



CHEMICAL KINETICS

CHAPTER -4



Introduction

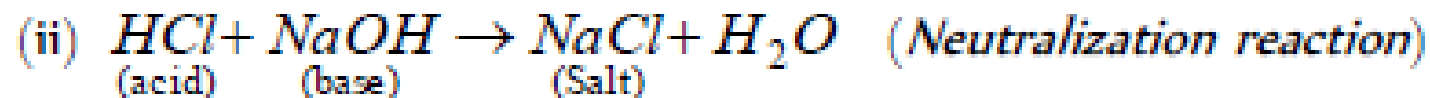
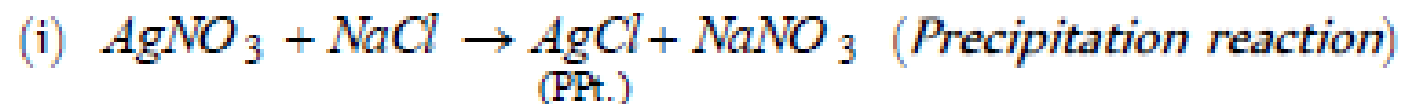
- *The branch of physical chemistry which deals with the rate at which the chemical reactions occur, the mechanism by which the chemical reactions take place and the influence of various factors such as concentration, temperature, pressure, catalyst etc., on the reaction rates is called the chemical kinetics.*

Type of Chemical Reaction

On the basis of reaction rates, the chemical reactions have been classified into the following three types,

(i) **Very fast or instantaneous reactions** : These reactions occur at a very fast rate generally these reactions involve ionic species and known as ionic reactions. It is almost impossible to determine the rates of these reactions.

Examples



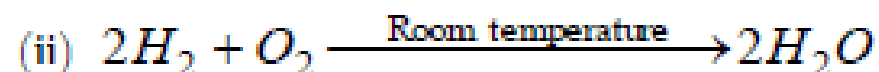
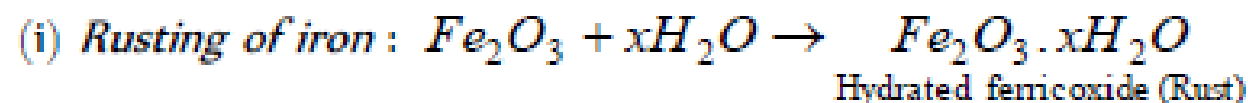
(2) **Moderate reaction** : These reactions proceed with a measurable rates at normal temperature and it is *these reactions are studied in chemical kinetics*. Mostly these reactions are molecular in nature.

Examples



(3) **Very slow reactions** : These reactions are extremely slow and take months together to show any measurable change.

Examples



Rate/Velocity of Reaction

The rate (speed or velocity) of a reaction is the change in concentration in per unit time.

$$\frac{\Delta x}{\Delta t} \text{ or } \frac{dx}{dt} = \left(\frac{x_2 - x_1}{t_2 - t_1} \right)$$

where Δx or dx is the concentration change, *i.e.*, $(x_2 - x_1)$ in the time interval Δt or dt , *i.e.*, $(t_2 - t_1)$.

Concentration is generally expressed in active mass, *i.e.*, mole L

- The rate measured over a long time interval is called *average rate* and the rate measured for an infinitesimally small time interval is called *instantaneous rate* and

$$\text{Instantaneous rate} = (\text{Average rate})_{\Delta t \rightarrow 0}$$

Expression for General Reaction

- For the reaction $aA + bB \rightarrow cC + dD$

Rate of disappearance of a reactant is negative

$$-\frac{d[A]}{dt} = \text{Rate of disappearance of } A$$

$$-\frac{d[B]}{dt} = \text{Rate of disappearance of } B$$

Rate of formation of a product is positive

$$\frac{d[C]}{dt} = \text{Rate of formation of } C$$

$$\frac{d[D]}{dt} = \text{Rate of formation of } D$$

- In terms of stoichiometric coefficient rate may be expressed as

$$\frac{dx}{dt} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

Units

- The rate of reaction is always *positive*.
- The rate of chemical reaction decreases as the reaction proceeds.
- Unit of rate of a reaction = $\frac{\text{Unit of conc.}}{\text{Unit of time}} = \text{mole L}^{-1} \text{ time}^{-1}$

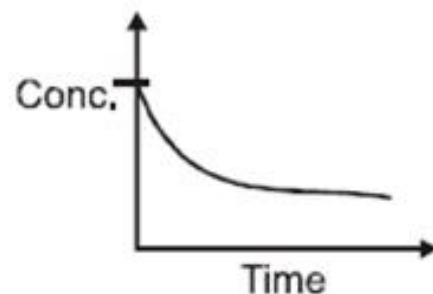
In term of gaseous reaction the unit is *atm time* and

$$\text{Rate in atm time} = \text{Rate in mole L}^{-1} \text{time}^{-1} \times RT$$

Factors Affecting the Rate of Reaction

- | | | |
|---------------------|-----------------------|---------------------------------------|
| 1. Concentration | 2. Temperature | 3. Nature of reactants and products |
| 4. Catalyst | 5. pH of the solution | 6. Dielectric constant of the medium. |
| 7. Radiations/light | 8. Pressure | 9. Electrical and magnetic field. |

1. **Effect of concentration :** We known from law of mass action that Rate is proportional to concentration of reactants. " So rate of reaction decreases with passage of time, since concentration of reactants decreases.



2. **Effect of temperature :** Will be discussed later.

Nature of Reactant and Product

3. Effect of nature of reactants and Products :

(a) Physical state of reactants :

Gaseous state > Liquid state > Solid state

Decreasing order of rate of reaction.

because collisions in homogeneous system are more effective than heterogenous system.

(b) Physical size of reactants : As we decreases the particle size rate of reaction increases since surface area increases.

(c) Chemical nature of reactants :

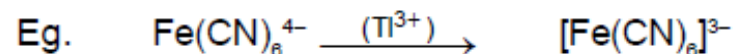
- ☐ If more bonds are to be broken, the rate of reaction will be slow.
- ☐ Similarly bond strength is more, rate of reaction will be slow.

Other Factors-

4. Effect of Catalyst :

- Presence of positive catalyst lower down the activation energy hence increases the rate of reaction.
- Presence of negative catalyst increases activation energy hence decreases the rate of reaction.

5. Effect of pH of solution :



This reaction takes place with appreciable rate in acidic medium, but does not take place in basic medium.

- ## 6. Effect of dielectric constant of the medium :
- More is the dielectric constant of the medium greater will be the rate of ionic reactions.
- ## 7. Effect of radiations/light :
- Radiation are useful for photochemical reaction.
- ## 8. Effect of pressure :
- Pressure is important factor for gaseous reaction.
- ## 9. Effect of electrical & Magnetic field :
- Electric and magnetic fields are rate determining factors if a reaction involves polar species.

Rate Law-

The representation of rate of reaction in terms of the concentration of the reactants is called the rate law. It can only be established by experiments.

Generally rate law expressions are not simple and these may differ for the same reaction on conditions under which the reaction is being carried out.

But for large number of reactions starting with pure reactants we can obtain simple rate laws. For these reactions :

$$\text{Rate} \propto (\text{conc.})^{\text{order}}$$

$$\text{Rate} = K (\text{conc.})^{\text{order}} \quad \text{This is the differential rate equation or rate expression.}$$

Where K = Rate constant = specific reaction rate = rate of reaction when concentration is unity

unit of K = $(\text{conc})^{1-\text{order}} \text{ time}^{-1}$

Order of Reaction

The total number of molecules or atoms whose concentration determine the rate of reaction is known as order of reaction.

Order of reaction = Sum of exponents of the conc. terms in rate law

For the reaction $x\text{A} + y\text{B} \rightarrow \text{Products}$

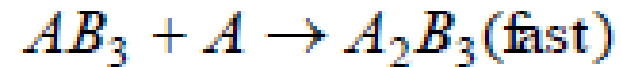
The rate law is $\text{Rate} = [\text{A}]^x [\text{B}]^y$

Then the overall order of reaction. $n = x + y$

where x and y are the orders with respect to individual reactants.

