



University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi - 110092



Engineering Chemistry-I (BS-109)

Chemical Kinetics

Dr. Shruti Khanna Ahuja

Assistant Professor

USAR, GGSIPU

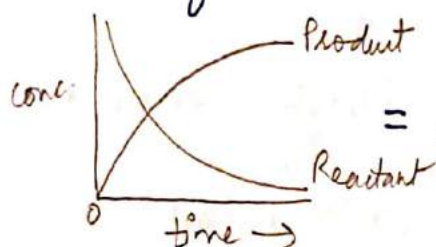
: CHEMICAL KINETICS :

→ The branch of chemistry which deals with the study of the speeds or the rates of chemical reactions, the factors affecting the rates of the reactions and the mechanism by which the reactions proceed is known as chemical kinetics.

- Rate of reaction: It is the change in the concentration of anyone of the reactants or products per unit time.



rate of reaction = $\frac{\text{Decrease in the conc. of reactant R}}{\text{Time interval}}$



= $\frac{\text{Increase in the concentration of product P}}{\text{Time interval}}$

t_1 In. conc. of reactant = R_1 , product = P_1

t_2 Fin. conc. of reactant = R_2 , product = P_2

$$\therefore \Delta R = R_2 - R_1 \quad , \quad \Delta P = P_2 - P_1 \quad , \quad \Delta t = t_2 - t_1$$

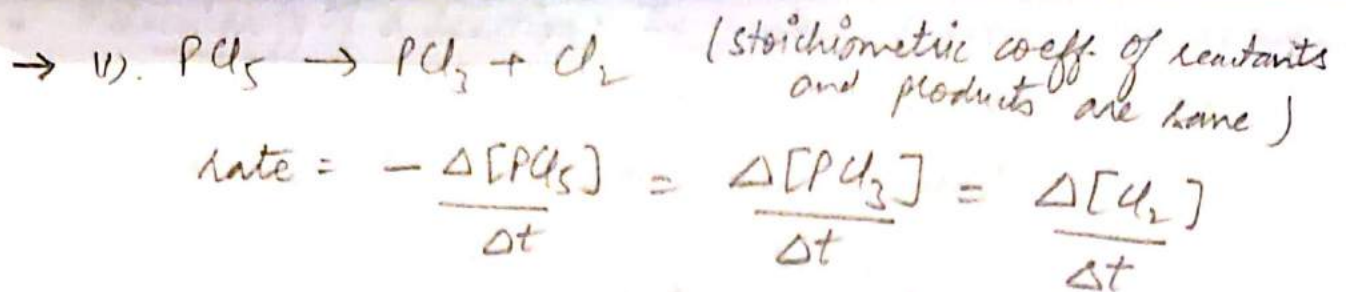
$$\text{Rate} = -\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$$

Rate of reaction is always positive

$$\text{Unit} = \text{mol L}^{-1} \text{s}^{-1} \\ \text{mol L}^{-1} \text{min}^{-1}$$

For a reaction, $A + B \rightarrow C + D$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = +\frac{\Delta[C]}{\Delta t} = +\frac{\Delta[D]}{\Delta t}$$



rate of decomposition of $\text{N}_2\text{O}_5 = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$

rate of formation of $\text{NO}_2 = \frac{\Delta[\text{NO}_2]}{\Delta t}$

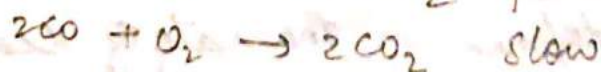
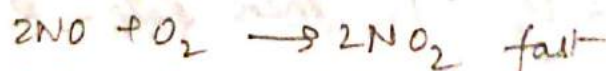
rate of formation of $\text{O}_2 = \frac{\Delta[\text{O}_2]}{\Delta t}$

Here, rate of reaction can't be equal to ^{rate of} disappearance of reactant or appearance of product as their stoichiometries are not same.

$$\therefore \text{Rate of reaction} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

• Factors affecting rate of reaction:

(1). Nature of the reactants



(2) Conc of reactants : More it is, more is the rate.

(3). Temperature : Rate of reaction increases with inc. in temp^r.

(4). Catalyst : Speeds up the reaction

(5) Surface area of the reactants : Smaller the particle size, greater is the surface area, faster is the reaction.

