

Chemical Kinetics

→ The branch of physical chemistry that deals with speed (rate) of reaction and its mechanism is c/d Chemical kinetics.

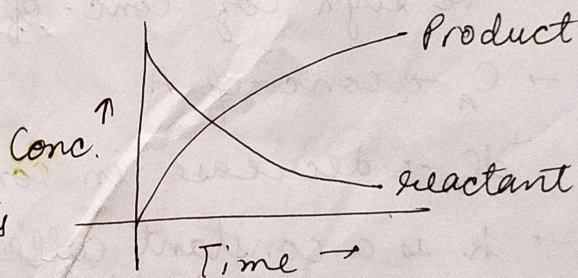
→ Rate of a rxⁿ is actually the speed with which reactants get converted to products.

→ Rate of a rxⁿ depends on nature of reactants and products as well as their concentration.

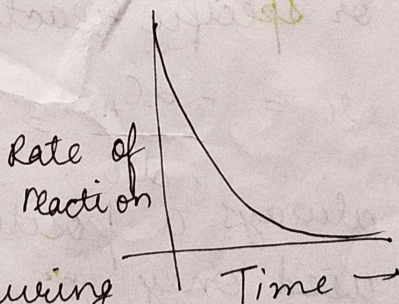
→ Rate or Velocity of a rxⁿ: → The change in concentration of reactant or product per unit time is c/d rate of rxⁿ.

→ As rxⁿ proceeds, reactant conc. ↓ (decrease) while product conc. ↑.

→ With time, this reaction rate decreases (initially fast because more reactants are present).



→ After some time, rate becomes too small to be observed.



→ If the change in conc. during time Δt is ΔC

then, average rate = $\pm \frac{\Delta C}{\Delta t}$

+ve sign suggests conc. of Product $\uparrow$ ing with time
-ve " " " " reactant $\downarrow$ ing " "

When $\Delta t \rightarrow 0$

$$\text{then rate } r = \pm \frac{dC}{dt} \quad (1)$$

- Here dC is the infinitesimal change in conc. in infinitesimal small time dt .
- This differential form (1) is called Instantaneous rxn rate.

Rate Constant

→ Consider a rxnⁿ
 $A \longrightarrow B$

$$r = - \frac{dC_A}{dt} = k C_A$$

-ve sign coz conc. of reactant ↓ with time

→ $C_A \rightarrow$ conc. of A

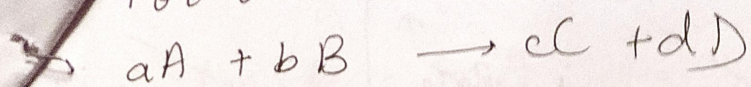
$dC_A \rightarrow$ decrease in conc. of A during small dt .

→ k is a constant called Rate constant or velocity constant or specific reaction rate

$$r = - \frac{dC_A}{dt} = + \frac{dC_B}{dt} = k C_A$$

→ Rate is always a positive ~~conc~~ quantity. Negative sign is used only for implying a decrease in concentration.

For a reaction.



$$r = -\frac{1}{a} \frac{dC_A}{dt} = -\frac{1}{b} \frac{dC_B}{dt} = +\frac{1}{c} \frac{dC_C}{dt} = +\frac{1}{d} \frac{dC_D}{dt}$$
$$= k C_A^a C_B^b$$

$$\text{If } C_A = C_B = 1,$$

$$\text{then } r = k$$

→ Therefore, rate constant is defined as the reaction rate when concentration of all reactants are unity.

Factors affecting rate of a rxn: →

a) Nature of reactants: →

→ Since a rxn involves bond breaking in reactants, rxn rate depends on nature of reactants.