Complex Reaction

- If reaction is in the form of reaction mechanism then the order is determined by the slowest step of mechanism.



(Here, the overall order of reaction is equal to two.)

Example of Order of Reaction

Reaction	Rate law	Order
(i) $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$	$R = K [\text{N}_2\text{O}_5]^1$	1
(ii) $5\text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) \longrightarrow 3\text{Br}_2(\ell) + 3\text{H}_2\text{O}(\ell)$	$R = K [\text{Br}^-] [\text{BrO}_3^-] [\text{H}^+]^2$	$1 + 1 + 2 = 4$
(iii) $\text{H}_2(\text{Para}) \longrightarrow \text{H}_2(\text{ortho})$	$R = K [\text{H}_2(\text{Para})]^{3/2}$	$3/2$
(iv) $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \longrightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$	$R = K [\text{NO}_2]^2 [\text{CO}]^0$	$2 + 0 = 2$
(v) $2\text{O}_3(\text{g}) \longrightarrow 3\text{O}_2(\text{g})$	$R = K [\text{O}_3]^2 [\text{O}_2]^{-1}$	$2 - 1 = 1$
(vi) $\text{H}_2 + \text{Cl}_2 \xrightarrow{h\nu} 2\text{HCl}$	$R = K [\text{H}_2]^0 [\text{Cl}_2]^0$	$0 + 0 = 0$

The reaction (ii) does not take place in one single step. It is almost impossible for all the 12 molecules of the reactants to be in a state of encounter simultaneously. Such a reaction is called **complex reaction** and takes place in a sequence of a number of **elementary reactions**. For an elementary reaction the sum of stoichiometric coefficients = order of the reactions. But for complex reactions order is to be experimentally calculated.

Question

In a catalytic experiment involving the Haber's process, $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$, the rate of reaction was measured as rate = $2 \times 10^{-4} \text{ M.s}^{-1}$. If there were no side reactions, express the rate of reaction in terms of (a) N_2 (b) H_2 ?

For each reaction below, express the rates of change of [product] and [reactant] in the correct relationship to each other.



Types of Order of Reaction

Zero order reactions :

For a zero order reaction

General rate law is, Rate = $k [\text{conc.}]^0 = \text{constant}$

If C_0 is the initial concentration of a reactant and C_t is the concentration at time 't' then

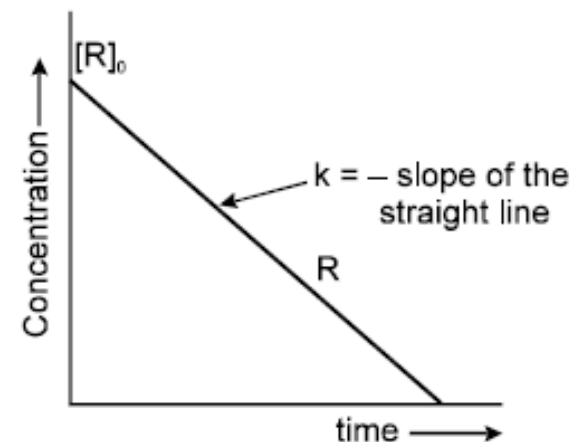
$$\text{Rate} = k = \frac{C_0 - C_t}{t} \quad \text{or} \quad kt = C_0 - C_t \quad \text{or} \quad C_t = C_0 - kt$$

Unit of K is same as that of Rate = $\text{mol lit}^{-1} \text{sec}^{-1}$.

$$\text{Time for completion} = \frac{C_0}{k}$$

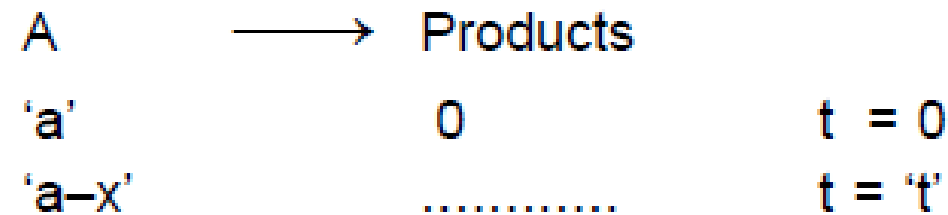
$$t_{1/2} \text{ (half life period)} \quad \text{at } t_{1/2}, C_t = \frac{C_0}{2}, \text{ so } kt_{1/2} = \frac{C_0}{2} \Rightarrow t_{1/2} = \frac{C_0}{2k}$$

$$\therefore t_{1/2} \propto C_0$$



First Order of Reaction

Let a 1st order reaction is



Let $\frac{dx}{dt}$ be the rate of reaction at time 't'

$$\therefore \frac{dx}{dt} = k(a-x)^1 \quad \text{or} \quad \frac{dx}{a-x} = k dt.$$

$$\text{On solving } t = \frac{2.303}{k} \log \frac{a}{a-x} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

Equation of 1st Order

- Time period 0 to T

$$k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

- Time period t₁ to t₂

Interval formula :

$$k = \frac{2.303}{(t_2 - t_1)} \log \frac{C_1}{C_2}$$

Half Life

Half life time ($t_{1/2}$)

$$k = \frac{2.303}{t_{1/2}} \log \frac{2C_0}{C_0} \Rightarrow$$

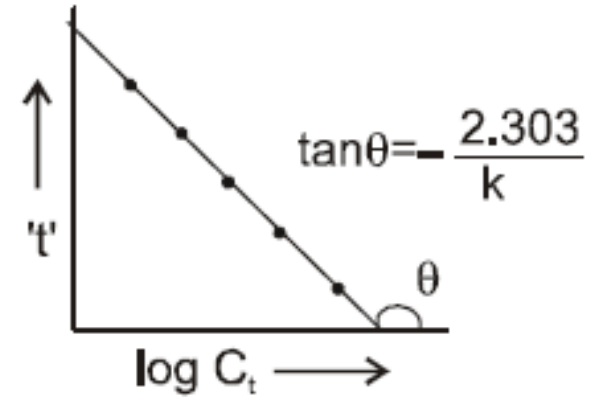
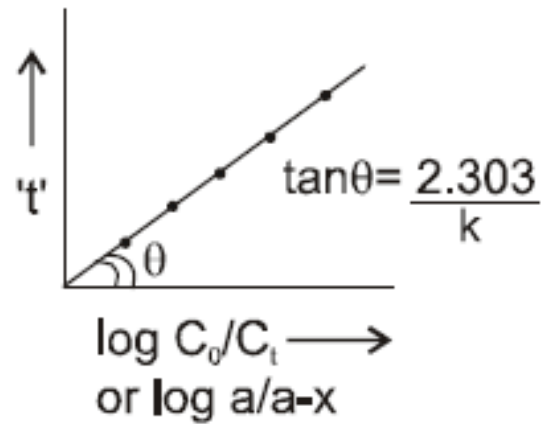
$$t_{1/2} = \frac{2.303 \log 2}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

\therefore Half life period for a 1st order reaction is a constant quantity.

Graphical Representation of 1st order

Graphical Representation :

$$t = -\frac{2.303}{k} \log C_t + \frac{2.303}{R} \log C_0$$



Question

Calculate $\frac{t_{0.75}}{t_{0.50}}$ for a 1st order reaction :

At least how many half-lives should elapse for a 1st order reaction $A \longrightarrow$ products so that the reaction is at least 95% completed ? (log 2 = 0.3)

(A) 4

(B) 5

(C) 6

(D) 7

Question for Practice

Rate of formation of SO_3 in the following reaction $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ is 100 g min^{-1} . Hence rate of disappearance of O_2 is :

- (A) 50 g min^{-1} (B) 40 g min^{-1} (C) 200 g min^{-1} (D) 20 g min^{-1}

The rate constant of the reaction $\text{A} \rightarrow 2\text{B}$ is $1.0 \times 10^{-3} \text{ mol lit}^{-1} \text{ min}^{-1}$, if the initial concentration of A is $1.0 \text{ mole lit}^{-1}$ what would be the concentration of B after 100 minutes.