• Rate law and rate constant :

For a reaction, $aA + bB \rightarrow \text{products}$

$$\text{Rate} \propto [A]^a [B]^b \quad (\text{Acc. to Law of Mass Action})$$

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

As observed experimentally, rate of reaction may not depend on 'a' and 'b',

$$\therefore \text{Rate} \propto [A]^\alpha [B]^\beta \quad \left(\alpha, \beta \text{ may or may not be equal to } a \text{ and } b \right)$$
$$\text{or, Rate} = k [A]^\alpha [B]^\beta$$

Rate Law (Differential rate law)

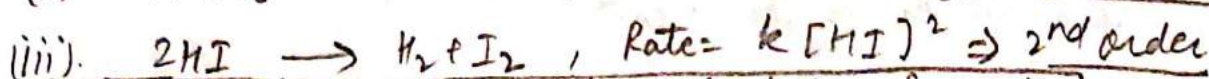
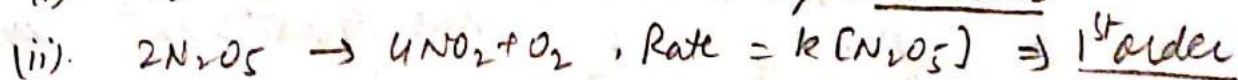
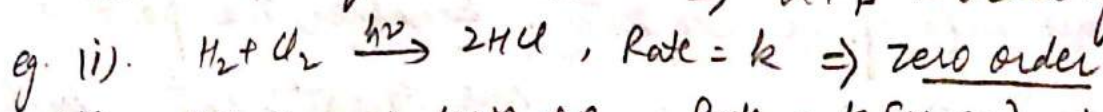
[A] & [B] : molar conc. of A & B resp.

k : rate const. or velocity const.

→ If $[A] = [B] = 1$, then $\text{Rate} = k$

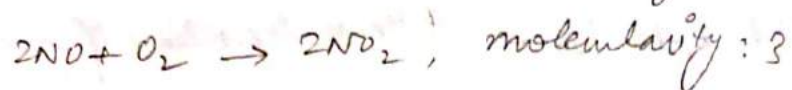
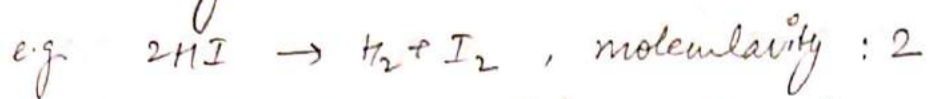
\therefore 'k' is defined as the rate of reaction when the molar concentration of each reactant is unity.

→ Order of a reaction: The sum of the exponents (powers) to which the molar concentrations in the rate law eqⁿ are raised. $\Rightarrow \alpha + \beta = \text{order of above reaction}$



* Order of a reaction is always determined experimentally

- molecularity of a reaction: The number of atoms, ions or molecules that must collide with another simultaneously to result into a chemical reaction.



- molecularity is applicable only to elementary (single-step) reactions
- The overall molecularity of a complex (multi-step) reaction has no significance.
- For complex reactions, molecularity of the slowest step is considered (slow step is the rate determining step)

- Units of rate constant, 'k':

(i) zero order:

$$\text{Rate} = -\frac{d[A]}{dt} = k_0 \quad A \rightarrow P$$

$$\Rightarrow \text{units} = \underline{\text{mol l}^{-1} \text{sec}^{-1}}$$

(ii) 1st order:

$$\text{Rate} = -\frac{d[A]}{dt} = k_1 [A]$$

$$\Rightarrow k_1 = \frac{\text{mol l}^{-1}}{\text{s}} \times \frac{1}{\text{mol l}^{-1}} = \underline{\text{s}^{-1}}$$

(iii) 2nd order:

$$\text{Rate} = -\frac{d[A]}{dt} = k_2 [A]^2$$

$$\Rightarrow k_2 = \left(\frac{\text{mol l}^{-1}}{\text{s}}\right) \times \frac{1}{(\text{mol l}^{-1})^2} = \underline{\text{mol}^{-1} \text{l s}^{-1}}$$

(iv) 3rd order:

$$\text{Rate} = -\frac{d[A]}{dt} = k_3 [A]^3$$

$$\Rightarrow k_3 = \left(\frac{\text{mol l}^{-1}}{\text{s}}\right) \times \frac{1}{(\text{mol l}^{-1})^3} = \underline{\text{mol}^{-2} \text{l}^2 \text{s}^{-1}}$$

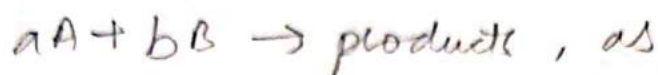
In general, for n^{th} order, $\text{rate} = -\frac{d[A]}{dt} = k[A]^n$

$$\text{units of } k : (\text{conc.})^{1-n} \cdot \text{t}^{-1}$$

$$\text{conc.} : (\text{mol l}^{-1})$$

- Integrated Rate Laws (time dependence of conc.)

So far, we have discussed rate laws for a general reaction



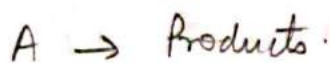
$$\text{Rate} = -\frac{d[R]}{dt} = k[A]^a[B]^b : \text{Differential rate eq}^n$$

∴ Integrated rate laws are studied by integrating the above differential eqⁿs.

↓
does not give accurate order of reaction

in order to predict the conc. at any time and to determine the order of the reaction accurately.

