Sem 4. Unit 2nd

Chapter: Chemical kinetics

Chemical Kinetics:-

→ Study of Rates of reactions and factors affecting Rate

Ex:- i) $AgNO_3 + NaCl \longrightarrow \underset{ppt.}{AgCl} + NaNO_3$ ---- fast Rn.

ii) Rusting of Fe in air & moisture to form --- slow Rn.
$Fe_2O_3 \cdot xH_2O$ (Rust).

iii) Pseudo order Rns. and n=1

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$ ---- intermediate Rn.
Cane sugar (excess) Glu- (Ald.) Fru. (ketone)

$\underset{(starch)}{C_6H_{10}O_5} + H_2O \xrightarrow{H^+} 2\,C_6H_{12}O_6$ ---- intermediate Rn.

(ester) $CH_3COOC_2H_5 + \overset{(excess)}{H_2O}$ (excess) $\xrightarrow{H^+} CH_3COOH + C_2H_5OH$ ---- " "

Conclusion:- Speed is diff. or Rate is different

Rate = ? It can be defined as the change in conc. of Reactants or Products per unit time.

In Gen, Rate = $\frac{\text{conc.}}{\text{time}}$ = $\text{conc}\cdot\text{time}^{-1}$ = atm time^{-1} = bar time^{-1}.

By convention, conc. = moles/lit = molarity = Active Mass.
time = sec.

∴ Rate = moles/lit/sec = Ms^{-1}

Also, for Reactants, Rate = $\frac{\text{Decrease in Conc of R}}{\text{time taken}} = -\frac{\Delta[R]}{\Delta t}$

for Products, Rate = $\frac{\text{Increase " " " P}}{\text{" "}} = +\frac{\Delta[P]}{\Delta t}$

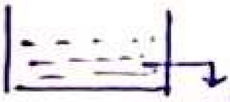
Q:- for 1st order Rn; Unit of Rate = ?
for zero " ", " " "
for 2nd " ", " " "
for nth " ", " " "
→ Sol:- $[mL^{-1}s^{-1}]$

Hint:- What may be the order of Rn:
i) Unit of Rate will never change.
ii) Unit of Rate constant varies with order of Rn.

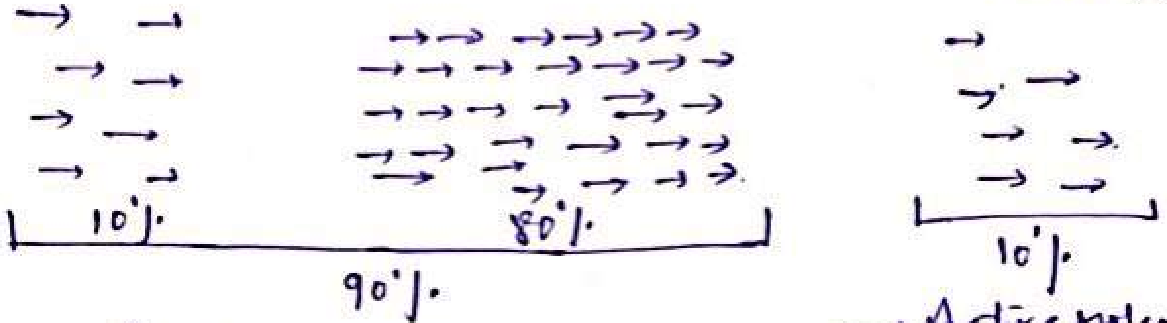
* iii) P/T on → Fract-Order Rns.

Basic:-

In Gen, during any ch Rxn., distribution of velocity is as follows:-



chemical + molecules.

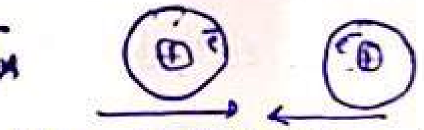


⟿ Passive molecules
⟿ In effective collisions
⟿ donot possess E_{Thr} but less than that = E_R

⟿ Active molecules
⟿ effective collisions
⟿ Possess E_{Thr}.