- (A) 0.1 mol lit^{-1} (B) 0.2 mol lit^{-1} (C) 0.9 mol lit^{-1} (D) 1.8 mol lit^{-1}

For a reaction $2\text{A} + \text{B} \rightarrow \text{product}$, rate law is $-\frac{d[\text{A}]}{dt} = k[\text{A}]$. At a time when $t = \frac{1}{k}$, concentration of the reactant is : (C_0 = initial concentration)

- (A) $\frac{C_0}{e}$ (B) $C_0 e$ (C) $\frac{C_0}{e^2}$ (D) $\frac{1}{C_0}$

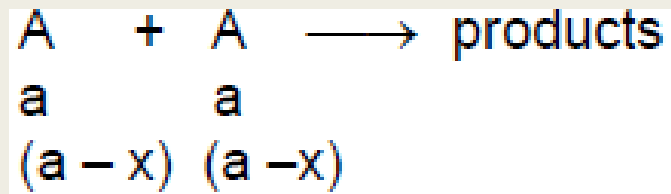
Write the units of the rate constants for a (i) Zeroth order, (ii) half order, (iii) first order, (iv) $3/2$ order, (v) second order, (vi) $5/2$ order, (vii) third order reactions.

First Order Growth of Reaction

$$k = \frac{2.303}{t} \log_{10} \left(\frac{a + x}{a} \right)$$

Second Order of Reaction

- If Reactant are same



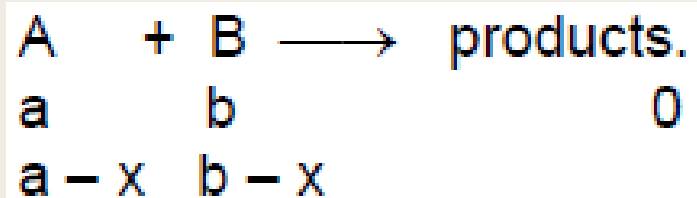
$$\therefore \frac{dx}{dt} = k (a-x)^2$$

$$\Rightarrow \int_0^x \frac{dx}{(a-x)^2} = \int k dt$$

$$\Rightarrow \left(\frac{1}{(a-x)} \right)_0^x = kt$$

$$\Rightarrow \frac{1}{(a-x)} - \frac{1}{a} = kt \quad \text{or} \quad \frac{1}{C_t} - \frac{1}{C_0} = kt$$

If reactant are different



Rate law

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

$$\int_0^x \frac{dx}{(a - x) (b - x)} = \int_0^t k dt$$

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

Pseudo 1st Order of Reaction

A second order (or of higher order) reactions can be converted into a first order reaction if the other reactant is taken in large excess. Such first order reactions are known as pseudo first order reactions.

∴ For $A + B \longrightarrow \text{Products}$ [Rate = $K [A]^1 [B]^1$]

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

Now if 'B' is taken in large excess $b \gg a$.

$$\therefore k = \frac{2.303}{-bt} \log \frac{(a-x)}{a} \quad \Rightarrow \quad k = \frac{2.303}{bt} \log \frac{a}{a-x}$$

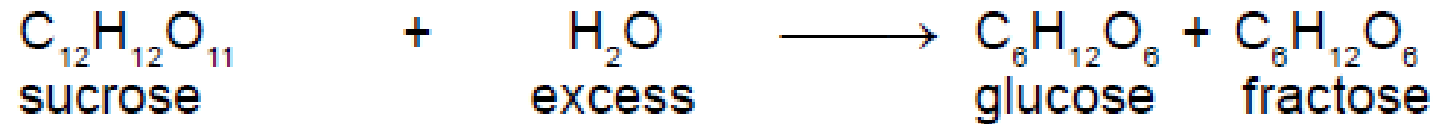
∴ 'b' is very large can be taken as constant

$$\Rightarrow kb = \frac{2.303}{t} \log \frac{a}{a-x} \quad \Rightarrow \quad k' = \frac{2.303}{t} \log \frac{a}{a-x}$$

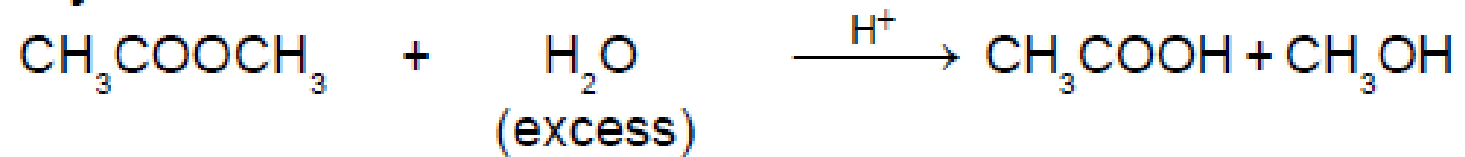
Examples

- **Examples of Pseudo 1st order reactions :**

(a) Hydrolysis of canesugar :



(b) Hydrolysis of esters :



Conclusion

	Zero Order	First-Order	Second-Order	n th order
Differential Rate law	$-\frac{\Delta[A]}{\Delta t} = k[A]^0$	$-\frac{\Delta[A]}{\Delta t} = k[A]$	$-\frac{\Delta[A]}{\Delta t} = k[A]^2$	$-\frac{\Delta[A]}{\Delta t} = k[A]^n$
(Integrated Rate law)	$[A]_t = [A]_0 - kt$	$\ln [A]_t = -kt + \ln [A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{(A_t)^{n-1}} - \frac{1}{(A_0)^{n-1}} = (n-1)kt$
Linear graph	$[A]_t$ v/s t	$\ln [A]$ v/s t	$\frac{1}{[A]}$ v/s t	$\frac{1}{(A_t)^{n-1}}$ v/s t
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$ (depends on $[A]_0$)	$t_{1/2} = \frac{0.693}{k}$ (independent of $[A]_0$)	$t_{1/2} = \frac{1}{k[A]_0}$ (depends on $[A]_0$)	$t_{1/2} \propto \frac{1}{(A_0)^{n-1}}$

Method for calculation of Order of Reaction

Initial rate method :

- By comparison of different initial rates of a reaction by varying the concentration of one of the reactants while others are kept constant

$$r = k [A]^a [B]^b [C]^c \quad \text{if} \quad \begin{array}{l} [B] = \text{constant} \\ [C] = \text{constant} \end{array}$$

then for two different initial concentrations of A we have

$$r_{01} = k [A_0]_1^a \quad \& \quad r_{02} = k [A_0]_2^a$$

$$\Rightarrow \frac{r_{01}}{r_{02}} = \left(\frac{[A_0]_1}{[A_0]_2} \right)^a$$

or in log form we have

$$a = \frac{\log(r_{01}/r_{02})}{\log([A_0]_1/[A_0]_2)}$$

Question

For the reaction $A + B \longrightarrow \text{products}$
the following data were obtained :

initial rate (<i>mole/liter.sec</i>)	0.030	0.059	0.060	0.090	0.089
[A] (<i>mole/liter</i>)	0.10	0.20	0.20	0.30	0.30
[B] (<i>mole/liter</i>)	0.20	0.20	0.30	0.30	0.50

Write the rate equation for this reaction. Be sure to evaluate k.

(A) $\cdot 2$

(B) $\cdot 3$

(C) $\cdot 4$

(D) $\cdot 5$

Solution

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

$$\text{From data I.} \quad 0.030 = K [0.10]^x [0.20]^y \quad (1)$$

$$\text{From data II.} \quad 0.059 = K [0.20]^x [0.20]^y \quad (2)$$

$$\text{From III.} \quad 0.060 = K [0.20]^x [0.30]^y \quad (3)$$

divide 1 equation by (2)

$$\frac{0.030}{0.059} = \frac{K[0.10]^x [0.20]^y}{K[0.20]^x [0.30]^y}$$

$$\Rightarrow x = 1$$

Then divide (2) equation by (3)

$$\frac{0.059}{0.060} = \frac{K[0.20]^x [0.20]^y}{K[0.20]^x [0.30]^y}$$

$$\Rightarrow y = 0$$

Put the value of x and y in (1) equation

$$0.030 = K[0.10]^1 [0.20]^0$$

$$K = \frac{0.030}{0.10} = 0.3 \text{ Sec}^{-1}$$

Half Life Method

Method of half lives :

The half lives of each order is unique so by comparing half lives we can determine order

for n^{th} order reaction $t_{1/2} \propto \frac{1}{[R_0]^{n-1}}$

$$\frac{t_{1/2}}{t'_{1/2}} = \frac{(R_0')^{n-1}}{(R_0)^{n-1}}$$

integrated rate law method :

It is method of hit and trial. By checking where the kinetic data (experimental data) best fits into which integrated rate law , we determine the order. It can also be done graphically.