① Zero order reaction: e.g. $\text{CH}_3\text{COCH}_3 + \text{Br}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{Br} + \text{HBr}$



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

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

Integrating both sides

$$\int_{A_0}^A dA = -k \int_0^t dt$$

$$\Rightarrow [A] - A_0 = -k[t - 0] \Rightarrow \boxed{[A_0] - [A] = kt} \quad \text{--- (1)}$$

→ Half-life period ($t_{1/2}$): Time in which half of the reactant has reacted

⇒ $[A] = \frac{[A_0]}{2}$, substituting this in eqⁿ (1),

$$\Rightarrow [A_0] - \frac{[A_0]}{2} = kt_{1/2} \Rightarrow \boxed{t_{1/2} = \frac{[A_0]}{2k}}$$

(B). First order reaction: eg. $N_2O_4 \rightarrow 2NO_2$

$A \rightarrow \text{Products}$

Ini. conc. of A : 'a'

after time 't', x moles/l of it have decomposed

\Rightarrow conc. of A after time 't' = $(a-x)$

or, conc. of product after time 't' = x

$$\therefore \text{Rate} = \frac{d[P]}{dt} = k[A]$$

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

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

on integrating, we get

$$\int \frac{dx}{(a-x)} = k \int dt \Rightarrow -\ln(a-x) = kt + I \quad \text{--- (1)}$$

integration const

at $t=0$, $x=0$

\therefore from eqⁿ (1), $-\ln a = I$, substituting this eqⁿ (1),

$$\Rightarrow -\ln(a-x) = kt - \ln a \Rightarrow \ln a - \ln(a-x) = kt$$

$$\Rightarrow kt = \ln \left(\frac{a}{a-x} \right) \quad \text{or,} \quad k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\text{or, } x = a(1 - e^{-kt}) \quad \text{--- (3)}$$

if $a = \text{ini. conc. } [A]_0$, $(a-x) = [A]$

$$\text{then, } kt = \ln \frac{[A]_0}{[A]}$$

$$\text{or, } \frac{[A]}{[A]_0} = e^{-kt} \quad \text{--- (4)}$$

$$\text{then, } k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \quad \text{--- (2)}$$

\rightarrow Half-life: at $t_{1/2}$, $[A] = \frac{[A]_0}{2}$

$$\Rightarrow k = \frac{2.303}{t_{1/2}} \log \left(\frac{[A]_0}{[A]_{1/2}} \right) \Rightarrow k = \frac{2.303}{t_{1/2}} \log 2$$

$$\Rightarrow t_{1/2} = \frac{0.693}{k} \quad \text{--- (5)}$$

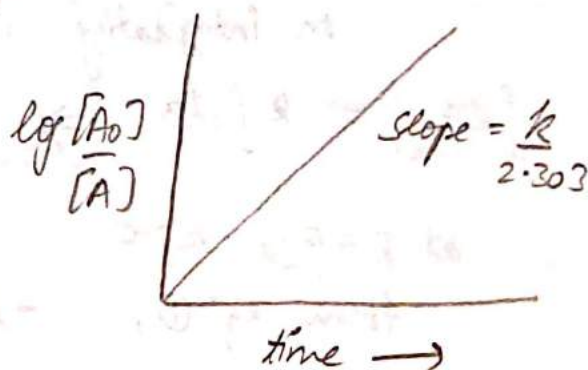
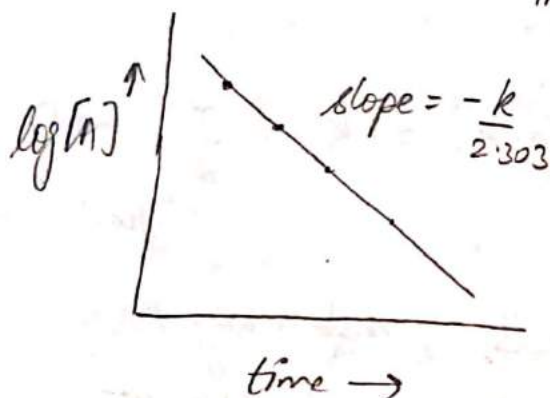
→ eqⁿ ② can be written as:

$$\frac{kt}{2.303} = \log \frac{[A_0]}{[A]} = -\log [A] - \log [A_0]$$

$$\Rightarrow \log [A] = \log [A_0] - \frac{k}{2.303} \cdot t$$

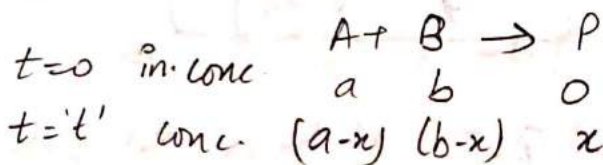
$$(y = c + mx)$$

\downarrow intercept \downarrow slope



→ If $x = a$, then from eqⁿ (3),
 $a = a(1 - e^{-kt})$, which is possible only when $t = \infty$
 \Rightarrow first order reaction is never completed.

