

Theories of Reaction Rates:

There are two important approaches (THEORIES) of Reaction Kinetics.

I. Collision Theory (II) Transition State Theory

I. Collision Theory: Developed by Arrhenius & Vant Hoff.

Postulates of Collision Theory (i) For a reaction to take place, the collision between reacting molecules must occur.

(ii) All the collisions do not lead to product formation.

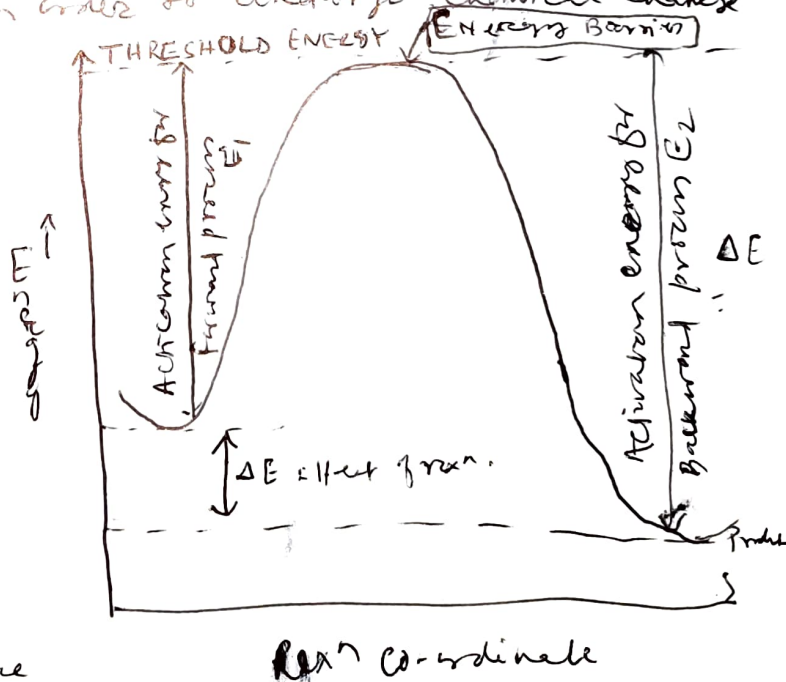
(iii) only those collisions result into chemical reactions (product formation) in which the colliding molecules possess a certain minimum amount of energy, called "THRESHOLD ENERGY".
Threshold energy is defined as the minimum amount of energy which must be associated with the molecules, so that their mutual collisions results into product formation. The collisions which yield product formation are called Effective collisions.

The activation of molecules can also be expressed in "ENERGY OF ACTIVATION" term, defined as the excess energy that the reacting molecules acquire to attain the "Threshold energy" in order to undergo chemical change.

Energy of Activation

= Threshold Energy - Energy possessed by the molecule.

(iv) The colliding molecule must be properly oriented, if the reaction is to take place. If orientation is not proper, product formation is not possible, even though the energy required is much higher than in case of properly oriented molecules.



If every collision leads to product formation, then rate of the reaction will be determined by the frequency with which reactant collide. The calculated rate will be the optimum rate observed experimentally.

* Let the molecules colliding do not have forces of attraction & repulsion & ~~molecules~~ are rigid hard spheres.

~~Let us consider a bimolecular elementary reaction~~



$\therefore$ The number of collision per unit volume per unit time

$$Z_{AA} = \frac{1}{\sqrt{2}} \pi \sigma^2 \bar{u} N_A^*$$

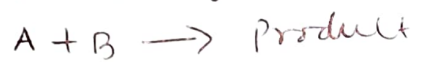
where σ = Diameter of the molecule A

$\bar{u}$ = Average speed of the molecule.

N_A^* = Number of molecules per unit volume.

Av speed $\bar{u} = \sqrt{\frac{8KT}{\pi m_A}}$ (K = Boltzman const, m_A = mass of single molecule)

Let us consider a general elementary rxn.



The number of collision per unit volume per unit time between A & B is given by

$$Z_{AB} = \pi \sigma_{AB}^2 \left(\frac{8KT}{\pi \mu} \right)^{1/2} N_A^* N_B^* \quad \text{--- (1)}$$

$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$ is closest approach for the collision. (sum of the radii of molecule A & B). μ = Reduced mass $\mu = \frac{m_A m_B}{m_A + m_B}$, N_A^* N_B^* no of molecules of A & B per unit volume of the vessel.