E_{Thr} = ? i) It is that minimum amt of energy which must be possessed by the reactants so that they can bring abt effective collisions & can form products.

ii) " " " " " " " " is reqd to overcome inter-electron repulsions.



inter ē Repulsions
⟶ they may not collide
⟶ they just collide
⟶ they bounce back.

* Acc. to kinetics, lab always want harsh & violent movements.

E_R = ? It is the average amt of energy possessed by the reactants.

E_P = ? " " " " " " " " products.

* Effective collisions are always less (2-3, 10%)

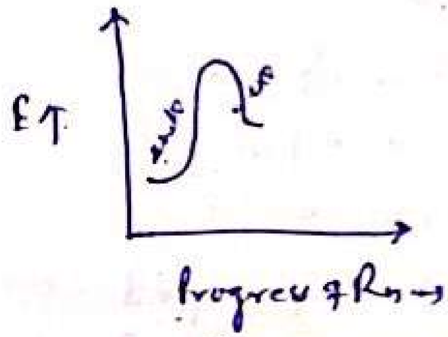
* Active molecules population is v. less (" ").

Thus, each & every ch. Rn. needs Activation Energy

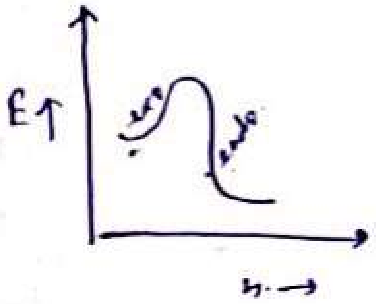
i.e, $E_r + E_a = E_{Thr}$.

Ea = ? It can be defined as the minimum amt. of energy supplied (additional) from outside to the reactants, so that they can reach to E_{Thr} and hence can form products.

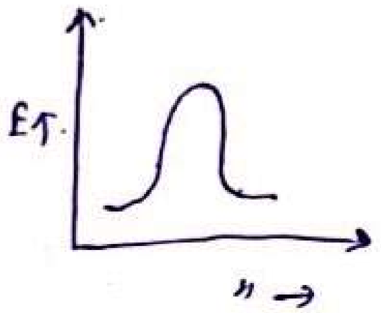
Graphically:-



∘ this Rn is endothermic
$\Delta E|_{\Delta H} = +ve$



∘ this Rn is exothermic
$\Delta E|_{\Delta H} = -ve$



$\Delta E|_{\Delta H} = 0$
[Athermic Rns.]

Also, Acc. to Energetics,

Exothermic Rns.