(C). Second Order Reaction: eg. $2HI \rightarrow H_2 + I_2$



$$\text{rate eqⁿ: } \frac{d[P]}{dt} = k_2[A][B]$$

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

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

resolving into partial fraction:

$$\frac{1}{(a-x)(b-x)} = \frac{1}{(b-a)} \left[\frac{1}{(a-x)} - \frac{1}{(b-x)} \right]$$

$$\Rightarrow k_2 dt = \frac{1}{(b-a)} \left[\frac{1}{(a-x)} - \frac{1}{(b-x)} \right] dx$$

on integration,

$$\Rightarrow k_2 \int dt = \frac{1}{(b-a)} \int \left[\frac{1}{(a-x)} - \frac{1}{(b-x)} \right] dx$$

k_2 = second
order
rate
const

$$\Rightarrow k_2 \int dt = \frac{1}{(b-a)} \left[\int \frac{dx}{(a-x)} - \frac{dx}{(b-x)} \right]$$

$$\Rightarrow k_2 t + I = \frac{1}{(b-a)} \left[-\ln(a-x) + \ln(b-x) \right]$$

$$\Rightarrow k_2 t + I = \frac{1}{(b-a)} \left[\ln \frac{(b-x)}{(a-x)} \right] \quad \text{--- (1)}$$

at $t=0$, $x=0$

$$\Rightarrow I = \frac{1}{(b-a)} \ln \left(\frac{b}{a} \right)$$

on substituting the value of 'I' in eqⁿ (1),

$$\Rightarrow k_2 t + \frac{1}{(b-a)} \ln \left(\frac{b}{a} \right) = \frac{1}{(b-a)} \left[\ln \left(\frac{b-x}{a-x} \right) \right]$$

$$\Rightarrow k_2 t = \frac{1}{(b-a)} \left[\ln \left(\frac{b-x}{a-x} \right) - \ln \left(\frac{b}{a} \right) \right]$$

$$\Rightarrow k_2 (b-a) t = \ln \left[\frac{a(b-x)}{b(a-x)} \right]$$

$$\Rightarrow k_2 = \frac{2.303}{(b-a)t} \log \left(\frac{a(b-x)}{b(a-x)} \right)$$

Case : When reactants are same, $2A \rightarrow P$

initial conc a 0
conc at t $a-x$ x

$$\Rightarrow \frac{dx}{dt} = k_2 (a-x)^2 \Rightarrow \frac{dx}{(a-x)^2} = k_2 dt$$

on integration, we get

$$\Rightarrow (-1) \left[\frac{1}{(a-x)} \right] = k_2 t + I$$

$$\Rightarrow \frac{1}{(a-x)} = k_2 t + I$$

$$\Rightarrow \text{at } t=0, x=0$$

$$\Rightarrow \frac{1}{a} = I \quad \Rightarrow \frac{1}{(a-x)} = k_2 t + \frac{1}{a}$$

$$\Rightarrow k_2 = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right] = \frac{1}{t} \left(\frac{x}{a(a-x)} \right)$$

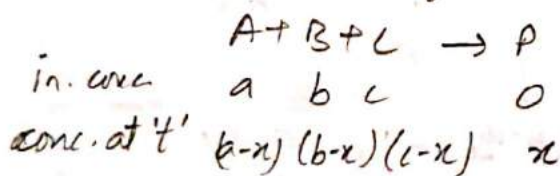
• Half time period $t_{1/2}$:

$$\text{at } t_{1/2}, x = \frac{a}{2}$$

$$\Rightarrow t_{1/2} = \frac{1}{k_2} \left(\frac{x}{a(a-x)} \right) = \frac{1}{k_2} \left(\frac{a/2}{a-a/2} \right) = \boxed{\frac{1}{ak_2}}$$

$$\therefore \text{at } a=1, \quad \boxed{t_{1/2} = \frac{1}{k_2}}$$

(D) Third order reaction: eg. $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$



$$\text{when } a=b=c, \quad \frac{dx}{dt} = k_3 (a-x)^3$$

$$\Rightarrow \frac{dx}{(a-x)^3} = k_3 dt$$

k_3 third order rate const.

on integration,

$$\Rightarrow \frac{1}{2} \left(\frac{1}{(a-x)^2} \right) = k_3 t + I$$

$$\Rightarrow \frac{1}{2(a-x)^2} = k_3 t + I$$

$$\text{at } t=0, x=0 \Rightarrow I = \frac{1}{2a^2}$$

$$\Rightarrow \frac{1}{2(a-x)^2} - \frac{1}{2a^2} = k_3 t$$

$$\Rightarrow k_3 = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right] = \frac{1}{2t} \left[\frac{a^2 - (a-x)^2}{a^2(a-x)^2} \right]$$

$$\Rightarrow \boxed{k_3 = \frac{1}{t} \frac{x(2a-x)}{2a^2(a-x)^2}}$$

• Half time period, $t_{1/2}$ $x = a/2$

$$\Rightarrow k_3 = \frac{1}{t_{1/2}} \frac{a/2 (2a - \frac{a}{2})}{2a^2 (a - \frac{a}{2})^2}$$