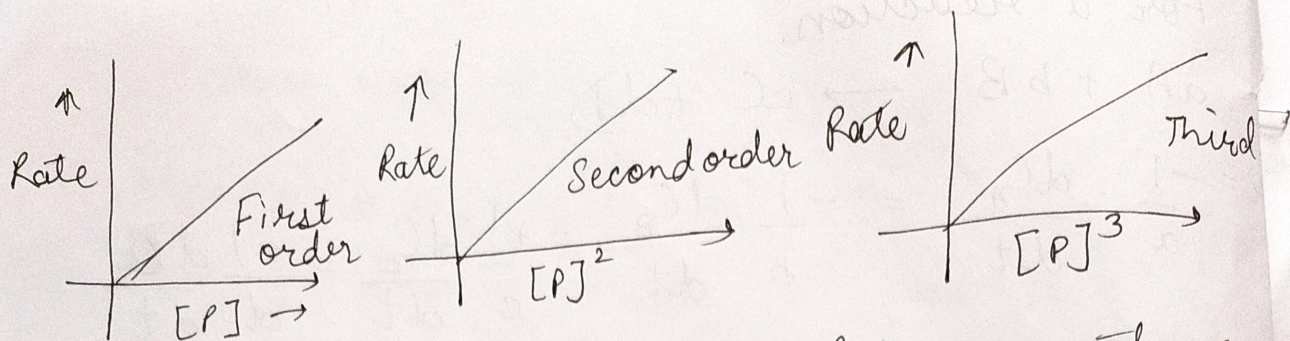
→ If the reactant molecules are simple, rxn rate would be faster and vice versa.

b) Effect of Concentration: →

→ According to Law of mass action, "Reaction rate is directly proportional to the molar concentration of reactant molecules."

e.g. Rusting of iron becomes faster during rainy season because humidity is higher in rainy season.

→ Effect of concentration on rate of reaction can be depicted from rate law equations

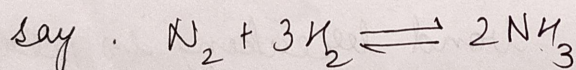


→ some rxⁿ that are reversible in nature, are also affected by conc. of Product $[P]$

c) Effect of Pressure: →

→ Pressure affects those reactions in which no. of moles of reactants and no. of products are not same ($\Delta n \neq 0$)

$$\Delta n = n_{\text{products}} - n_{\text{reactants}}$$



$$\Delta n = 2 - 4 = -2 \quad (\text{No. of moles decreasing in products})$$

→ Since, products has lesser no. of moles, pressure will decrease. Therefore, if we increase pressure, rxⁿ will move in forward direction (Le Chatelier's principle)

→ Those reactions which take place in solution state, ~~have~~ their rate depends on equilibrium constant and can be determined by using transition state theory.

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

$\Delta G^\ddagger$ - free energy of activated complex

Taking log

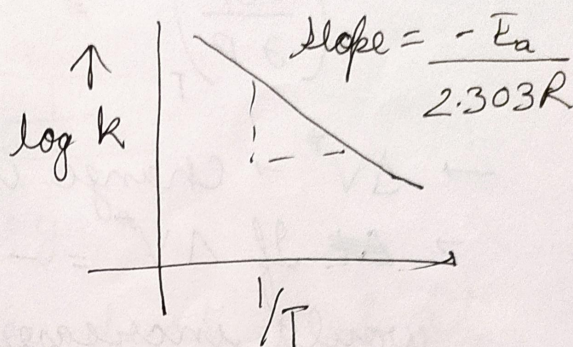
$$\ln k = \ln A - \frac{E_a}{RT}$$

or

$$\log k = \log A - \frac{E_a}{2.303RT}$$

Taking differentiation

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$



Integrating between T_1 and T_2

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

[If rate constants at two different temperature are known, E_a can be calculated]

→ A minimum energy is required with reactant molecules to undergo a chemical change. This minimum energy is c/d

Threshold energy.

→ However, most molecules have some thermal energy. To acquire threshold energy, molecules collide among themselves.

The difference b/w threshold energy and the energy possessed by molecules ~~at~~ is c/d Activation energy.

$K^{\circ} \rightarrow$ equilibrium constant. $\neq$

$\rightarrow$ Taking differentiation w.r.t P at const

Temperature

$$-\left(\frac{\partial G^{\circ}}{\partial P}\right)_T = -\Delta V^{\circ} = RT \left[\frac{\partial (\ln K^{\circ})}{\partial P} \right]$$

$\rightarrow \Delta V^{\circ} \rightarrow$ change in volume.

$\rightarrow$ ~~At~~ If $\Delta V^{\circ} = -ve$, then Pressure increase would increase rxn rate and vice versa

d) Effect of Temperature $\rightarrow$

$\rightarrow$ Most of the rxns show a 2-3 times increase in rxn rate when temp change is 10°C (between 25°C to 35°C).

$$\left[\frac{k_{t+10}}{k_t} \right] \approx 2-3$$

$\rightarrow$ This ratio is c/d Temperature coefficient.

