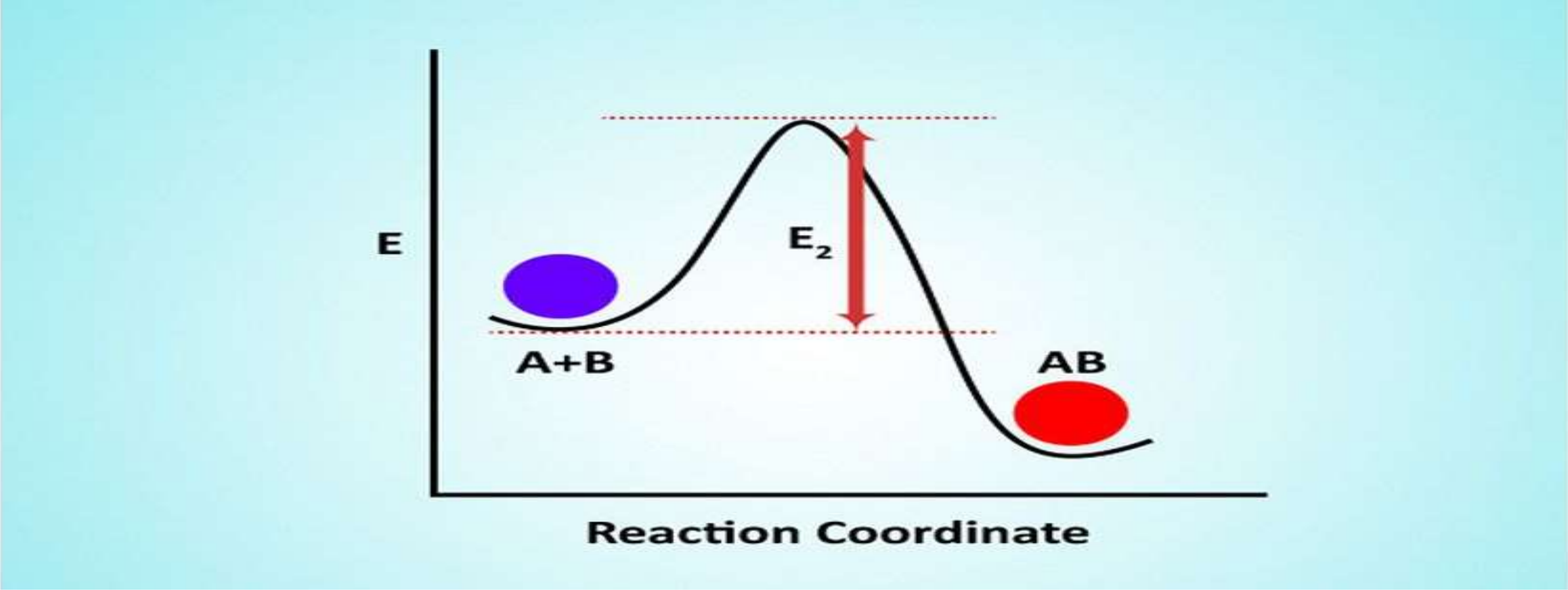
Chemical Kinetics 2



General methods for the determination of order of reaction

1. Hit and trial method(By using integral rate equations)

i).Substitution method

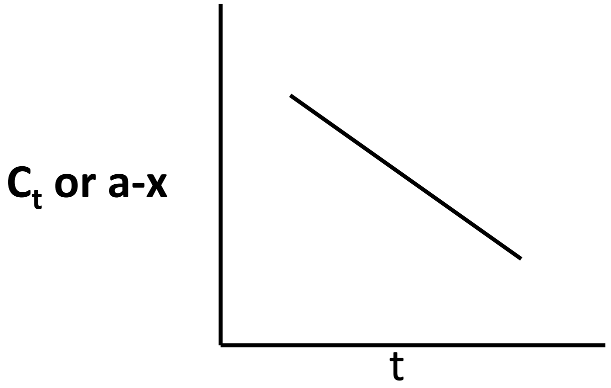
- Different C_t and C_o values at different 't' values are substituted in integral rate equations
- The rate equation which gives the constant value of k gives the order of the reaction
- $k = \frac{1}{t}[Co - Ct]$ ……… for zero order
- $K = \frac{2.303}{t} \log \frac{Co}{Ct}$ ………..for 1st order
- $k = \frac{1}{t}\left[\frac{1}{Ct} - \frac{1}{Co}\right]$………for second order