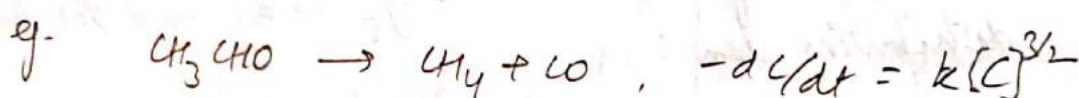
$$= \frac{1}{t_{1/2}} \frac{3a^2/4}{a^4/2} = \frac{1}{t_{1/2}} \frac{3a^2}{4} \times \frac{2}{a^4}$$

$$\Rightarrow k_3 = \frac{1}{t_{1/2}} \frac{3}{2a^2} \Rightarrow \boxed{t_{1/2} = \frac{1}{k_3} \cdot \frac{3}{2a^2}}$$

$\Rightarrow t \propto \frac{1}{a^2}$ time reqd. for completion of reaction is inversely proportional to sq. of in. conc

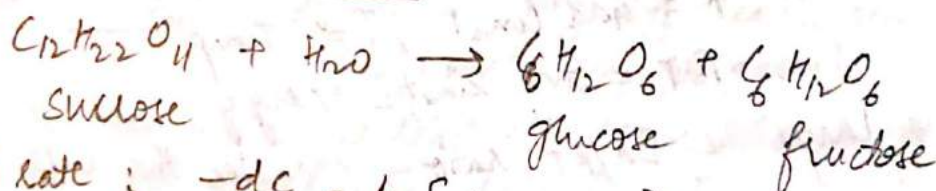
→ Fractional order reaction: Rate of reaction is proportional to fractional power of conc. of reactant

i.e. $-\frac{dc}{dt} = k c^{1/2}$



In such reactions, mechanisms involve atoms or free radicals as intermediates.

→ Pseudo unimolecular reaction:



expected rate: $-\frac{dc}{dt} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}] [\text{H}_2\text{O}]$

but in solⁿ, amt. of water is excessively high as compared to sugar, so $[\text{H}_2\text{O}]$ is taken as const.

$$\Rightarrow -\frac{dc}{dt} = k' [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

$$\boxed{k' = \frac{1}{t} \ln \frac{a}{a-x}}$$

• Effect of temperature on reaction rates (Arrhenius Equation)

→ Chemical reactions proceed faster at higher temp. As the temp rises, molecules move faster and collide more vigorously, enabling bond cleavages and rearrangements.

→ Rate of a reaction doubles for a 10° rise in temperature as proved by Swedish chemist Arrhenius wherein, he combined the concepts of activation energy (E_a) and the Boltzmann distribution law:

$$k = A e^{-\frac{E_a}{RT}} \quad \text{--- (1)}$$

where, k = rate const.

A = pre-exponential factor

E_a = Activation energy

R = Gas const., T = Temp.

RT = avg. kinetic energy

(keeping the conc. const., if we ↑ temp., rate of reaction ↑
ie. rate const. k also ↑)

⇒ Larger the E_a/RT ratio, smaller the rate (hence the -ve sign)

⇒ High Temp and low activation energy favor larger rate constants, and thus speed up the reaction.

→ Taking log on both sides of eqⁿ (1),

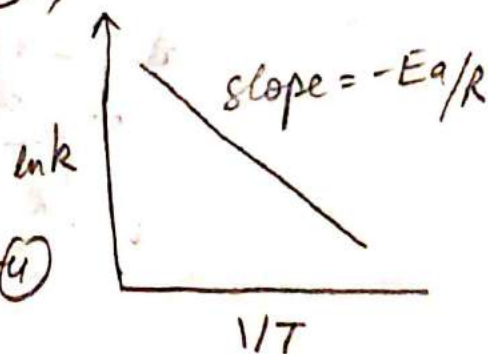
$$\boxed{\ln k = \ln A - \frac{E_a}{RT}} \quad (y = mx + c)$$

at temp^r T_1

at temp^r T_2

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \text{--- (3)}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad \text{--- (4)}$$