Ostwald's isolation method :

This method is useful for reaction which involve a large number of reactants. In this method, the concentration of all the reactants are taken in large excess except that of one, so if

$$\text{rate} = k [A]^a [B]^b [C]^c = k_0 [A]^a$$

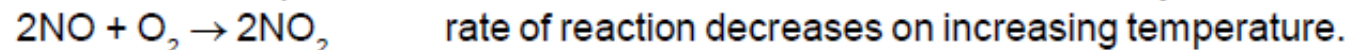
Then value of 'a' can be calculated by previous methods and similarly 'b' and 'c' can also be calculated

Effect of Temperature on rate of Reaction

The effect of temperature on reaction rate was expressed in terms of **temperature coefficient** which was defined as the ratio of rate of reaction at two different temperature differing by 10°C (usually these temperatures were taken as 25°C and 35°C)

$$\text{T.C.} = \frac{K_{t+10}}{K_t} \approx 2 \text{ to } 3 \text{ (for most of the reactions)}$$

For some reactions temperature coefficient is also found to be less than unity. For example



Question

For a reaction T.C. = 2, Calculate $\frac{k_{40^\circ\text{C}}}{k_{25^\circ\text{C}}}$ for this reaction.

(A) $\sqrt{8}$

(B) $\sqrt{7}$

(C) $\sqrt{6}$

(D) $\sqrt{4}$

Sol.
$$\frac{k_2}{k_1} = (\text{T.C.})^{\frac{\Delta t}{10}} = (2)^{\frac{15}{10}} = (2)^{\frac{3}{2}} = \sqrt{8}$$

Question

Pressure measurement :

Progress of gaseous reaction can be monitored by measuring total pressure at a fixed volume & temperature.

1st order reaction $A(g) \longrightarrow nB(g)$; Find the expression for K in terms of P_0 , P_t and n

Arrhenius Theory

It is based upon kinetic theory of gases.

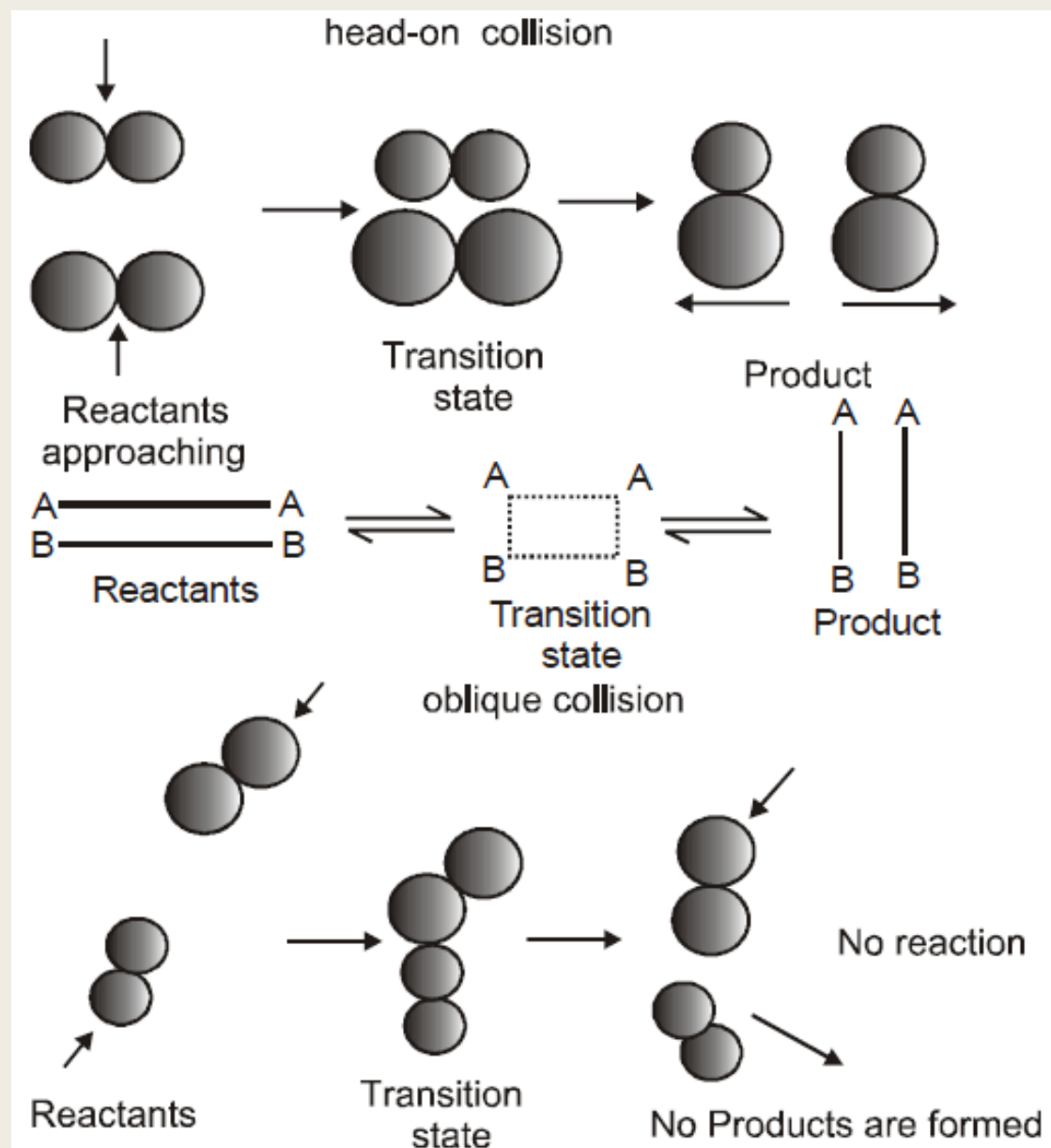
Arrhenius proposed a theory of reaction rate which states as follows :

- A chemical reaction takes place due to the collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z).
- Every collision does not bring a chemical change. The collision that actually produce the products are effective collision. For a collision to be effective the following two barriers are to be cleared.

Energy barrier : The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur is known as threshold energy.

“The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy (E_a)”

Orientation barrier : Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper direction to make collision effective. Following diagrams can explain importance of suitable direction for collision.



Important Points

- Collision to be effective the colliding molecules must possess some certain minimum energy called threshold energy of the reaction.
- Reactant molecules having energy equal or greater than the threshold are called active molecules and those having energy less than the threshold are called passive molecules.
- At a given temperature there exists a dynamic equilibrium between active and passive molecules. The process of transformation from passive to active molecules being endothermic, increase of temperature increases the number of active molecules and hence the reaction.
Passive molecules \rightleftharpoons Active molecules, $\Delta H = +ve$