$A - \Delta \rightarrow B$

$A \longrightarrow B + \Delta$

$A \longrightarrow B \quad \Delta E = E_p - E_r \; [\because E_p < E_r]$

$\Delta E|_{\Delta H} = -ve$

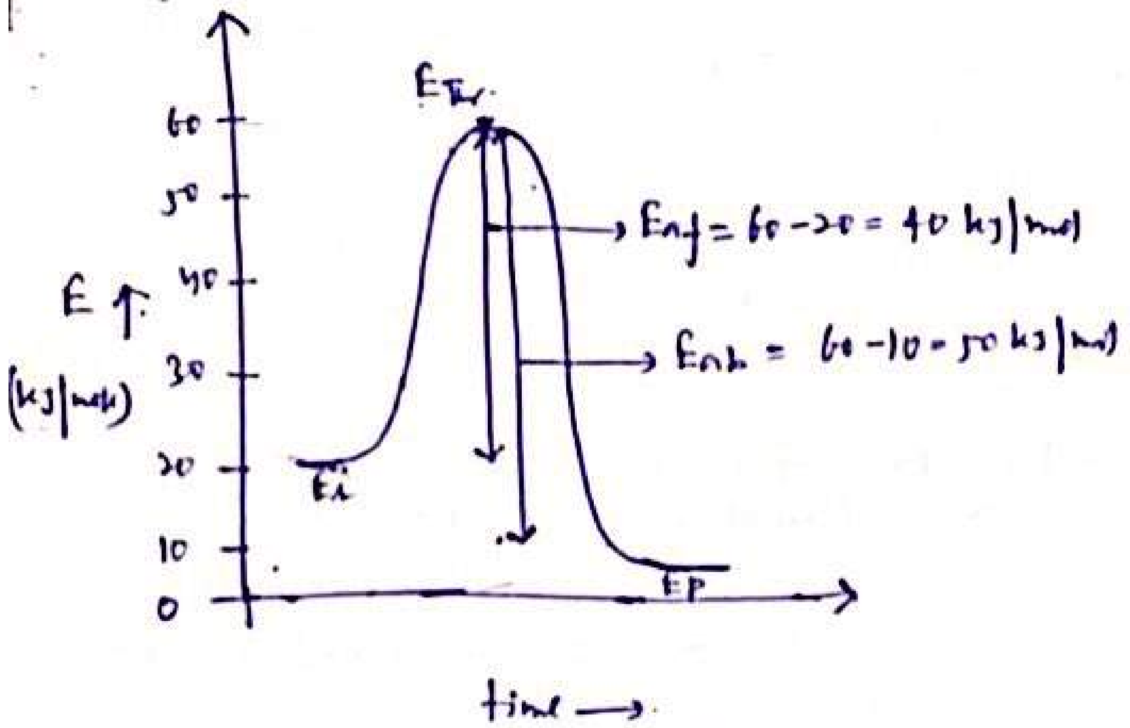
Endothermic Rns.

$A + \Delta \rightarrow B$.

$A \longrightarrow B - \Delta$

$A \longrightarrow B \quad \Delta E = E_p - E_r \; [\because E_p > E_r]$

$\Delta E|_{\Delta H} = +ve$



→ forward Rxn is Exothermic
Backward " " Endothermic

→ $\Delta E | \Delta H = -ve$

→ $E_{af} = 40$ kJ/mol

→ $E_{ab} = 50$ kJ/mol.

∴ $\Delta E | \Delta H = E_{af} - E_{ab} = 40 - 50 = -10$ kJ/mol.

OR $\Delta E | \Delta H = E_p - E_r = 10 - 20 = -10$ kJ/mol.

In Gen, $\boxed{\Delta E / \Delta H = E_{af} - E_{ab} = E_p - E_r}$

Rate conventions:-

① Concentration $[A]$ ✓ $\{A\}$ ✗ (A) ✗

OR c_A for solids & liquids
p_A for gases.

Also, conc. = Active Mass
= Molarity
$= \frac{X}{MV}$

② a) Average Rate, $\frac{\Delta x}{\Delta t} = \frac{\text{*Avg change in Conc.}}{\text{" " " time}}$

Acc. to kinetics
we are interested to calculate rate at particular moment of time ∴ diff. term is used.

b) Differential Rate $\frac{dx}{dt}$
OR Instantaneous Rate

In Gen, $\left(\frac{\Delta x}{\Delta t}\right)_{t \to 0} = \frac{dx}{dt}$

③ Rate constant = k

Ex:- $nA \longrightarrow$ Products. n = Order of Rn.
$= 0, 1, 2, 3, 1/2, 3/2, 5/2$

Acc. to Rate Law,

$$\frac{dx}{dt} \propto [A]^n$$

OR $\frac{dx}{dt} = k[A]^n$

OR $k = \frac{dx/dt}{[A]^n} = \frac{\text{conc}\cdot\text{time}^{-1}}{[\text{conc}\cdot]^n} = \frac{m\,l^{-1}\,s^{-1}}{(m\,l^{-1})^n}$

$= (m\,l^{-1})^{1-n}\cdot s^{-1}$

Ex:- if $n = 0$ k Units $= m\,l^{-1}\,s^{-1}$ = Rate of Rn.