General methods for the determination of order of reaction

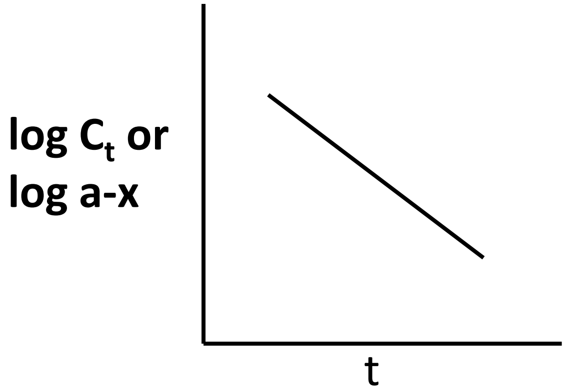
1. Hit and trial method(By using integral rate equations)

ii. Graphical method

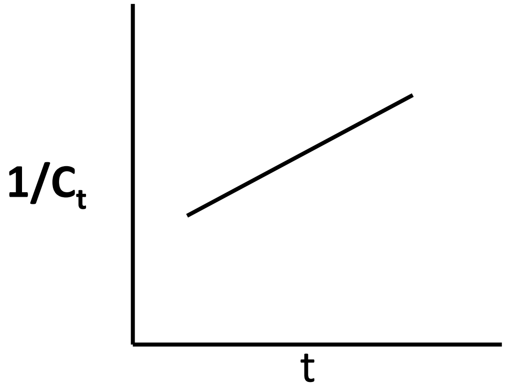
- Different integral rate equations are converted in to the equation of straight lines.
- Graph is plotted. The equation which gives straight line plot determines the order of the reaction
- $C_t = - kt + C_o$……for zero order
- $\log C_t = -\frac{kt}{2.303} + \log C_o$ …for 1st order
- $\frac{1}{C_t} = kt + \frac{1}{C_o}$ …. For 2nd order



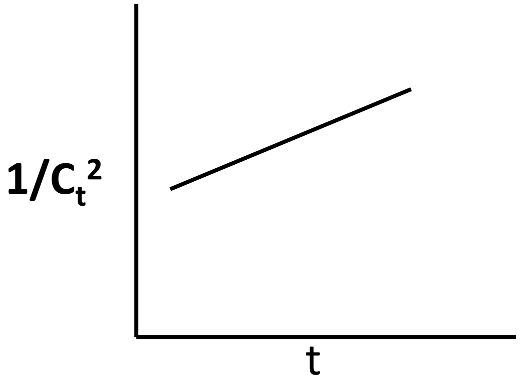
Zero order



1st order



2nd order



3rd order

General methods for the determination of order of reaction

2. Van’t Hoff’s differential method(By using differential rate equations)

- $\frac{dx}{dt} \alpha\, C^1$ for 1st order, $\frac{dx}{dt} \alpha\, C^2$ for 2nd order $\frac{dx}{dt} \alpha\, C^3$ for 3rd order
- For nth order , we can write $\frac{dx}{dt} \alpha\, C^n$ or $\frac{dx}{dt} = k\, C^n$ or $r = k\, C^n$ …………1

at two different concentrations we can write equation 1 as

$r_1 = k\, C_1^n$ ……………………………………2 $r_2 = k\, C_2^n$…………………3

Divide equation 2 by 3 we get

$\frac{r_1}{r_2} = \frac{kC_1^n}{kC_2^n} = \left(\frac{C_1}{C_2}\right)^n$ Now take log of this equation i.e.

$\log \frac{r_1}{r_2} = n \log \frac{C_1}{C_2}$ or $n = \log \frac{r_1}{r_2} \Big/ \log \frac{C_1}{C_2}$ Or $n = \frac{\log r_1 - \log r_2}{\log C_1 - \log C_2}$

General methods for the determination of order of reaction

3. Half life period method (Fractional change method)

- $t_{1/2}\ \alpha\ \frac{1}{a^0}$ for 1st order, $t_{1/2}\ \alpha\ \frac{1}{a^1}$ for 2nd order $t_{1/2}\ \alpha\ \frac{1}{a^2}$ for 3rd order
- So in general $t_{1/2}\ \alpha\ \frac{1}{a^{n-1}}$ ……………1

at two different initial concentrations, we can write equation 1 as

- $(t_{1/2})_1\ \alpha\ \frac{1}{{a_1}^{n-1}}$ ………2 $(t_{1/2})_2\ \alpha\ \frac{1}{{a_2}^{n-1}}$ …………3

Divide equation 2 by 3 we get

- $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{{a_2}^{n-1}}{{a_1}^{n-1}} = \left(\frac{a_2}{a_1}\right)^{n-1}$ Now take log of this equation
- we get $\log\frac{(t_{1/2})_1}{(t_{1/2})_2} = n\text{-}1 \log\frac{a_2}{a_1}$
- Or $n-1 = \frac{\log (t_{1/2})_1 - \log (t_{1/2})_2}{\log a_2 - \log a_1}$ or $n = 1 + \left[\frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log a_2 - \log a_1}\right]$