Concept of Activation

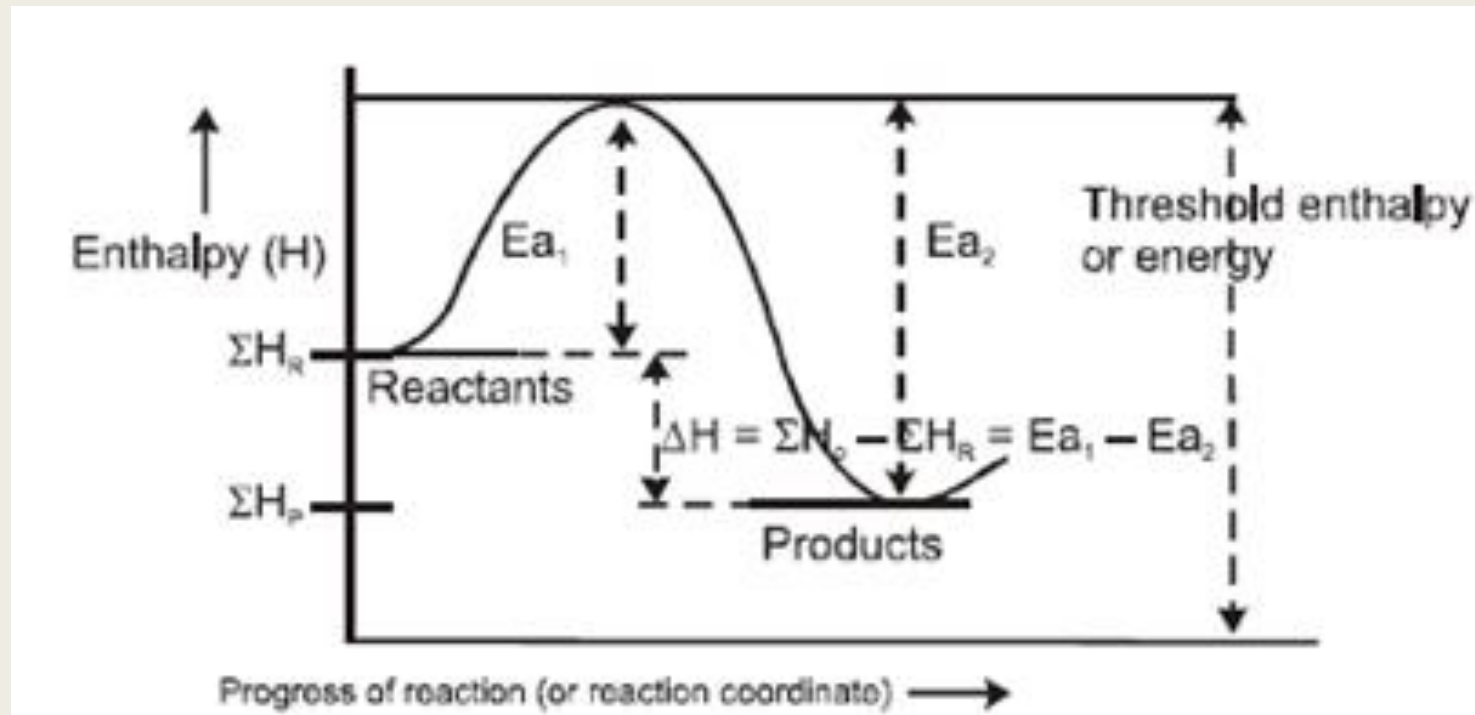
The extra amount of energy which the reactant molecules (having energy less than the threshold) must acquire so that their mutual collision may lead to the breaking of bond(s) and hence the energy is known as energy of activation of the reaction. It is denoted by the symbol E_a . Thus,

$$E_a = \text{Threshold energy} - \text{Actual average energy}$$

E_a is expressed in kcal mol⁻¹ or kJ mol⁻¹.

The essence of Arrhenius Theory of reaction rate is that there exists an energy barrier in the reaction path between reactant(s) and product(s) and for reaction to occur the reactant molecules must climb over the top of the barrier which they do by collision. The existence of energy barrier and concept of E_a can be understood from the following diagram.

Diagram



ΣH_R = Summation of enthalpies of reactants

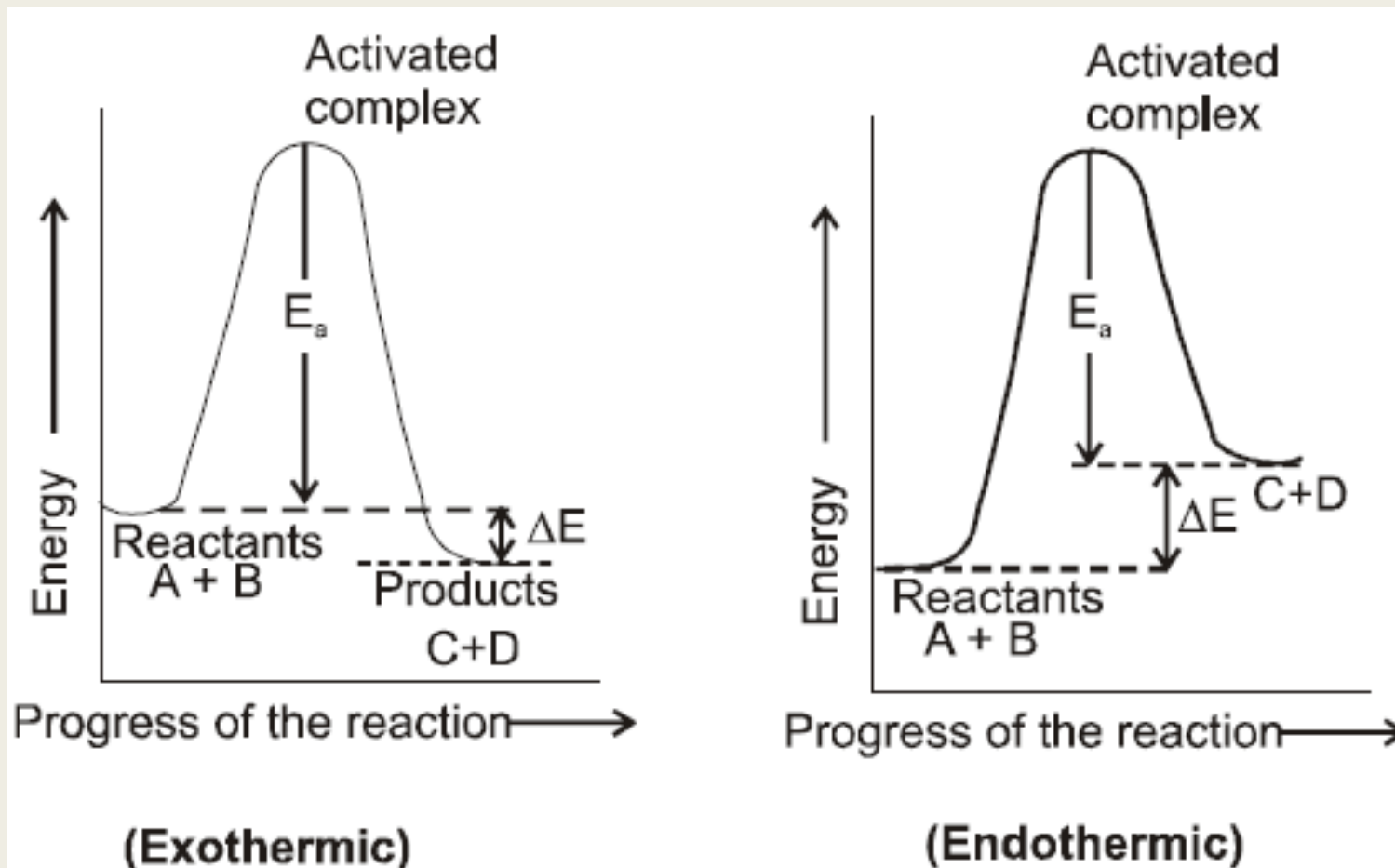
ΣH_P = Summation of enthalpies of products