Eqn (1) provides the maximum possible rate of the rxn if $A + B \rightarrow \text{Product}$

$$-\left[\frac{dN_A^*}{dt} \right]_{\text{max}} = Z_{AB} = \pi \sigma_{AB}^2 \left(\frac{8KT}{\pi \mu} \right)^{1/2} N_A^* N_B^*$$

The amount of A & B per unit volume will be related to N_A^* & N_B^* by the relations

$$[A] = \frac{N_A^*}{N_A} \quad \& \quad [B] = \frac{N_B^*}{N_A}$$

where N_A = Avogadro's const

$$-\left[\frac{d[A]}{dt} \right] = k_2 [A][B]$$

$$-\frac{1}{N_A} \left[\frac{dN_A^*}{dt} \right]_{\text{max}} = k_2 \left[\frac{N_A^*}{N_A} \right] \left[\frac{N_B^*}{N_A} \right]$$

$$- \left[\frac{dN_A^*}{dt} \right] = k_2 \frac{1}{N_A} N_A^* N_B^* \quad - (2)$$

Comparing (1) & (2)

$$k_2 = N_A \pi \sigma_{AB}^2 \left(\frac{8KT}{\pi \mu} \right)^{1/2} \quad - (3) \quad \checkmark$$

e.g. At Maximum rate for most of the bimolecular rxn can be calculated at 1 atm & 0°C. $\sigma = 3 \times 10^{-9} \text{ dm}$
 $\bar{u} = 5 \times 10^3 \text{ dm/sec}$

$$N_A^* = N_B^* = \left(\frac{6.023 \times 10^{23} \text{ mol}^{-1}}{22.414 \text{ dm}^3 \text{ mol}^{-1}} \right) \approx 2.8 \times 10^{22} \text{ dm}^{-3}$$

$$\begin{aligned} - \frac{d(N_A^*)}{dt} &= \pi \sigma_{AB}^2 \bar{u} N_A^* N_B^* \\ &= 3.14 (3 \times 10^{-9} \text{ dm})^2 (5 \times 10^3 \text{ dm s}^{-1}) (2.8 \times 10^{22} \text{ dm}^{-3})^2 \\ &= 1.11 \times 10^{32} \text{ dm}^{-3} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} - \left[\frac{d[A]}{dt} \right] &= - \frac{1}{N_A} \left(\frac{dN_A^*}{dt} \right)_{\text{max}} \\ &= \frac{(1.11 \times 10^{32} \text{ dm}^{-3} \text{ s}^{-1})}{(6.023 \times 10^{23} \text{ mol}^{-1})} \approx 2 \times 10^8 \text{ mol dm}^{-3} \text{ s}^{-1} \end{aligned}$$

Failure of Collision Theory: The theory fails in many cases.
 e.g.

1. The Chain reaction proceed at a very fast rate which is much higher than the theoretical value calculated from Collision theory.

2. The bimolecular polymerization of ethylene takes place at a rate which is slower than the theoretical value calculated from Collision theory.

In order to account for this deviation the orientation factor p is introduced, called Steric factor. value of p varies from 1 to 10^{-9} .

Weakness of Collision Theory:

(i) Collision theory does not give explanation for abnormally high rates.

(ii) Collision theory fails to correlate steric factor p with the characteristic of reactant molecule.

(3) Collision theory is unable to explain reversible & complicated reaction.

Causes of Weakness of Collision Theory:

1. In collision theory, the calculations are based on the assumption that molecules are elastic hard spheres, which is true only for ideal gases.
2. With larger molecules, many collisions would take place where vulnerable reactive parts would not be brought together although molecules have high energy. In consequence many such collisions of activated molecules become infrequent. the steric factor p becomes much less than unity.
3. In calculation of Δ for energy of activation, only translational energy has been considered. No account is taken of the internal motions of the reacting molecules. There may be contributions from rotational & vibrational motions towards energy of activation. If such contributions are appreciable, the observed rate of reaction would be greater than the calculated rate.
4. Collision theory is totally based on chemical mechanism which is very crude and requires modification.