General methods for the determination of order of reaction

4. Ostwald's isolation method

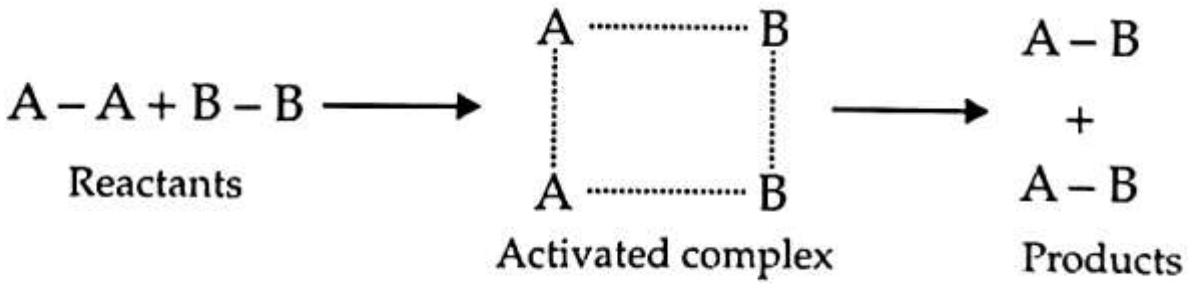
- In this method one of the reactants is isolated and others are taken in excess

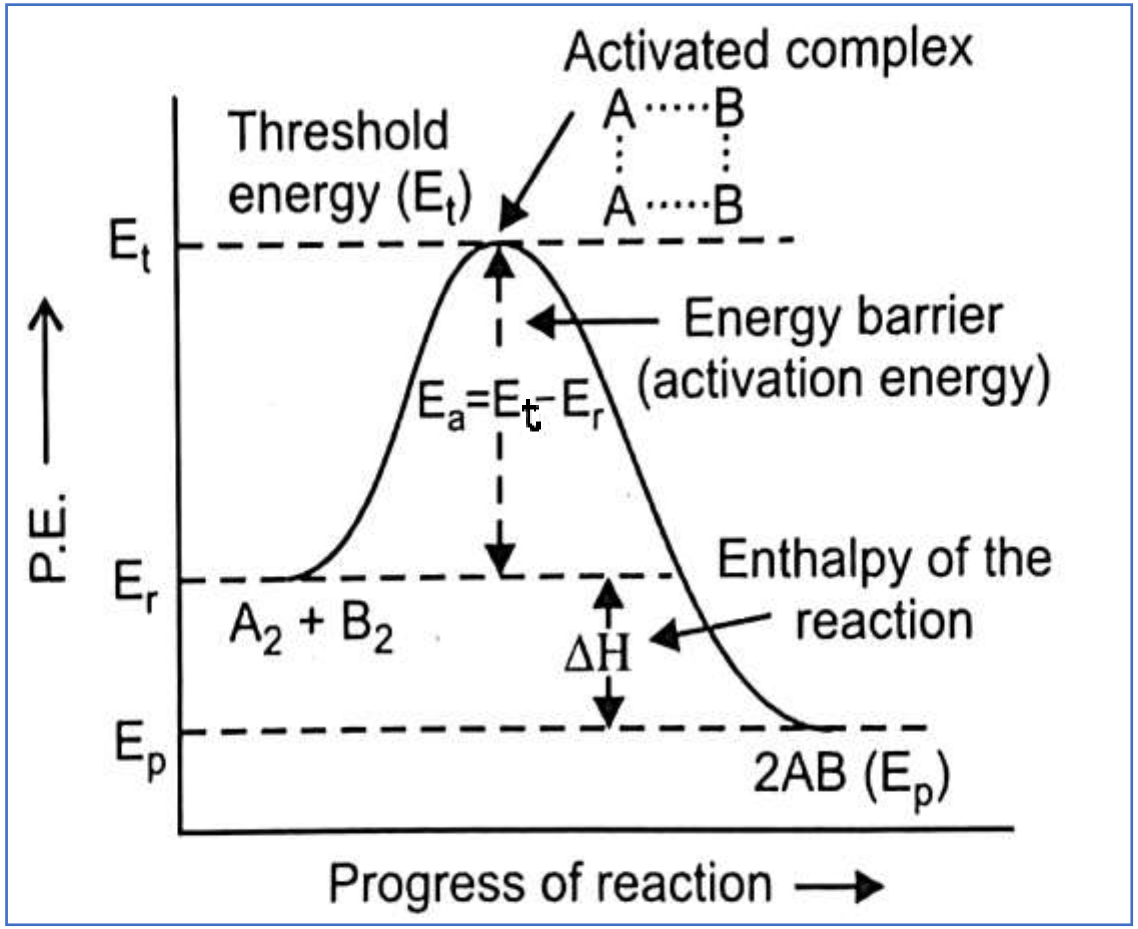
- aA + bB + cC → Products
- If A is isolated, B & C are taken in excess and change in conc. Of A will give order w.r.t A let it be x
- Similarly B & C are isolated and the order is determined and let it be y and z
- So overall order n = x + y + z