ΔH = Enthalpy change during the reaction

Ea_1 = Energy of activation of the forward reaction

Ea_2 = Energy of activation of the backward reaction

Graph of Exothermic and Endothermic Process

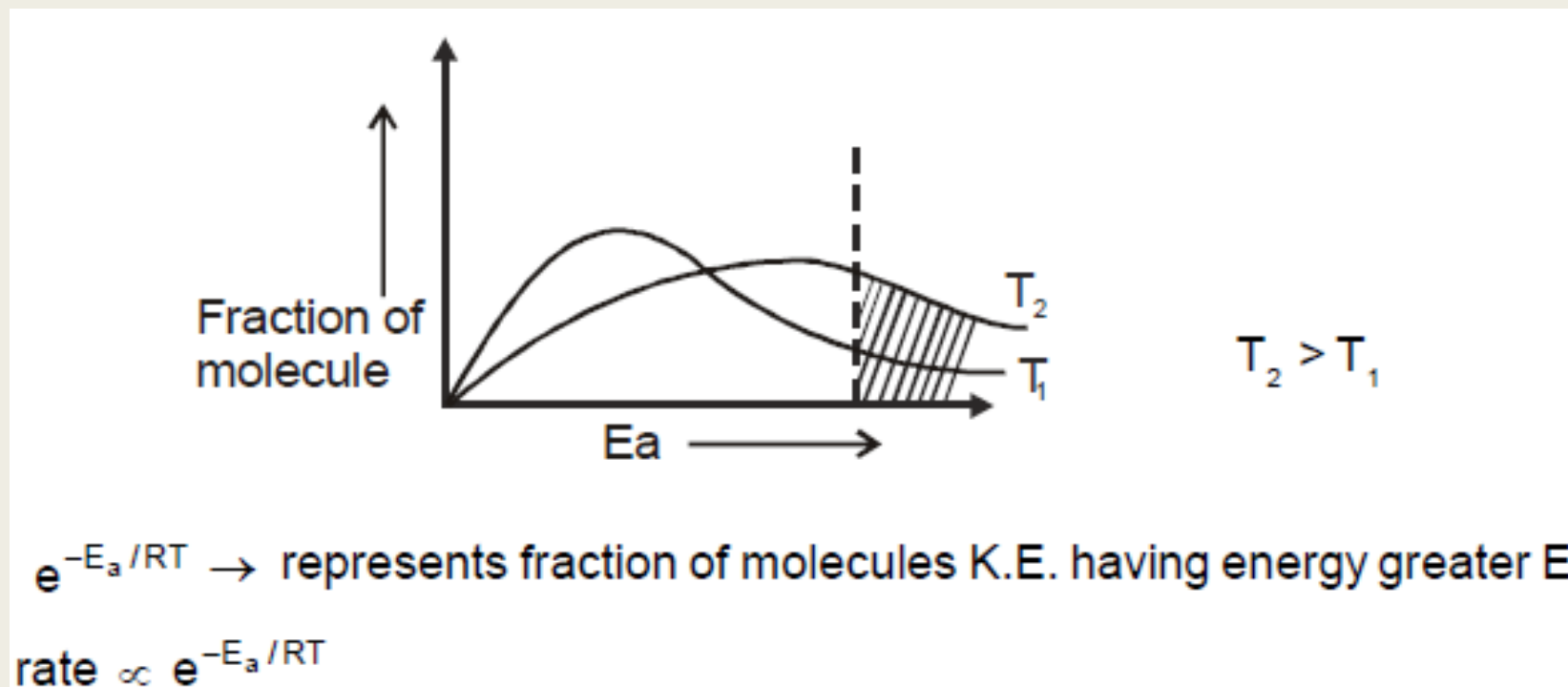


Rate of any chemical reaction = Collision frequency \times fraction of the total number of effective collision
= Collision frequency \times fraction of the total number of collision in which
K.E. of the colliding molecules equals to E_a or exceeds over it.

Important Points

Collision frequency is the number of collisions per unit volume per unit time. It is denoted by the symbol Z . Z is directly proportional to \sqrt{T} . By 10°C rise in temperature, so it is the fraction of the total number of effective collision that increases markedly resulting into marked increase in the reaction rate.

Collision Frequency Graph



dependence of rate on temperature is due to dependence of k on temperature.

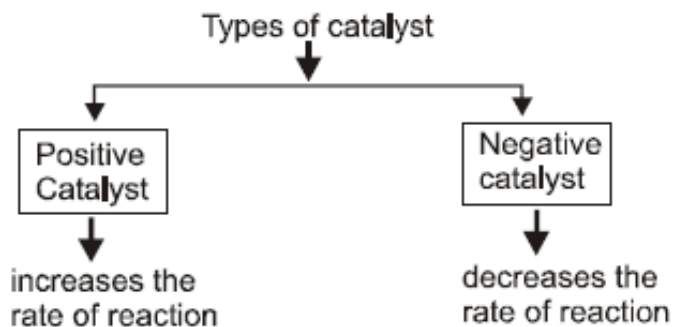
$$k \propto e^{-E_a/RT}$$

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

[Arrhenius equation]

Catalyst and Catalysis

A **catalyst** is a substance, which increases the rate of a reaction without itself being consumed at the end of the reaction, and the phenomenon is called **catalysis**.



Catalyst are generally foreign substances but sometimes one of the product may act as a catalyst and such catalyst is called “**auto catalyst**” and the phenomena is called **auto catalysis**.

General Characteristics of Catalyst

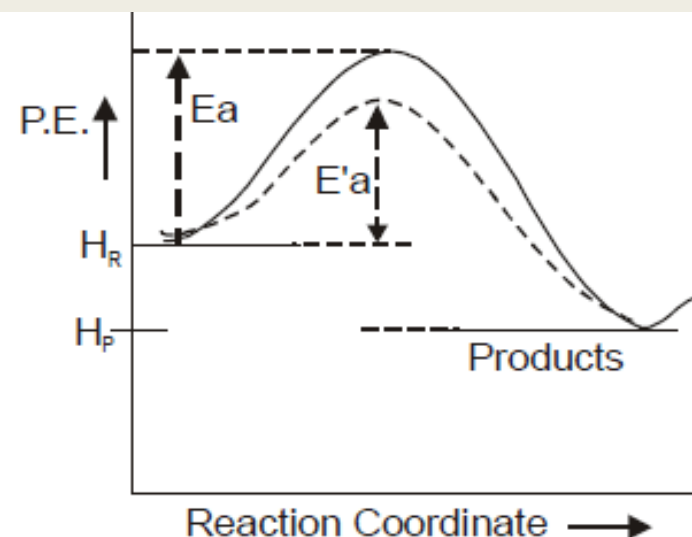
- A catalyst does not initiate the reaction. It simply fastens it.
- Only a small amount of catalyst can catalyse the reaction.
- A catalyst does not alter the position of equilibrium i.e. magnitude of equilibrium constant and hence ΔG° . It simply lowers the time needed to attain equilibrium. This means if a reversible reaction in absence of catalyst completes to go to the extent of 75% till attainment of equilibrium, and this state of equilibrium is attained in 20 minutes then in presence of a catalyst the reaction will go to 75% of completion before the attainment of equilibrium but the time needed for this will be less than 20 minutes.

A catalyst drives the reaction through a low energy path and hence E_a is less. That is, the function of the catalyst is to lower down the activation energy.

E_a = Energy of activation in absence of catalyst.

E'_a = Energy of activation in presence of catalyst.

$E_a - E'_a$ = lowering of activation energy by catalyst.