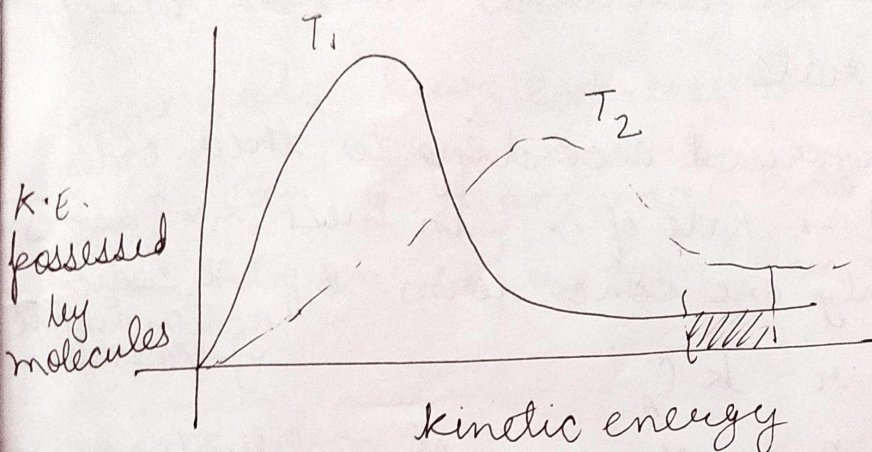
$\rightarrow$ For quantitative assessment, Arrhenius gave a relation b/w absolute Temp. T and rate constant k .

$$-E_a/RT$$

$$k = A e$$

$\rightarrow A \rightarrow$ Pre-exponential factor / frequency factor
 $E_a \rightarrow$ Activation energy

$$\text{Activation energy} = \text{Threshold energy} - \text{Avg. energy of molecules}$$



$T_2 > T_1 \rightarrow$ It is clearly evident that at higher temperature, K.E. possessed by molecules increase. So, they collide more often. Therefore, more molecules acquire threshold energy and thus rx^n rate increases.

e) Effect of catalyst: $\rightarrow$

$\rightarrow$ A catalyst increases rx^n rate by decreasing the activation energy.

$\rightarrow$ Unit of rate and rate constant: $\rightarrow$

For rate = $\text{mole litre}^{-1} \text{s}^{-1}$

For rate constant $k = (\text{mole litre}^{-1})^{1-n} \text{s}^{-1}$

where $n = \text{order of } rx^n$.

Order of a reaction. $\rightarrow$

$\rightarrow$ An order of a reaction may be defined as the sum total of those reactant molecules which affect the rxn rate.

$\rightarrow$ Rxn can be categorised according to their order

a) First Order rxn $\rightarrow$ Rate of rxn in these rxn ~~are~~ affected by only one conc. term. e.g. All radioactive decay reactions

$$\text{i.e. } r = k C_A$$

b) Second Order rxn $\rightarrow$ If rate is affected by two concentration terms

$$\text{i.e. } r = k C_A^2 \quad (\text{when one type of reactant})$$

or

$$r = k C_A C_B \quad (\text{when 2 types of reactant molecules are present})$$

c) Third order rxn $\rightarrow$ Rate is affected by three concentration terms.

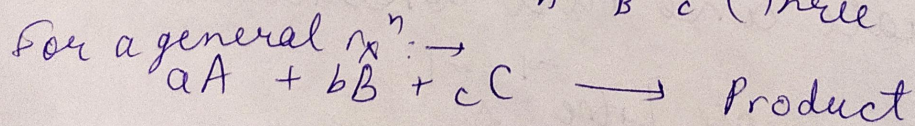
$$r = k C_A^3 \quad (\text{one type of reactant})$$