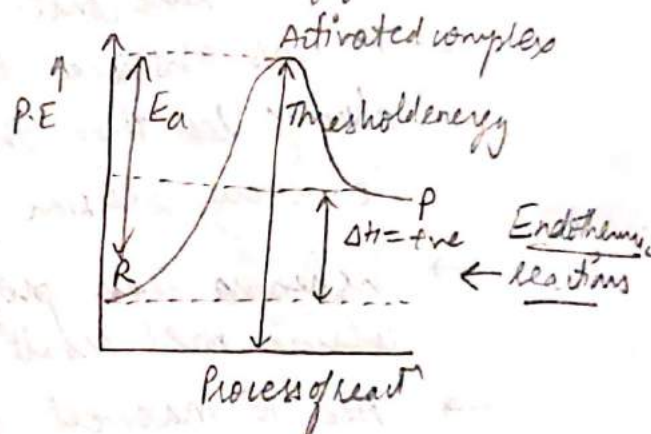
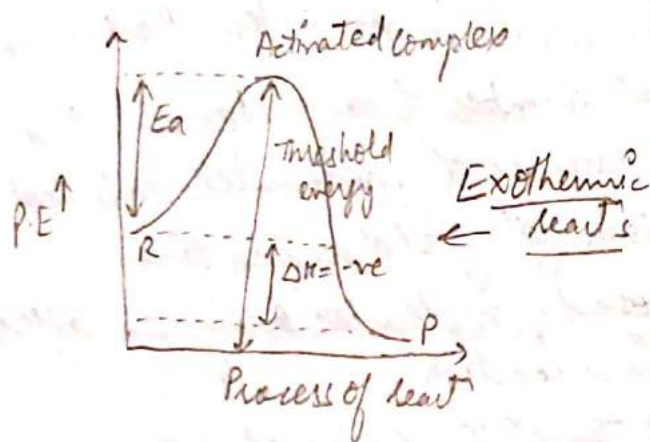


subtracting eqⁿ (4) from (3)

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

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

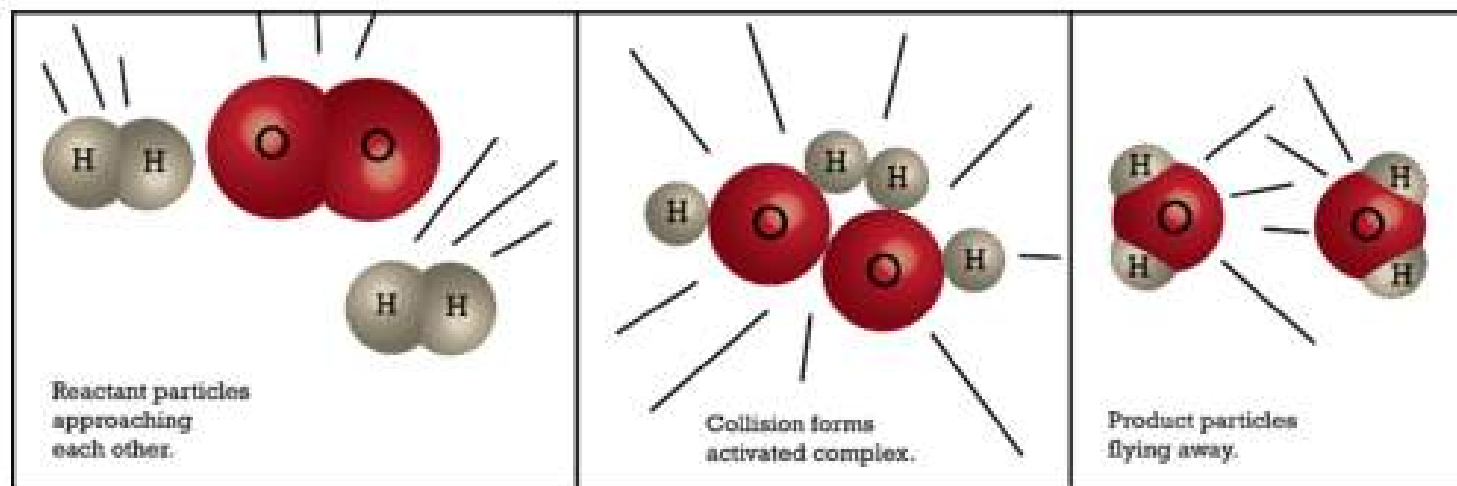
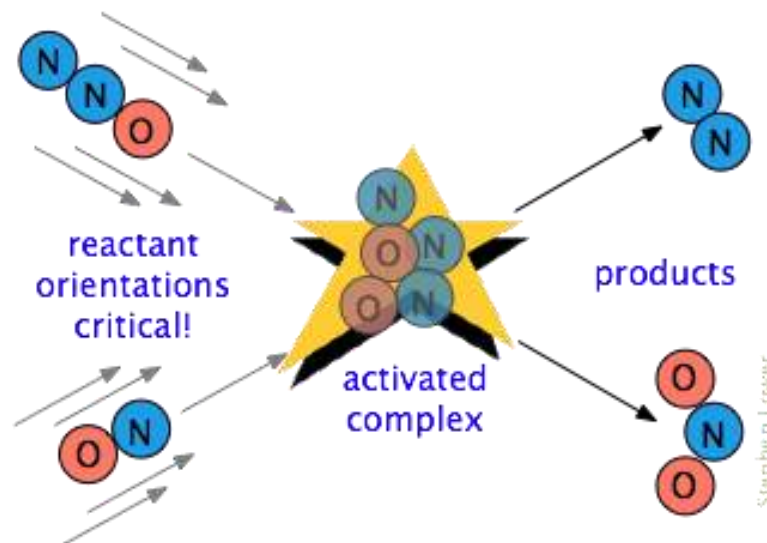
→ Physical significance of E_a : Minimum amount of energy that is required to activate atoms or molecules so that they can undergo a chemical reaction or transformation. Or, the difference between the minimum energy required to bring about molecular arrangement and the average energy reactant molecules is known as activation energy.