Imp Arrhenius Equation and Collision Theory:

Arrhenius eqn is $k_2 = A e^{(-E_a/RT)}$
and according to Collision Theory Rate cont is given by,

$$k_2 = p N_A \bar{v}_{AB}^2 \left(\frac{8kT}{\pi \mu} \right)^{1/2} e^{(-E_0/RT)} \quad \text{--- (I)}$$

Eqn (I) can be written as

$$k_2 = K \sqrt{T} e^{(-E_0/RT)} \quad \text{--- (II)}$$

where K is independent of temperature $= \left(p N_A \bar{v}_{AB}^2 \left(\frac{8k}{\pi \mu} \right)^{1/2} \right)$

Relation between E_a & E_0 (Activation energy & Min Energy) may be obtained through the expression.

$$\frac{d \ln \left(\frac{k_2}{k_0} \right)}{dT} = \ln \left(\frac{A}{k_0} \right) - \frac{E_a}{RT}$$

$$\frac{d \ln (k_2/k_0)}{dT} = \frac{E_a}{RT^2}$$

$$\ln \frac{k_2}{k_0} = \ln \frac{K}{K_0} + \frac{1}{2} \ln \left(\frac{T}{T_0} \right) - \frac{E_0}{RT}$$

$$\frac{d \ln (k_2/k_0)}{dT} = \frac{1}{2T} + \frac{E_0}{RT^2} \therefore E_a = \frac{RT}{2} + E_0$$

Thus, activation energy E_a shows temperature dependence since E_0 is usually much larger than $RT/2$ the difference between the Arrhenius activation energy E_a & the minimum energy E_0 of the simple kinetic theory is not sufficient.

$$k_2 = K\sqrt{T} e^{\left\{ \frac{-(E_a - RT/2)}{RT} \right\}}$$

$$\therefore k_2 = K\sqrt{T} e^{1/2} e^{(-E_a/RT)}$$

Comparing with Arrhenius Eqⁿ.

$$A = K\sqrt{T} e^{1/2}$$

$$\text{i.e. } A = P N_A \pi \sigma_{AB}^2 \left(\frac{8k}{\pi \mu} \right)^{1/2} \sqrt{T} e^{1/2}$$

$$\therefore A = P N_A \frac{\Sigma_{AB}}{N_A^* N_B} e^{1/2}$$

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Collision theory of unimolecular Gaseous Reⁿ:

Lindemann Theory: according to this theory a unimolecular reⁿ $A \rightarrow \text{Product}$ takes place through the following mechanism:



where A^* is the energized molecule. The vibrational energy of A exceeds the threshold limit giving rise to product. A^* is a molecule with high energy (NOT AN ACTIVATED complex)

A^* is produced with collision of molecule A , kinetic energy of the second molecule is converted into vibrational energy of the first.

Imp The 2nd molecule can be either a product-molecule or a ~~foreign~~ ^{foreign} molecule present in the system which do not appear in the stoichiometry of the reⁿ $A \rightarrow P$.

In Lindemann mechanism, a time lag exists between the energization of A to A^* & decomposition of A^* to product. S.S.A. can be applied to A^* .

$$\text{Rate of formation} = k_1 [A]^2 \quad \text{--- (1)}$$

$$\text{Rate of decomposition} = k_{-1} [A] [A^*] + k_2 [A^*] \quad \text{--- (2)}$$

$$\frac{d[A^*]}{dt} = 0 = k_1 [A]^2 - k_{-1} [A] [A^*] - k_2 [A^*] \quad \text{--- (3)}$$

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2} \quad - (4)$$

$$\text{Rate of Rxn} = r = -\frac{d[A]}{dt} = k_2[A^*] = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2} \quad - (5)$$

Rate Law (5) has no definite order.

If $k_1[A] \gg k_2$

$$r = \frac{k_1 k_2 [A]}{k_{-1}} \quad - (6) \quad \text{1st order. in}$$

gases rxn under high pressure condition this holds good

If $k_2 \gg k_{-1}[A]$

$$r = k_1[A]^2 \quad (7) \quad \text{2nd order at low pressure}$$

Experimental rate is defined as.

$$r = k_{uni}[A] \quad - (8) \quad \text{where } k_{uni} = \text{unimolecular rate const.}$$

Compare (8) & (4)

$$k_{uni} = k' = \frac{k_1 k_2 [A]}{k_{-1}[A] + k_2} = \frac{k_1 k_2}{[k_{-1} + k_2]/[A]} \quad - (9)$$

~~Another~~

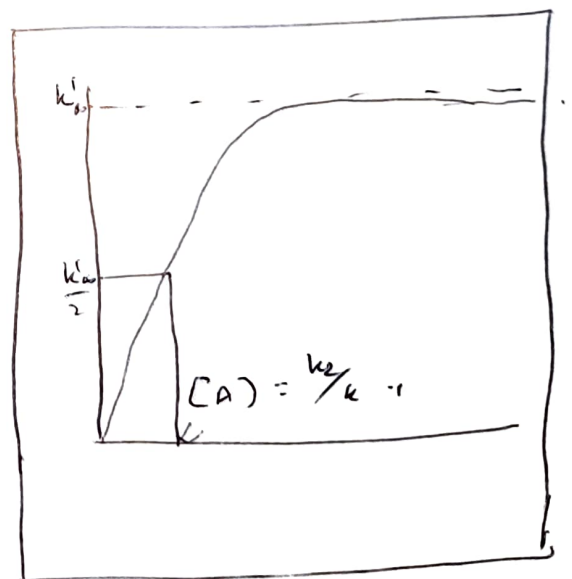
Limitation of Lindemann Theory:

$$\text{Eqn (9) can be written as } k' = \frac{k_2 k_1 / k_{-1}}{1 + (k_2 / k_{-1})[A]} \quad - (10)$$