$$= k C_A^2 C_B \quad (\text{two " " "})$$

$$= k C_A C_B^2 \quad (\text{" " " "})$$

$$= k C_A C_B C_C \quad (\text{Three " " "})$$

For a general rxn $\rightarrow$



$$\text{rate} = k C_A^a C_B^b C_C^c$$

$$\text{Then } n (\text{order}) = a + b + c$$

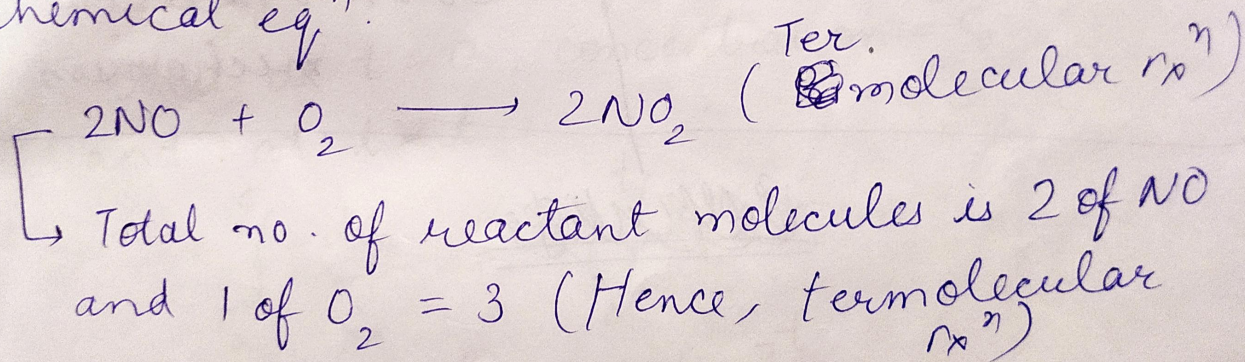
where a is order w.r.t. A , b is order w.r.t. B and c is order w.r.t. C .

order can also be defined, "The sum total of powers (exponents) of all reactants ~~to~~ terms to which their concentration are raised in a rate law expression".

Order can be fractional and zero too.
" is an experimentally determined quantity

Molecularity: -

Molecularity of a rxⁿ is defined as the total no. of reactant molecules in a balanced chemical eqⁿ.



→ Molecularity is never zero or fractional.

→ Theoretical concept (may or may not be equal to order of rxⁿ)

→ usually defined for simple elementary rxⁿ.

Order

- Experimental quantity determined by reaction rate
- Can be fractional or zero.
- Not determined from balanced chemical eqⁿ (experiments needed)
- Describes mechanism

Molecularity

- Theoretical quantity determined from balanced eqⁿ of a determining step.
- Always a whole number and never zero or fractional
- Determined from balanced eqⁿ
- Doesn't describe mechanism

Diff. type

Integration of Rate Expressions

①

First Order Reaction: $\rightarrow$



Differential rate expression

$$r = -\frac{dc_A}{dt} = \frac{dc_P}{dt} = k C_A$$

Separate the variables

$$\frac{-dc_A}{C_A} = k_1 dt$$

Integrate the eqⁿ considering
that at $t=0$, concentration = C_0
and at $t=t$ " " = C

$$\int_{C_0}^C \frac{-dc_A}{C_A} = k_1 \int_0^t dt$$

$$[-\ln C_A]_{C_0}^C = k_1 [t]_0^t$$

$$-\ln \frac{C}{C_0} = k_1 t$$

$$\text{or } C = C_0 e^{-k_1 t}$$

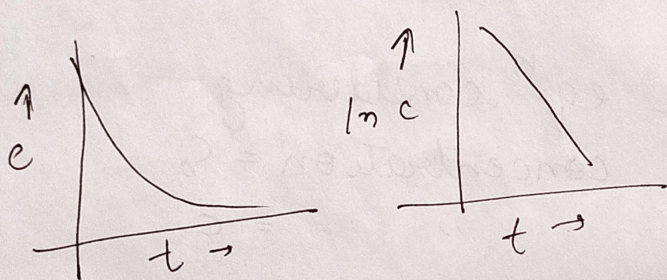
$$\text{or } k_1 = \frac{1}{t} \ln \frac{C_0}{C}$$

→ If the initial conc. of reactant is "a" and "x" moles of it react to form product. At time t, the remaining reactant will be a-x

$$\text{so } C_0 \propto a$$

$$C \propto (a-x)$$

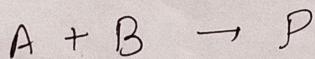
$$k_1 = \frac{1}{t} \ln \frac{a}{a-x}$$



→ For a first order reaction, conc. of reactant decreases exponentially with time.

B) Second Order reaction: →

a) When reactants are different: →



Initial conc. of A = a } i.e. at t = 0
Initial " " B = b

After time t, x moles of A and x moles of B react to form x moles of product.

herefore at time = t

reactant concentrations are
($a-x$) and ($b-x$).