- COLLISION THEORY: It explains why diff. react's occur at diff. rates (particularly for gases)
 - It states that for a chemical reaction to occur, the reacting particles must collide with another. The rate of react depends on the freq. of collisions.
 - A collision will be effective in producing chemical change only if the species brought together possess a certain minimum amount of energy (E_a).
 - The colliding particles must be oriented in a manner favorable to the necessary rearrangement of atoms.
 - Not all collisions are equal or bring about a chemical change.



Schematic illustration of Collision Theory and Activated Complex Theory



An activated complex is a short-lived state in which the colliding particles are at the peak of the potential energy curve

So, when two gases A and B react, react becomes possible when A & B collide. So, number of collisions per second (Z) in a given volume can be obtained from kinetic theory:

$$Z_{AB} = n_A n_B \sigma_{AB}^2 \left(\frac{8\pi k_B T}{\mu} \right)^{1/2}, \text{ where,}$$

n_A, n_B : number of molecules of A & B reacted in 1 sec, which can be obtained from rate const. 'k'.

σ = collision diameter

μ = reduced mass

k_B = Boltzmann const

→ It was observed that number of molecules reacted is always less than the number of molecules collided, i.e. every collision does not yield a reaction.

→ Arrhenius then proposed, molecules having E_a after collision will result in a reaction.

→ Acc. to Maxwell, at temp^r T , ratio of total number of collisions and number of collisions giving E_a to molecules is $e^{-E_a/RT}$

$$\Rightarrow Z' = Z \cdot e^{-E_a/RT} \quad \text{and} \quad -\frac{dn_A}{dt} = Z' \rightarrow \text{ideally rate of relative collision}$$

Z = tot. no. of collision
 Z' = no. of collision giving E_a to molecules

$$\Rightarrow -\frac{dC_A}{dt} = k C_A C_B$$

where $C_A = \frac{n_A}{N_A}$ (Avogadro's no.)

$$\Rightarrow -\frac{1}{N_A} \frac{dn_A}{dt} = k \frac{(n_A \cdot n_B)}{(N_A)^2}$$

$C_B = \frac{n_B}{N_A}$

$$\Rightarrow k = -\frac{N_A}{n_A n_B} \frac{dn_A}{dt} = \frac{N_A}{n_A n_B} \cdot Z' \Rightarrow \boxed{\frac{N_A}{n_A n_B} \cdot Z e^{-E_a/RT} = k}$$

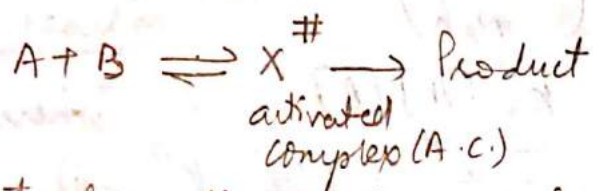
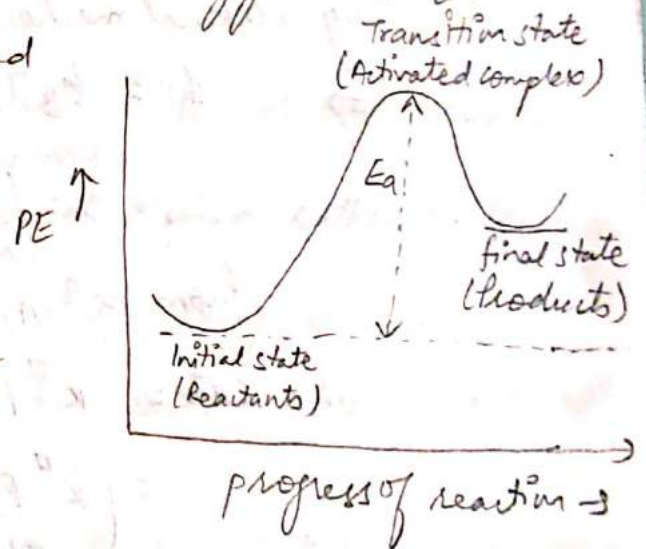
freq. factor

