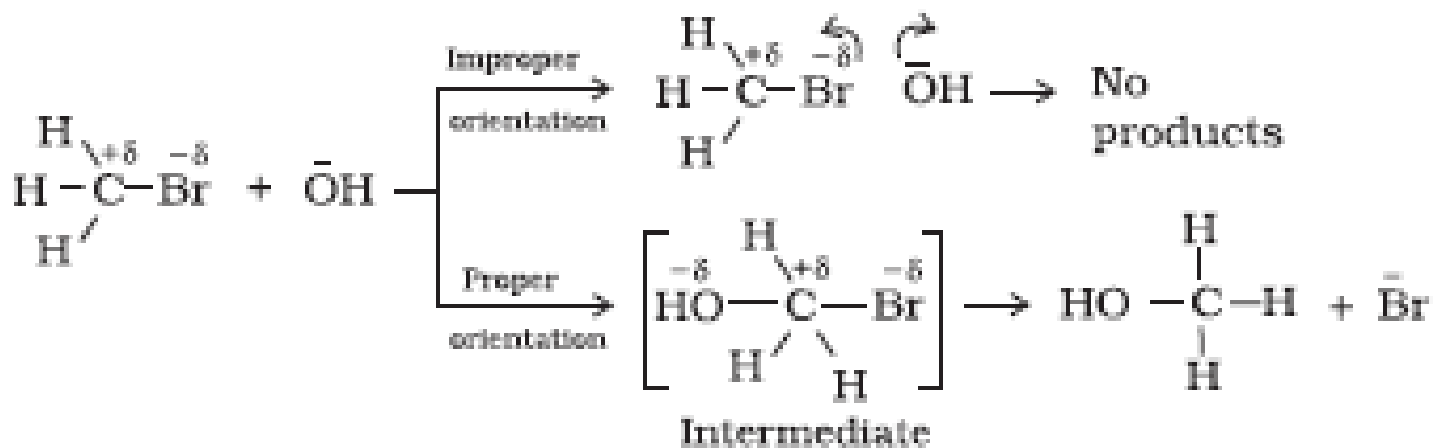


Fig. 4.12: Diagram showing molecules having proper and improper orientation

Probability or steric factor

- To account for effective collisions, another factor P , called the probability or steric factor is introduced.
- It takes into account the fact that in a collision, molecules must be properly oriented i.e.,

$$\text{Rate} = PZ_{AB}e^{-E_a/RT}$$

- Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

**End of the chapter
chemical kinetics**