Differential rate expression

$$x = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[P]}{dt} = k_2[A][B]$$

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

k_2 = second order rate constant

Separate the variables

$$\frac{dx}{(a-x)(b-x)} = k_2 dt \quad (1)$$

$\frac{1}{(a-x)(b-x)}$ in terms of partial fractions
can be written as: $\rightarrow$

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

Putting this value in (1) and
integrating

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

$\frac{1}{a-b}$ is a constant in the given eqⁿ
so kept outside the integration

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

$$= \frac{1}{(a-b)} \ln \frac{a-x}{b-x} = k_2 t + C \quad (2)$$

C is constant of integration

Since at $t=0$, $x=0$, put value in (2)
to determine value of C

$$C = \frac{1}{a-b} \ln \left(\frac{a}{b} \right) \quad (3)$$

Put value of (3) in (2)

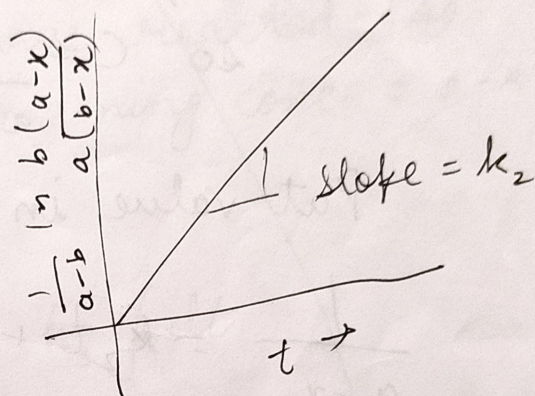
$$\frac{1}{(a-b)} \ln \frac{a-x}{b-x} = k_2 t + \frac{1}{(a-b)} \ln \left(\frac{a}{b} \right)$$

Rearranging and solving

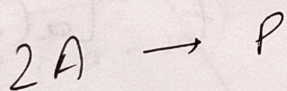
⑤

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

$$= \frac{1}{(a-b)t} \ln \frac{b(a-x)}{a(b-x)}$$



b) when both reactants are same: $\rightarrow$



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

At $t=0$, initial conc = a

At $t=t$, x moles reacted to form product so $(a-x)$ remained.

Separate variables

$$\frac{1}{(a-x)^2} = k_2 dt$$

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

$$\text{or } \frac{1}{a-x} = k_2 t + C \quad (4)$$

$C = \text{Integration const.}$

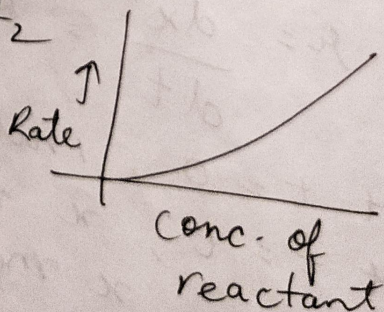
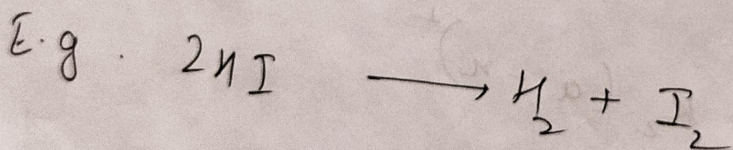
$$t = 0, x = 0$$

$$\text{so } C = \frac{1}{a}$$

Put value in (4)

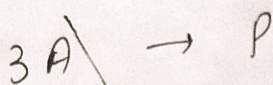
$$\frac{1}{a-x} = k_2 t + \frac{1}{a}$$

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



(7)

c) Third Order reaction: $\rightarrow$
(Not in course)



Differential eq.

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

At $t = 0$, conc = a
At $t = t$, x moles

have reacted, so
remaining conc. = $a-x$

Separate variables

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

$$= \frac{1}{2(a-x)^2} = k_3 t + C \quad (5)$$

C = Integration const.

$$\text{At } t = 0, x = 0$$

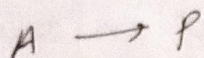
$$\text{so } C = \frac{1}{2} a^2$$

Put value of C in (5)

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

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

D) Zero Order reaction: $\rightarrow$



$\rightarrow$ Rate not affected by change in conc. of one or more reactants.

$$r = -\frac{d[A]}{dt} = k_0$$

$$-d[A] = k_0 dt$$

At $t=0$, conc. be A_0

$t=t$ " " A

$$-\int_{A_0}^A d[A] = k_0 \int_{t=0}^{t=t} dt$$

$$k_0 t = [A_0] - [A]$$

$$\boxed{k_0 = \frac{1}{t} [A_0 - A]}$$

Half-Life

Half life of a reaction is the time in which the reactant concentration is reduced to half of its initial concentration.