Concept of activation energy- Energy barrier

- **If reactants do not possess threshold amount of energy then extra amount of energy is supplied from outside.**
- **The excess amount of energy which is to be supplied is called as activation energy**
- **Activation Energy (E_a) = Threshold energy (E_t) – Energy possessed by the reactant molecules(E_r)**

- **Consider a reaction $A_2(g) + B_2(g) \rightarrow 2AB(g)$**





- **If activation energy is low then the reaction is fast**
- **And if the activation energy is high then the reaction is slow**

Calculation of activation energy from Arrhenius equation

- Arrhenius equation gives dependence of rate of reaction on temperature. It relates rate constant k with T as

- $K = A\,e^{-Ea/RT}$ here E_a is activation energy and A is frequency factor and exponential factor gives fraction of molecules having energy equal to or greater than E_a

❖ For calculation of E_a, take log of Arrhenius equation

- $\ln k = \ln A - \frac{E_a}{RT}$ …………1

- Now at two different temperatures we can write

- $\ln k_1 = \ln A - \frac{E_a}{RT_1}$ …………..2 & $\ln k_2 = \ln A - \frac{E_a}{RT_2}$ ………………..3

Calculation of activation energy from Arrhenius equation

- **Subtract eqn 2 from eqn. 3, we get**
- $\ln k_2 - \ln k_1 = \ln A - \frac{E_a}{RT_2} - \left(\ln A - \frac{E_a}{RT_1} \right) = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$
- Or $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ or $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_2}{T_1 T_2} \right)$

Calculation of activation energy from Arrhenius equation

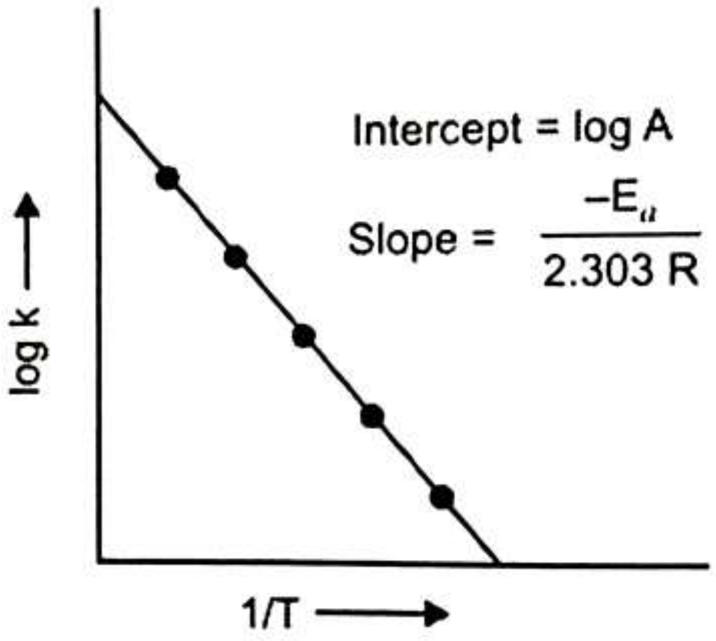
- E_a can also be determined graphically as

- $\ln k = \ln A - \frac{E_a}{RT}$ can be written as $\ln k = -\frac{E_a}{RT} + \ln A$
- $2.303 \log k = -\frac{E_a}{RT} + 2.303 \log A$ or $\log k = -\frac{E_a}{2.303\,RT} + \log A$ ………………..1

- Eqn 1 is of straight line

- Plot of log k vs 1/t gives a straight line
- From slope of straight line, We can get E_a

- $E_a = -\,2.303 \times R \times \text{Slope}$



Collision theory of reaction rates

- For reaction to take place, molecules undergo collisions.
- No. of effective collisions is only a fraction of total collisions.
- So we can write Rate = Z x f

  here Z is collision frequency and 'f' is fraction of effective collisions

- Now according to Maxwell – Boltzmann law of distribution of energies
- $f = \frac{\Delta N}{N} = e^{-Ea/RT}$ (Boltzmann fraction) So rate = $Z \times e^{-Ea/RT}$ …………………………..1

❖ For determining Z, Kinetic molecular theory of gases is used & following assumptions are made

1. The molecules are hard and rigid sphere
2. Molecules are non-interacting
3. Binary collisions are allowed while ternary collisions are ignored.