→ For complicated gaseous molecules, rate tends to be smaller than collision theory predicts by a factor of 10^5 . To account for this, an additional factor "p" called probability factor or steric factor is used in the above eqⁿ.

$$k = p \frac{N_A}{n_A n_B} \cdot z e^{-E_a/RT}$$

• ACTIVATED COMPLEX THEORY : (Also known as Transition State Theory)

- An activated complex is an unstable arrangement of atoms that is in between the reactants and the products and exists momentarily at the peak of activation energy barrier.
- Because of its high energy, the activated complex exists for an extremely short period of time (about 10^{-13} s)
- There is equal likelihood that the activated complex either reforms the original reactants or goes on to form products



Here, rate of reactⁿ depends on 2 factors : (1) conc. of activated complex (2) freq. of decomposition of A.C.

$$\Rightarrow \text{rate} = (\text{conc. of A.C.}) (\text{freq. of decomposition of A.C.}) \quad \text{--- (1)}$$

(1) conc. of A.C. : reactⁿ is in equilibrium with A.C.,
so eq^m const. $K^{\ddagger} = \frac{[X^{\ddagger}]}{[A][B]}$

$$[X^{\ddagger}] = K^{\ddagger} [A][B] \quad \text{--- (2)}$$

conc. of
A.C.

12). Freq. of decomposition of A.C.: Since, A.C. is in a process of decomposition, so one of its vibrational degrees of freedom will change to translational degree of freedom. So, let E_{vib} be the average vibrational energy which results in bond breaking.

by Planck's eqⁿ: $E_{vib} = h\nu$

by classical mechanics: $E_{vib} = k_B T$

k_B = Boltzmann const.

$$\Rightarrow h\nu = k_B T = \left(\frac{R}{N_A}\right) T$$

$$\nu = \left(\frac{R}{N_A h}\right) T \quad \text{--- (3)}$$

from eqⁿ (1), (2) & (3), we get

$$\begin{aligned} \text{rate} &= k^\ddagger [A][B] \left(\frac{RT}{N_A h}\right) \\ &= \left(k^\ddagger \frac{RT}{N_A h}\right) [A][B] \end{aligned}$$

$$\text{rate} = k_2 [A][B]$$

where k_2 = rate const

$$\text{and } k_2 = \left(\frac{RT}{N_A h}\right) k^\ddagger = \left(\frac{k_B T}{h}\right) k^\ddagger \quad \text{--- (4)}$$

from thermodynamics, equilibrium constant is expressed in terms of ΔG° (standard free energy).

$$\Delta G^\circ = -RT \ln K$$

$$\text{So, } (\Delta G^\circ)^\ddagger = -RT \ln k^\ddagger \quad \& \quad (\Delta G^\circ)^\ddagger = (\Delta H^\circ)^\ddagger - T(\Delta S^\circ)^\ddagger$$

$$\therefore k^\ddagger = e^{-(\Delta G^\circ)^\ddagger / RT} = e^{-(\Delta H^\circ)^\ddagger / RT} \cdot e^{(\Delta S^\circ)^\ddagger / R}$$

on substituting the value of k^\ddagger in eqⁿ (4)

$$\Rightarrow \boxed{k_2 = \left(\frac{k_B T}{h}\right) e^{-(\Delta H^\circ)^\ddagger / RT} \cdot e^{(\Delta S^\circ)^\ddagger / R}}$$

Taking log both sides and diff. w.r.t. T

from eqⁿ ① & ②,

$$\text{rate} = \frac{dx}{dt} = k_1(a-x) - k_2 x \frac{(a-x_{eq})}{x_{eq}}$$

$$\text{or, } \frac{dx}{dt} = k_1 \frac{(x_{eq} - x)a}{x_{eq}}$$

$$\text{or, } \frac{dx}{(x_{eq} - x)} = \frac{a}{x_{eq}} k_1 dt$$

on integration,

$$-\ln(x_{eq} - x) = \frac{a}{x_{eq}} (k_1 t + I)$$

$$\Rightarrow -\frac{x_{eq}}{a} \ln(x_{eq} - x) = k_1 t + I$$

at $t=0$, $x=0$

$$\Rightarrow I = -\frac{x_{eq}}{a} \ln(x_{eq})$$

$$\Rightarrow k_1 t = -\frac{x_{eq}}{a} \ln(x_{eq} - x) + \frac{x_{eq}}{a} \ln(x_{eq})$$

$$\Rightarrow k_1 t = \frac{x_{eq}}{a} \ln\left(\frac{x_{eq}}{x_{eq} - x}\right)$$

→ Consecutive reactions: $A \xrightarrow{k_1} B ; B \xrightarrow{k_1'} C$

$$-\frac{d[A]}{dt} = k_1 [A] ; \quad \frac{d[C]}{dt} = k_1' [B]$$

$$+ \frac{d[B]}{dt} = k_1 [A] - k_1' [B]$$