$$\text{At } t = t_{1/2} \quad A' = \frac{A}{2}$$

For a first order rxⁿ: →

$$k_1 = \frac{1}{t_{1/2}} \ln \frac{a}{a - \frac{a}{2}} = \frac{1}{t_{1/2}} \ln 2 = \frac{0.693}{t_{1/2}}$$

$$\text{or } t_{1/2} = \frac{0.693}{k_1}$$

→ As there is no term of concentration in this expression, $t_{1/2}$ in first order rxⁿ is independent of initial concentration of reactants.

b) For a second order rxⁿ: →

$$k_2 = \frac{1}{t_{1/2}} \left[\frac{a/2}{a(a - a/2)} \right] = \frac{1}{t_{1/2}} \times \frac{a/2}{a(a/2)} = \frac{1}{a t_{1/2}}$$

$$\text{or } t_{1/2} = \frac{1}{k_2 a}$$

→ Here, $t_{1/2}$ is inversely proportional to initial conc. "a".

For n^{th} order rxⁿ: →

$$t_{1/2} = \frac{2^{n-1} - 1}{k_n (n-1) a_0^{n-1}}$$

Methods of determining order of a reaction:

a) Use of differential rate expressions: →

→ Method devised by Van't Hoff.

→ Rate for n^{th} order rxn given by: →

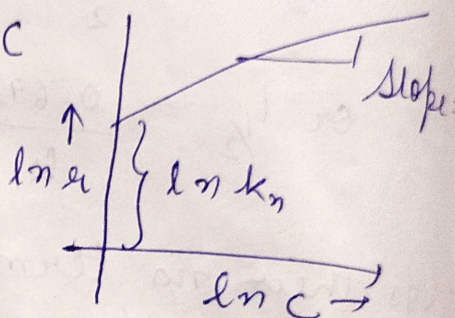
$$r = k_n C^n$$

Taking logs

$$\ln r = \ln k_n + n \ln C$$

→ On plotting $\ln r$ vs $\ln C$

slope gives n (order of the rxn) and intercept gives $\ln k$ value.



b) Use of integral rate expressions: →

→ This works on a hit and trial principle.

→ We have already derived expressions for first, second, zero and third order reactions.

→ If by using a particular expression, the value of k comes out to be constant then the assumed expression is thought to be applicable.

→ Method can be applied analytically and graphically.

isolation method

This is carried out by taking one of the reactants in large excess, so that the order of the rxn in terms of the other reactant (which is not in excess) can be calculated.

Likewise, order w.r.t all reactants are calculated keeping others in ~~an~~ excess.

→ Total n (order) of rxn = sum of orders w.r.t. all reactants.

c) ~~The~~ The Half life method: $\rightarrow$

$\rightarrow$ If all the reactants are present in same molar concentrations,

$$\text{then } t_{1/2} \propto \frac{1}{a_0^{n-1}}$$

$\rightarrow$ If two experiments with different values of " a_0 " (initial concentration) are carried out,

$$\text{then, } \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1} \right)^{n-1}$$

$$\text{or } \frac{\ln(t_{1/2})_1}{(t_{1/2})_2} = (n-1) \ln \frac{a_2}{a_1}$$

$$n = 1 + \frac{\ln(t_{1/2})_1}{\frac{(t_{1/2})_2}{\ln\left(\frac{a_2}{a_1}\right)}}$$

$\rightarrow$ Method given by Ostwald.

Arrhenius Eqⁿ: → Effect of Temp. on rxⁿ rate: → (1)
Eqⁿ for calculation of energy of activation
of a rxⁿ

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

k = rate const. at temp. T

A = Arrhenius pre-exponential factor (also c/d frequency factor)

→ E_a and A are c/d Arrhenius parameters.