Collision theory of reaction rates

❑ Two cases

1. When Bimolecular collisions are between similar molecules

- ➢ A + A → Products

$$z_{AA} = \frac{1}{\sqrt{2}} \pi v \sigma_A^2 n_A^2$$

Now $v = \sqrt{\frac{8kT}{\pi m_A}}$ So we can write

$$z_{AA} = \frac{1}{\sqrt{2}} \pi \sigma_A^2 n_A^2 \sqrt{\frac{8kT}{\pi m_A}} = 2\sigma_A^2 n_A^2 \sqrt{\frac{\pi kT}{m_A}}$$

$$z_{AA} = 2\sigma_A^2 n_A^2 \sqrt{\frac{\pi (R/N) T}{M_A/N}} = 2\sigma_A^2 n_A^2 \sqrt{\frac{\pi RT}{M_A}}$$

collisions cm^{-3} s^{-1}

$$\text{Rate} = -\frac{dn_A}{dt} = 2\sigma_A^2 n_A^2 \sqrt{\frac{\pi RT}{M_A}} \times e^{-E_a/RT}$$

molecules cm^{-3} s^{-1}

Collision theory of reaction rates

- For every collision two molecules react so rate of reaction will be double

$$\text{Rate} = -dn_A/dt = 2\times\left(2\sigma_A^2 n_A^2\sqrt{\frac{\pi RT}{M_A}}e^{-E_a/RT}\right) \text{ molecules cm}^{-3}\text{ s}^{-1}$$

$$\text{Rate} = 4\sigma_A^2 n_A^2\sqrt{\frac{\pi RT}{M_A}}e^{-E_a/RT} \text{ molecules cm}^{-3}\text{ s}^{-1}$$

- Now according to chemical kinetics
  Rate = k n_A^2 so compare with upper equation

$$k = \boxed{4\sigma_A^2\sqrt{\frac{\pi RT}{M_A}}}e^{-E_a/RT} \text{ cm}^3\text{ molecule}^{-1}\ s^{-1}$$

- Now comparing with Arrhenius equation, we can derive expression for frequency factor

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

$$\underline{A} = \underline{4\sigma_A^2\sqrt{\frac{\pi RT}{M_A}}} \text{ cm}^3\text{ molecule}^{-1}\ s^{-1}$$

Collision theory of reaction rates

❖ In terms of molar concentrations, different equations can be changed as follows

- $C_A = \frac{\text{molecules}}{\text{c.c.}} = \frac{n_A/N}{10^{-3}L} = \frac{n_A}{N} \times 10^3$ moles L^{-1} or $n_A = \frac{NC_A}{10^3}$ or $dn_A = \frac{N}{10^3} dC_A$ OR $dC_A = \frac{10^3}{N} dn_A$

- $\frac{dC_A}{dt} = \frac{10^3}{N}\frac{dn_A}{dt}$ or $-\frac{dC_A}{dt} = \frac{10^3}{N}\left(-\frac{dn_A}{dt}\right)$ or $-\frac{dC_A}{dt} = \frac{10^3}{N} 4\sigma_A^2 n_A^2 \sqrt{\frac{\pi RT}{M_A}} \times e^{-E_a/RT}$

- Now put the value of n_A,

- Rate = $-\frac{dC_A}{dt} = \frac{10^3}{N}\left(\frac{NC_A}{10^3}\right)^{₹} \times 4\sigma_A^2 \sqrt{\frac{\pi RT}{M_A}} e^{-E_a/RT}$

- Or Rate = $-\frac{dC_A}{dt} = \frac{N}{10^3} \text{X } 4\sigma_A^2 \; CA^2 \sqrt{\frac{\pi RT}{M_A}} e^{-E_a/RT}$ mol/L/s ……………………..1

- According to chemical kinetics
- Rate = k C_A^2 ……………………..2 compare eqn 1 sand 2

- $k = \frac{N}{10^3} \text{X } 4\sigma_A^2 \sqrt{\frac{\pi RT}{M_A}} e^{-E_a/RT}$ L/mol/s …………………………..3

Collision theory of reaction rates

- $k = \boxed{\frac{N}{10^3} \times 4\sigma_A^2 \times \sqrt{\frac{\pi RT}{M_A}}}\, e^{-E_a/RT}$ L/mol/s 3

- Compare equation 3 with Arrhenius equation $K = \boxed{A}\, e^{-Ea/RT}$

- $A = \frac{N}{10^3} \times 4\sigma_A^2 \times \sqrt{\frac{\pi RT}{M_A}}$ L/mol/s

Collision theory of reaction rates

- ❑ **Case II**
- ❖ **When the bimolecular collision is between two dissimilar molecules**
- ➢ **A + B → Products**

$$Z_{AB} = \sigma_{AB}^2 \sqrt{\frac{8\pi kT}{\mu}} n_A n_B \qquad \sigma_{AB} = \left(\frac{\sigma_A + \sigma_B}{2}\right),$$