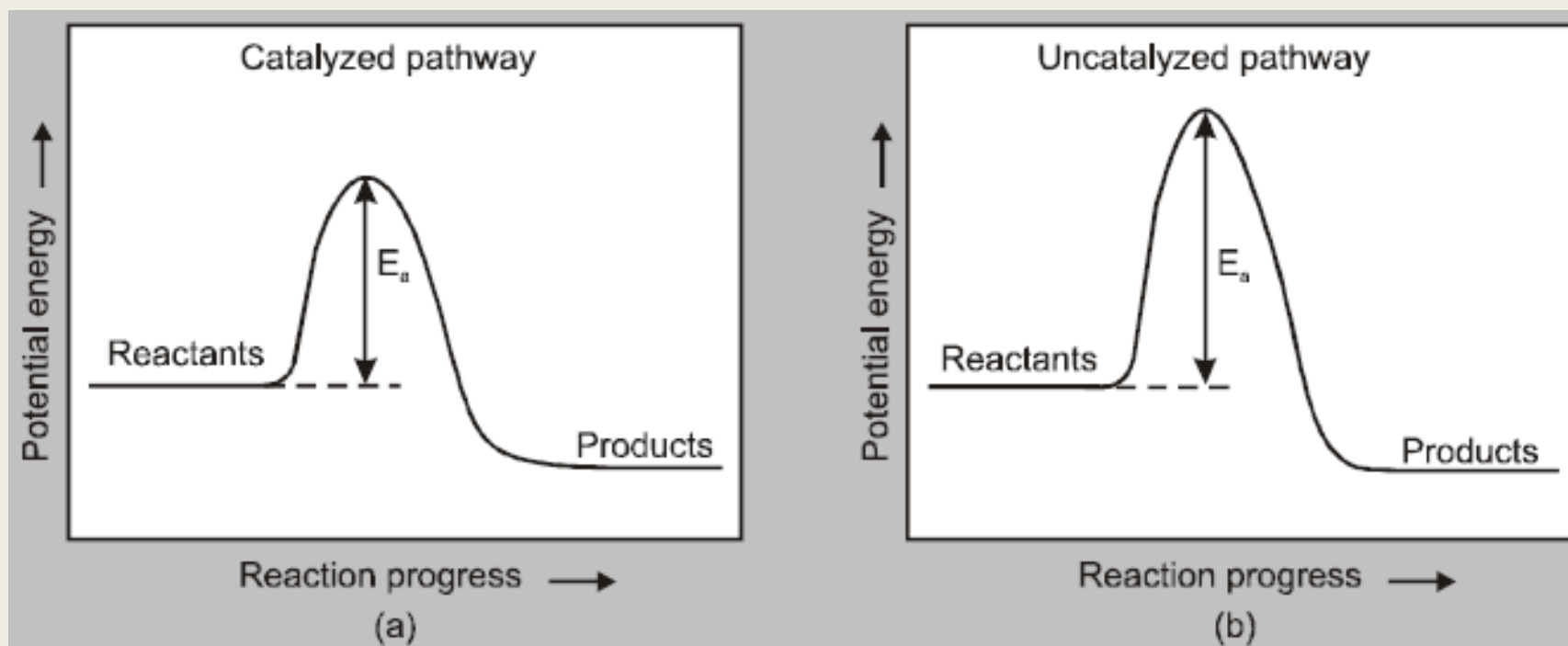
Comparison of ror with and without catalyst

If k and k_{cat} be the rate constant of a reaction at a given temperature T , and E_a and E'_a are the activation energies of the reaction in absence and presence of catalyst, respectively, the

$$\frac{k_{\text{cat}}}{k} = \frac{Ae^{-E'_a/RT}}{Ae^{-E_a/RT}} = Ae^{(E_a - E'_a)/RT}$$

Since $E_a - E'_a$ is positive so $k_{\text{cat}} > k$. the ratio $\frac{k_{\text{cat}}}{k}$ gives the number of times the rate of reaction will increase by the use of catalyst at a given temperature

Graph of catalyst or without Catalyst



Question

For the reaction $\text{CO(g)} + \text{Cl}_2\text{(g)} \longrightarrow \text{COCl}_2\text{(g)}$ under the same concentration conditions of the reactants, the rate of the reaction at 250°C is 1500 times as fast as the same reaction at 150°C . Calculate the activation energy of the reaction. If the frequency factor is $2.0 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, calculate the rate constant of the reaction at 150°C .

Solution

$$\text{Sol.} \quad \log \frac{k_2}{k_1} = \frac{E}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log 1500 = \frac{E}{2.303 \times 2} \times \frac{100}{523 \times 423}$$

$$E = \frac{3.1761 \times 2.303 \times 2 \times 523 \times 423}{100} = 32.36 \text{ kcal mol}^{-1}$$

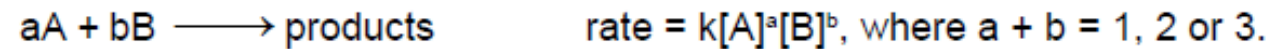
$$\log k = \log A - \frac{E}{2.303 RT} = \log (2.0 \times 10^{10}) - \frac{32360}{2.303 \times 2 \times 423} = 10.301 - 16.609 = -6.308$$

$$k = 4.92 \times 10^{-7} \text{ litres mol}^{-1} \text{ sec}^{-1}$$

Molecularity of Reaction

The number of molecules that react in an elementary step is the molecularity of the elementary reaction. Molecularity is defined only for the elementary reactions and not for complex reactions. No elementary reactions involving more than three molecules are known, because of very low probability of near-simultaneous collision of more than three molecules.

The rate law for the elementary reaction



For an elementary reaction, the orders in the rate law equal the coefficients of the reactants.

Comparison Between Order of reaction and Molecularity of Reaction

Molecularity of Reaction	Order of Reaction
<p>1. It is defined as the no. of molecules of reactant taking part in a chemical reaction</p> <p>eq $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}$ $m = 1$</p>	<p>1. It is defined as the sum of the power of concentration terms that appear in rate law.</p> <p>$\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}$. $\text{Rate} = k[\text{NH}_4\text{NO}_2]$</p>
<p>2. It is always a whole number</p> <p>It can neither be zero nor fractional.</p>	<p>2. It may be zero , fractional or integer.</p>
<p>3. It is derived from RDS in the mechanism of reaction.</p>	<p>3. It is derived from rate expression.</p>
<p>4. It is theoretical value.</p>	<p>4. It is experimental value.</p>
<p>5. Reactions with molecularity > 4 are rare.</p>	<p>5. Reactions with order of reaction > 4 are also rare.</p>
<p>6. Molecularity is independent of Pressure and temperature.</p>	<p>6. Order of reaction depends upon pressure and temperature.</p>

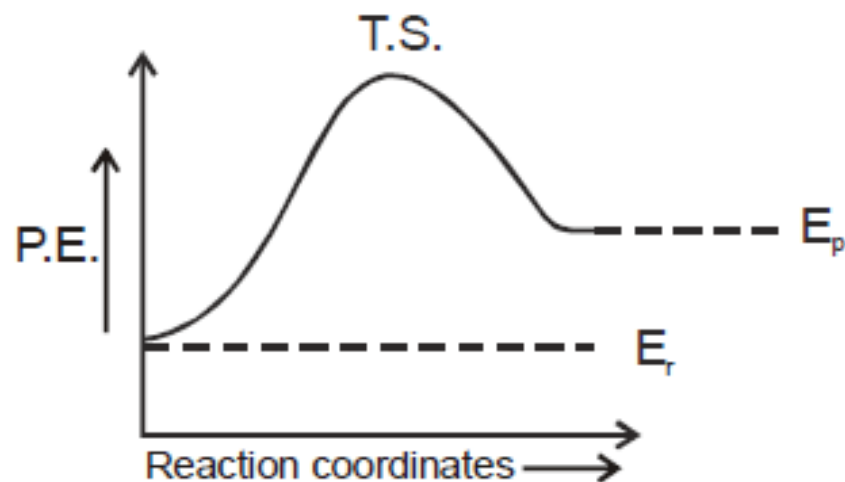
Mechanism of Reaction

Reactions can be divided into

- Elementary / simple / single step
- Complex / multi-step

ELEMENTARY REACTION :

These reaction take place in single step without formation of any intermediate



For elementary reaction we can define molecularity of the reaction which is equal to no of molecules which make transition state or activated complex because of collisions in proper orientation and with sufficient energy

Continue..

molecularity will always be a natural no

1 = unimolecular one molecule gets excited (like radioactivity)

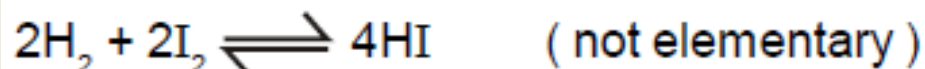
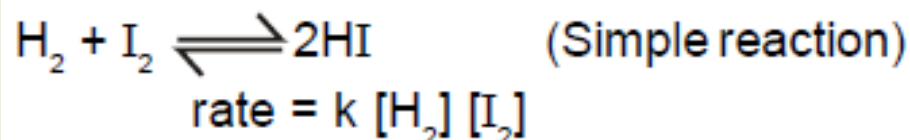
2 = bimolecular