Take log both sides

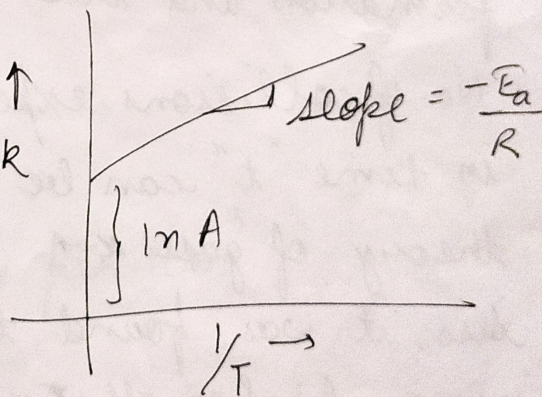
$$\ln k = \frac{-E_a}{RT} + \ln A$$

Taking differentiation

w.r.t. T

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

↑
 $\ln k$



→ Now integrate b/w T_1 and T_2 when corresponding rxⁿ rates are k_1 and k_2

→ E_a is assumed to be constant b/w T_1 and T_2 .

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

→ c/d Integrated Arrhenius eqⁿ

→ Arrhenius eqⁿ helps calculate Activation energy when rxⁿ rate at different T is known and vice versa.

Theories of Reaction rates

→ Two important theories have been proposed

a) Collision theory

b) Activated Complex theory

Collision Theory

→ This theory suggests that collisions between reacting molecules result in product formation and thus affect reaction rate

→ No. of collisions experienced by a molecule in time "t" can be obtained from Kinetic theory of gases.

→ Also, it was found that no. of collisions is way higher than those reactant molecules that get converted to products.

→ This theory suggests that a rxⁿ is feasible only if the molecules have a certain amount of energy c/d Threshold energy.

Since molecules are in constant motion, upon collision, they exchange energy among themselves. This results in some molecules acquiring energy sufficient to undergo chemical reaction.

→ If Z molecules per cm^3 per second of a gas undergo bimolecular collisions, and if E_a is activation energy, then no. of reacting molecules will be $Z e^{-E_a/RT}$

$$\frac{dx}{dt} = Z \cdot e^{-E_a/RT}$$

→ If the reacting molecules are of same type

$$\frac{dx}{dt} = k n^2$$

→ n = No. of molecules per cm^3

k = rate constant

$$k = \frac{Z}{n} e^{-E_a/RT}$$

→ According to kinetic theory of gases, no. of collisions b/w 2 molecules per cm^3 per second $\therefore \rightarrow$

$$Z = 4n^2 \sigma^2 \left(\frac{\pi RT}{M} \right)^{1/2}$$

σ = Collision diameter

M = Molecular wt.

$$k = 4\sigma^2 \left(\frac{\pi RT}{M} \right)^{1/2} e^{-E_a/RT}$$

or $k = Z' \cdot e^{-E_a/RT}$

where $Z' = 4\sigma^2 \left(\frac{\pi RT}{M} \right)^{1/2}$

→ Here, Z' is equivalent to A (pre-exponential factor) of Arrhenius eqⁿ and is c/d collision number.

→ Failure of Collision Theory: →

→ In a few rxⁿ, the theoretical and practical values of rate constants were found to differ a lot.

e.g. the gas phase rxⁿ b/w C2H5OH and acetic anhydride has theoretical value around 10^5 times more than value obtained by practical.

→ Therefore, a factor (Probability or Steric factor) was introduced.

$$k = P \cdot Z \cdot e^{-E_a/RT}$$

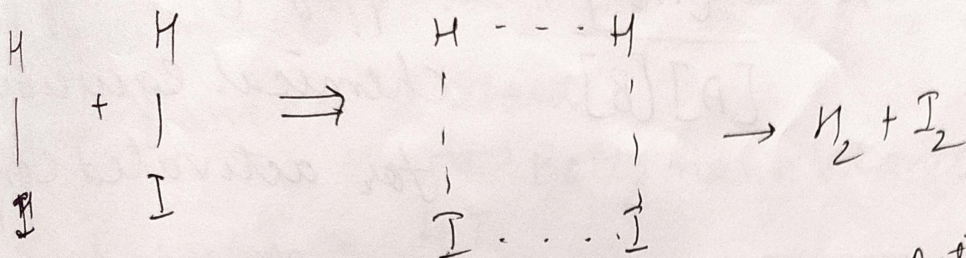
→ P varies from 1 to 10^{-9}

→ P was introduced because it was thought that a definite geometry is needed to undergo reaction.

Transition State Theory

OR

Activated Complex theory



→ Theory proposed by Eyring and Polanyi.