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B} \qquad \frac{1}{\mu} = \frac{m_A + m_B}{m_A m_B} \qquad \mu = \frac{m_A m_B}{m_A + m_B}$$

$$Z_{AB} = \sigma_{AB}^2 \sqrt{8\pi kT\left(\frac{m_A + m_B}{m_A m_B}\right)} n_A n_B \qquad m_A = \frac{M_A}{N}, m_B = \frac{M_B}{N} \text{ and } k = \frac{R}{N}$$

Collision theory of reaction rates

$$Z_{AB} = \sigma_{AB}^2 \sqrt{\frac{8\pi\left(\frac{R}{N}\right)T\left(\frac{M_A}{N}+\frac{M_B}{N}\right)}{\frac{M_A}{N}\times\frac{M_B}{N}}}\, n_A n_B = \sigma_{AB}^2\sqrt{\frac{8\pi RT(M_A+M_B)}{M_A M_B}}\, n_A n_B$$

collisions $cm^{-3}\ s^{-1}$

$$\text{Rate} = -\frac{dn_A}{dt} = -\frac{dn_B}{dt} = Z_{AB} \times e^{-E_a/RT}$$

Putting the value of Z_{AB}, we get

$$\text{Rate} = -\frac{dn_A}{dt} = -\frac{dn_B}{dt} = \sigma_{AB}^2\sqrt{8\pi RT\left(\frac{M_A+M_B}{M_A M_B}\right)}\, n_A n_B\, e^{-E_a/RT} \quad ①$$

molecules $cm^{-3}\ s^{-1}$

- Now according to chemical kinetics

  Rate = k $n_A n_B$ ……………..2
- Compare equations 1 & 2 We get

$$k = \sigma_{AB}^2\sqrt{8\pi RT\left(\frac{M_A+M_B}{M_A M_B}\right)}\, e^{-E_a/RT} \quad ③$$

cm^3 molecule $^{-1}s^{-1}$

- According to Arrhenius equation $k = A\, e^{-Ea/RT}$
- On comparing the Arrhenius equation with equation 3 we can obtain expression for frequency factor A

$$A = \sigma_{AB}^2\sqrt{8\pi RT\left(\frac{M_A+M_B}{M_A M_B}\right)}\ cm^3\ molecule^{-1}\ s^{-1}$$

Collision theory of reaction rates

- In terms of molar concentrations, different equations can be changed as follows

- $C_A = \frac{\text{molecules}}{\text{c.c.}} = \frac{n_A/N}{10^{-3}L} = \frac{n_A}{N} \times 10^3$ moles L^{-1} or $n_A = \frac{NC_A}{10^3}$ or $dn_A = \frac{N}{10^3}\, dC_A$ OR $dC_A = \frac{10^3}{N}\, dn_A$

- $\frac{dC_A}{dt} = \frac{10^3}{N}\frac{dn_A}{dt}$

- $C_B = \frac{\text{molecules}}{\text{c.c.}} = \frac{n_B/N}{10^{-3}L} = \frac{n_B}{N} \times 10^3$ moles L^{-1} or $n_B = \frac{NC_B}{10^3}$ or $dn_B = \frac{N}{10^3}\, dC_B$ OR $dC_B = \frac{10^3}{N}\, dn_B$

- $\frac{dC_B}{dt} = \frac{10^3}{N}\frac{dn_B}{dt}$

- Now rate = $-\frac{dC_A}{dt} = \frac{10^3}{N}\left(-\frac{dn_A}{dt}\right)$ Now put these values of rate $-\frac{dn_A}{dt}$, n_A & n_B, we get

- Rate = $-\frac{dC_A}{dt} = \frac{\cancel{10^3}}{\cancel{N}}\, \sigma_{AB}^2 \sqrt{8\pi RT\left(\frac{M_A+M_B}{M_AM_B}\right)}\; \frac{\cancel{N}C_A}{\cancel{10^3}}\; \frac{NC_B}{10^3}\, e^{-Ea/RT}$

- Rate = $-\frac{dC_A}{dt} = \frac{N}{10^3}\, \sigma_{AB}^2 \sqrt{8\pi RT\left(\frac{M_A+M_B}{M_AM_B}\right)}\; C_A\, C_B\, e^{-Ea/RT}$ mol/L/s

Collision theory of reaction rates

- **According to chemical kinetics**
- Rate = k C_A C_B ……………………..2 compare eqn 1 sand 2
- K = $\frac{N}{10^3}\sigma_{AB}^2\sqrt{8\pi RT\left(\frac{M_A+M_B}{M_AM_B}\right)}$ e $^{-Ea/RT}$ L/mol/s……………………..3
- Compare equation 3 with Arrhenius equation k = A e $^{-Ea/RT}$ to get expression for frequency factor A