3 = trimolecular

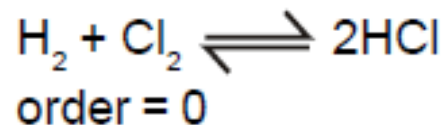
Molecularity ≤ 3 because the probability of simultaneous collision between 4 or more molecules in proper orientation is very low

For elementary reaction there is only single step and hence it is going to be rate determining step so order of an elementary reaction is its molecularity

Order of elementary reaction w.r.t. reactant = stoichiometric co-efficient of the reactant

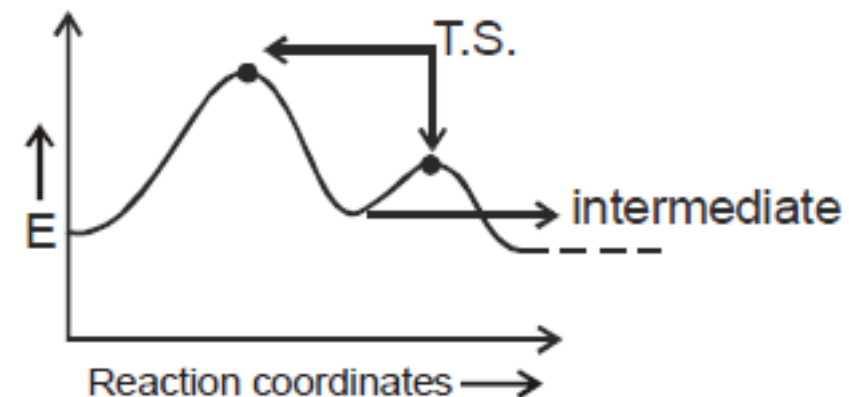


reaction obtained by multiplying an elementary reaction with some no will not be of elementary nature



Complex Reaction

Reaction which proceed in more than two steps. or having some mechanism. (sequence of elementary reaction in which any complex reaction proceeds)



For complex reaction each step of mechanism will be having its own molecularity but molecularity of net complex reaction will not be defined.

Order of complex reaction can be zero fractions whole no, even negative w.r.t. some species.

Order of reaction or rate law of reaction is calculated with the help of mechanism of the reaction generally using Rate determine step (R.D.S) if given.

Rate law of a reaction is always written in terms of conc. of reactant, products or catalysts but never in terms of conc. of intermediates.

Continue..

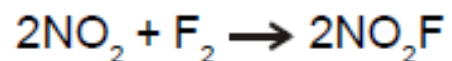
CALCULATION OF RATE LAW/ ORDER

(A) MECHANISM IN WHICH R.D.S. GIVEN

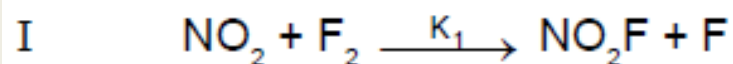
- (i) If R.D.S. involves only reactant, product or catalyst on reactant side
rate law of R.D.S. = rate law of reaction**

Question

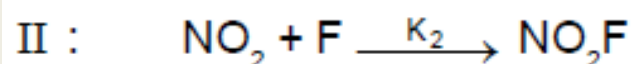
Calculate order and rate law of reaction



with help of mechanism



(slow) $\left[\begin{array}{l} \text{molecularity} = 2 \text{ for both} \end{array} \right.$



(fast)

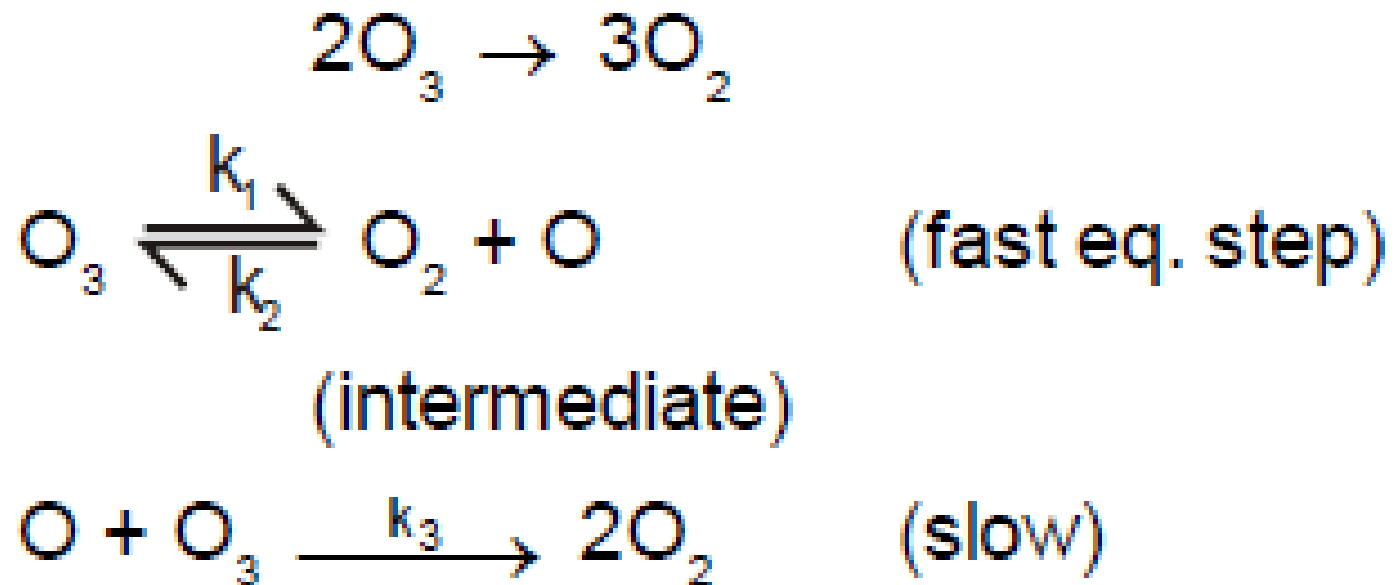
Calculate rate law



For Reversible Reaction

RDS is having intermediate on reactant side

To calculate order, we have to specify [intermediate] in expression of rate law in terms of conc. of [R], [P] or catalyst with the help of same equilibrium step given in mechanism.



solution

From R.D.S., $\text{rate} = k_3 [\text{O}_3] [\text{O}]$

According to equilibrium step.

$$K_{\text{eq.}} = \frac{k_1}{k_2} = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]}$$

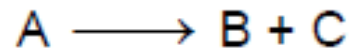
$$[\text{O}] = \left[\frac{k_1 [\text{O}_3]}{k_2 [\text{O}_2]} \right]$$

$$\text{Rate} = k_3 [\text{O}_3] [\text{O}] = k_3 [\text{O}_3] \left[\frac{k_1 [\text{O}_3]}{k_2 [\text{O}_2]} \right]$$

$$\text{Rate} = \frac{k_1 k_3}{k_2} \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

Radioactivity

All radioactive disintegration follow 1st order kinetics.



Int. nuclide

N_0

At time t.

N

decay constant

$$\boxed{\frac{-dN}{dt} = \lambda N}$$

No. of nuclei
of A at time t

rate decay(A)

*

λ = Not dependent on temperature.

$$\frac{-dN}{dt} = \lambda N \quad ; \quad \int \frac{-dN}{N} = \int \lambda dt$$

$$\boxed{N = N_0 e^{-\lambda t}}$$

$$\boxed{\lambda = \frac{1}{t} \ln \left(\frac{N_0}{N} \right)}$$

Half life & Average Life of Radioactivity

Half life :

$$t = t_{1/2} ; \quad N = \frac{N_0}{2}$$

$$\lambda = \frac{1}{t_{1/2}} \ln \left(\frac{N_0}{N_0/2} \right)$$

$$\lambda = \frac{\ln 2}{t_{1/2}}$$

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

Average life :

$$T_{\text{avg.}} = \frac{1}{\lambda} = 1.44 t_{1/2}$$

Unit of Radioactivity

curie (C_i) = 3.7×10^{10} dps

millicurie (mC_i) = 3.7×10^7 dps

microcurie (μC_i) = 3.7×10^4 dps

Rutherford (1 Rd) = 1×10^6 dps