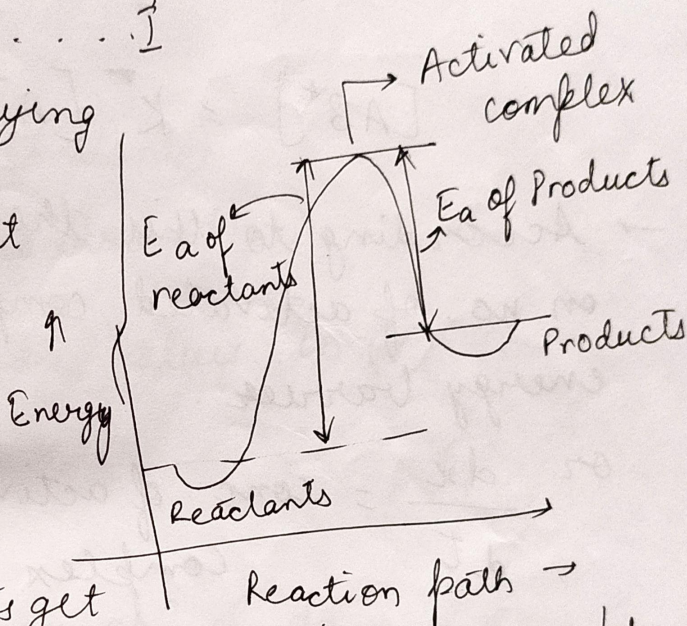
→ This theory suggested that as reactant molecules approach each other, their bond lengths change and also their energy.

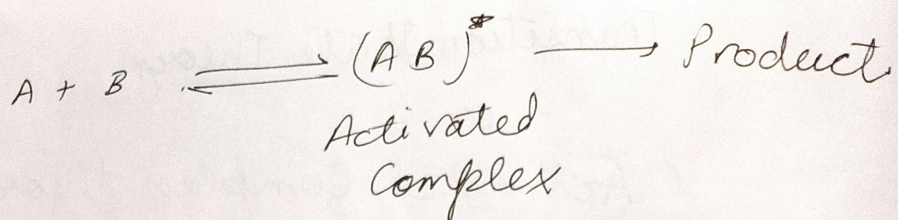
→ Before rxn, reactants get arranged in a definite configuration, now c/d activated complex.

→ Activated Complex can not be separated from the reaction mixture.

→ When this activated complex breaks, products are formed.

→ Rxn rate was considered proportional to disintegration of this activated complex.





$$K^* = \frac{[AB^*]}{[A][B]} \rightarrow \text{Applying Law of chemical equilibrium for activated complex}$$

$$[AB^*] = K^* [A][B]$$

→ According to this theory - rate of rxⁿ depends on no. of activated complex crossing the energy barrier.

or $\frac{dx}{dt} = \text{conc. of activated complex} \times \text{rate of disintegration of activated complex to products.}$

$$\frac{dx}{dt} = K^* [A][B] \times \text{rate of disintegration of activated complex}$$

→ This disintegration of activated complex will occur only when vibrational energy of bonds become critical enough to undergo bond breaking.

→ Rate of disintegration
of activated
complex

$$\nu = \frac{E_{\text{vibration}}}{h} \quad (1)$$

$E_{\text{vibration}} \rightarrow$ Avg. vibration energy at temp T

$h \rightarrow$ Planck's constant

$\rightarrow$ Boltzmann's Constant

$$E_{\text{vibration}} = k_B T$$

(Boltzmann Const). $k_B = \frac{R}{N}$ (gas constant)
(Avogadro's No.)

Putting various values in (1)

$$\nu = \frac{RT}{Nh}$$

Put this value in eqⁿ of $\frac{dx}{dt}$

$$\frac{dx}{dt} = \frac{k^* [A][B] RT}{Nh} \quad (2)$$

→ From Law of mass action, we know,
rate of rxⁿ is proportional to conc of
reactant molecules.

$$\frac{dx}{dt} = k[A][B] \quad (3)$$

Equating (2) and (3)

$$k[A][B] = \frac{K^* [A][B] RT}{Nh}$$

(I) $k = \frac{K^* RT}{Nh}$ [Mathematical expression for T.S. Theory]

From thermodynamics

$$\Delta G^* = -RT \ln K^* \quad (4)$$

$\Delta G^* =$ (free energy of activated complex - free energy of reactants)

also

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (5)$$

Equating (4) and (5)

$$\ln K^* = \frac{-(\Delta H^* - T\Delta S^*)}{RT}$$

or $K^* = e^{-(\Delta H^* - T\Delta S^*)/RT}$

Put this value in (I)

$$k = \frac{RT}{Nh} \cdot e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R}$$