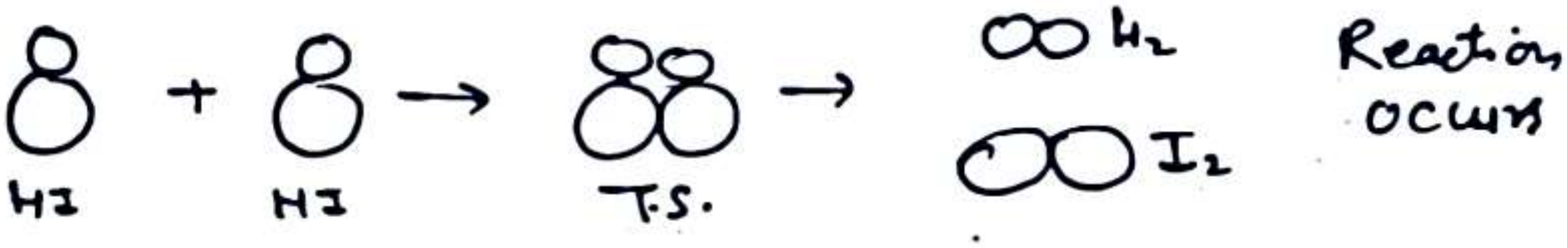
$$A = \frac{N}{10^3}\sigma_{AB}^2\sqrt{8\pi RT\left(\frac{M_A+M_B}{M_AM_B}\right)}\ \text{L/mol/s}$$

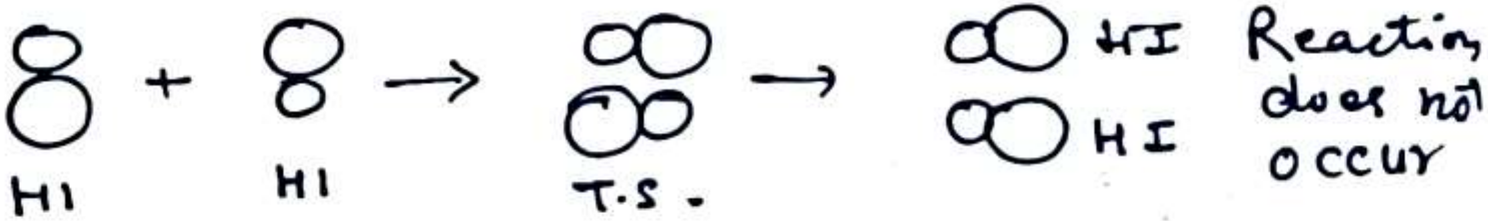
Limitations of Collision theory

- It fails in case of complex molecules
- It considers molecules as hard rigid spheres, the structure of molecules is completely ignored
- Activation energy can not be predicted with the help of this theory

☐ **Cause of limitations**

- It considers only energy factor, orientation factor is completely ignored





Modification of Collision theory

- Probability factor or steric factor ‘p’ is introduced in to the equation
- $k = p\,A\,e^{-Ea/RT}$
- P is the fraction of molecules having proper orientation

For like molecules

- $A = p\,\frac{N}{10^3}\,4\sigma_A^2 \times \sqrt{\frac{\pi RT}{M_A}}$ L/mol/s

For unlike molecules

- $A = p\,\frac{N}{10^3}\,\sigma_{AB}^2\sqrt{8\pi RT\left(\frac{M_A+M_B}{M_A M_B}\right)}$ L/mol/s

Transition State Theory or Theory of Absolute reaction rates

- **Developed by Erying and Polanyi**

☐ Assumptions

1. When two molecules possessing E_a come close, they form activated complex or transition state

$$A + B \rightleftharpoons X^{*} \longrightarrow \text{Products}$$

Activated complex

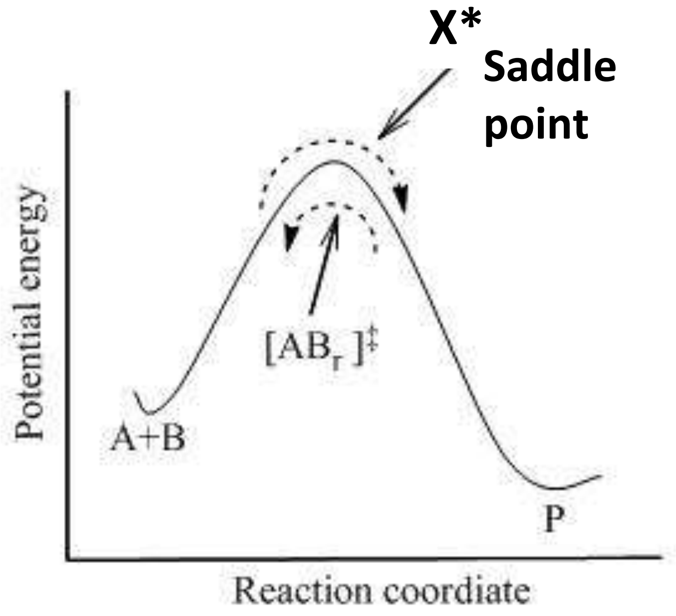
2. Activated complex has partial bonds. It can not be isolated. It is assumed that it possesses properties of real molecules like bond lengths and bond angles etc.