The plot of k' vs $[A]$ is a hyperbolic rate const k' is const in higher concn range but falls off at low concn range.

$$k' = k'_{\infty} / 2 \quad \text{when } k_{-1}[A] = k_2$$

& concn at which this is true is $[A]_{1/2} = \frac{k_2}{k_{-1}} = \frac{k'_{\infty}}{k'}$

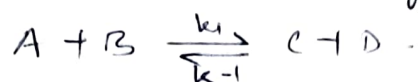


Plot of k' vs $[A]$

Temperature dependence of k_{eq} rate:

The dependence of rate constant on temperature can be derived from Van't Hoff eqn.

Let us consider a general rxn



$$K_{eq} = \frac{k_1}{k_{-1}} \quad - (1)$$

Van't Hoff eqn $\frac{d \ln K_{eq}}{dT} = \frac{\Delta E}{RT^2} \quad - (2)$

Hence $\frac{d \ln (k_1/k_{-1})}{dT} = \frac{\Delta E}{RT^2} \quad - (3)$

$$\therefore \frac{d \ln k_1}{dT} - \frac{d \ln k_{-1}}{dT} = \frac{\Delta E}{RT^2} \quad - (4) \quad [\Delta E = E_1 - E_{-1}]$$

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_{-1}}{dT} = \frac{E_1}{RT^2} - \frac{E_{-1}}{RT^2} \quad - (5)$$

so from eqn (5)

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} + I \quad \text{and} \quad \frac{d \ln k_{-1}}{dT} = \frac{E_{-1}}{RT^2} + J$$

If we take $I = C_{VT} = 0$

Then $\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad - (6)$

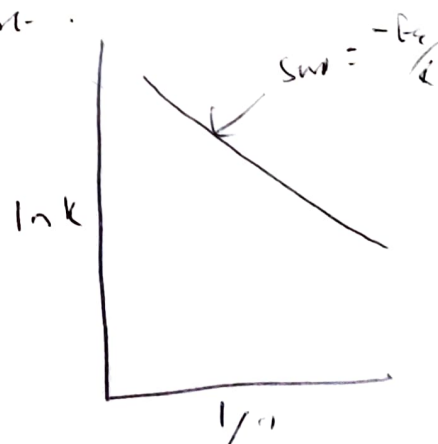
Integrating (6)

$$\text{i.e. } \frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

$$\therefore \ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \text{const.}$$

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

$A \equiv$ Pre-exponential factor.



Temperature Co-efficient of k_{obs} Rate - (Temp Co-efficient of a rxn is defined as the ratio of rate const of two temperatures differing by 10°C).

$$\ln k_T = -\frac{E_a}{RT} + \text{const.}$$

$$\ln k_{T+10} = -\frac{E_a}{R(T+10K)} + \text{const.}$$

$$\text{Hence } \frac{\ln k_{T+10}}{\ln k_T} = -\frac{E_a}{R(T+10K)} + \frac{E_a}{RT}$$

$$\ln \frac{k_{T+10K}}{k_T} = \frac{E_a}{R} \frac{(10K)}{T(T+10K)}$$

$$\therefore \frac{k_{T+10K}}{k_T} = e^{\left(\frac{(10K) E_a}{RT(T+10K)} \right)}$$

Main characteristics of Arrhenius Eqⁿ

1. Larger the value of Activation energy smaller is rate const.
2. Larger the activation energy, greater is the effect of a given temperature rise on k .
3. At lower temp, the increase in temp causes more change in value of k than at higher temperature.

At 300K.

$$\frac{k_{T+10K}}{k_T} = e^{\left\{ \frac{(10K)(80,000 \text{ J mol}^{-1})}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} (300K)(310K)} \right\}} \approx e^{1.03} \approx 2.8.$$

$\therefore$ For many rxn $E_a \approx 80 \text{ kJ mol}^{-1}$.

$\Rightarrow E_a$ increases ~ 2 to 3 for 10° rise .