3. At the top of the energy barrier known as saddle point, the activated complex may either change in to products or in to the reactants again

Transition State Theory or Theory of Absolute reaction rates

❑ Assumptions contd….

4. At saddle point the activated complex undergoes a loose vibration to change in to the products



5. The rate of reaction depends upon the rate at which activated complex breaks in to the products

6. Maxwell-Boltzmann distribution law is applicable to both reactants as well as the activated complex

Transition State Theory or Theory of Absolute reaction rates

- **According to Erying and Polanyi** $k = \frac{RT}{Nh}K^*$ ① **K* is equilibrium constant So** $K^* = \frac{[X^*]}{[A][B]}$
- **Also** $\Delta G^* = -RT \ln K^*$ **So** $\ln K^* = \frac{-\Delta G^*}{RT}$
- **Take exponential, we get** $K^* = e^{\frac{-\Delta G^*}{RT}}$
- **Putting the value in equation 1 we get** $k = \frac{RT}{Nh}e^{\frac{-\Delta G^*}{RT}}$ **Also** $\Delta G^* = \Delta H^* - T\Delta S^*$
- **So putting the value we get** $k = \frac{RT}{Nh}e^{-(\Delta H^* - T\Delta S^*)/RT}$
- **OR** $k = \frac{RT}{Nh}e^{\Delta S^*/R}.e^{-\Delta H^*/RT}$

Comparison of Transition State Theory and Collision theory

- **According to T.S.T** $k = \boxed{\frac{RT}{Nh} e^{\Delta S^*/R}} . e^{-\Delta H^*/RT}$
- **According to collision theory** $k = \boxed{p\ A}\ e^{-Ea/RT}$
- **Now compare the above equations** $(\Delta H^* \approx Ea)$ ✓
- **pA** $= \frac{RT}{Nh} e^{\Delta S^*/R}$ **So** $p = e^{\Delta S^*/R}$
- **RT/Nh corresponds to 'A' steric factor and 'p' is related to entropy of activation**

Comparison of Transition State Theory and Collision theory

S. No.	Collision Theory	Transition State Theory
1	Based upon hard rigid sphere model of molecules	Based upon microscopic properties of the reacting molecules and the activated complex
2	Only translational motion of the molecules is considered	It considers all the motions i.e translational, rotational and vibrational motion of the molecules
3	E_a used is experimentally determined	E_a used is theoretically determined
4	It is based upon Kinetic molecular theory of gases	It is based upon statistical mechanics & follows concepts of thermodynamics
5	It does not consider any loose vibration	It considers loose vibration of activated complex

Advantages of Transition State Theory over Collision theory

- Concept of formation of activated complex is more appropriate rather than mere collision of molecules to give products
- Correction factor (Steric factor) p was introduced arbitrarily in the collision theory whereas in TST it is already included in terms of entropy of activation
- TST follows thermodynamic principles

Questions

1. Why some reactions do not take place at room temperature but take place at higher temperature?
2. Derive expression for rate constant k and half life period of a reaction of zero order ? What are the units of k?
3. Why reactions of higher order rare?
4. What is half life period of a reaction? Drive a general expression for half life period of a reaction of nth order ?
5. Does the rate of a reaction remains constant through the reraction ? Why or why not?
6. Why different reactions take place at different rates?
7. How does a catalyst increase the rate of a reaction? What is its effect on equilibrium constant of a reaction.
8. Explain clearly the difference between rate law and law of mass action.
9. Show that half life period of a reaction is independent of the initial concentration of the reactants.
10. Derive an expression for the time required for completion of one third of a first order reaction?
11. Write expression for rate constant of second order of the type A + B → products with different initial concentrations. Show that if one of the reactants is present in excess, it becomes reaction of first order.
12. What is Boltzmann factor? What does it tell ? What are its units?
13. In Arrhenius equation, the units of pre exponential factor A are same as that of rate constant ? Show how?
14. Show diagrammatically how the rate of zero order reaction varies with concentration of the reactants?

Numericals

1. If half life period of a 1st order reaction is 10 minutes, then find out what percentage of reactants remain unreacted after one hour?
2. The half life of a certain 1st order reaction is 60 minutes. How long will it take for 90 % completion of the reaction?
3. 50% reaction is complete in 16 minutes. What fraction will react in 32 minutes if reaction follows 1st order kinetics?
4. Show that the time required for 99% completion of a 1st order reaction is twice the time required for 90 % completion of the reaction.
5. Show that the time required for 99.9 % completion of the 1st order reaction is about 10 times the time required for completion of half of the reaction.
6. A first order reaction is 40 % complete in 50 minutes. Calculate the rate constant. In what time will the reaction be 80 % complete?