$n = 1$ $= s^{-1}$

$n = 2$ $= m^{-1}\,l^{+1}\,s^{-1}$

$n = 3$ $= m^{-2}\,l^{+2}\,s^{-1}$

$n = 1/2$ $= m^{1/2}\,l^{-1/2}\,s^{-1}$

$n = 3/2$ $= m^{-1/2}\,l^{+1/2}\,s^{-1}$

In Gen i) What may be the time, value of k remains same.

ii) Units of k, for particular order of Rn. remains same.

iii) High value of k --- means --- fast Rn.
Low " " " ---- means ---. slow Rn.

Ex- $A \rightarrow B$ $k = 10^{4}\ s^{-1}$
$C \rightarrow D$ $= 10^{1}\ s^{-1}$
$K \rightarrow L$ $= 10^{-2}\ s^{-1}$
$P \rightarrow Q$ $= 10^{-3}\ s^{-1}$

a) Order of Rn = ? One → Units
b) slow ---- $P \rightarrow Q$
fast ---- $A \rightarrow B$.

iv) k changes with temperature..

④ Specific Rn. rate = k
→ It is the another name of Rate constant.

⑤ Specific rate
→ It is the rate, but when M=1
[that is when conc. of each of the reactant is taken as unity]

Ex:- $nA \rightarrow P$

a) $\frac{dx}{dt} = k[A]^{n} = k \times (1)^{n} = k$

b) $aA + bB \rightarrow P$.

$$\frac{dx}{dt} = k[A]^{a} \times [B]^{b} = k \times (1)^{a} \times (1)^{b} = k.$$

[Here, n, a, b = order of Rn]

SPEED OF A REACTION

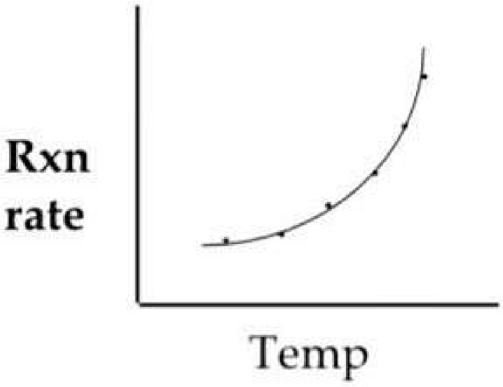
Chemical savvy says that reaction occurs when molecules or atoms come in contact (or collide together).

Some reactions are very fast

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$

Others are very slow

$4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$



Reaction rate vs. Temperature

In general, the rate of a reaction doubles for every 10° increase of temperature.

KINETIC MOLECULAR THEORY

- ***Kinetic Molecular Model***
- ***Collision Theory - explains factors which influence the speed of a chemical reaction.***
- ***Basic idea:***
- ***In a reaction, there must be a chemical changes***
  - ***For chemical change to occur***
    - ***Reactant bonds are broken***
    - ***Product bonds are formed***

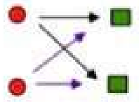
Factors influence reaction rate:

Rate $\propto$ [**Collision frequency** • **Orientation of molecules** • **Activation Energy**] **&** **Catalyst**

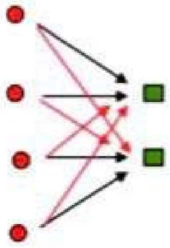
COLLISION FREQUENCY

- *1. Collision Theory - A collision must occur*
- *Collision frequency influence the rate of a reaction*
- *rate ∝ collision / time*

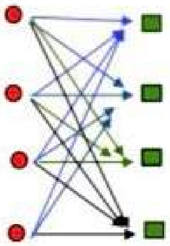
4 particle system
→ 4 collision

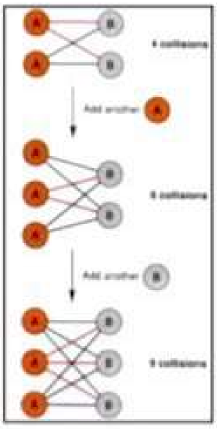


6 particle system
4 ● and 2 🟩
→ 8 collision



8 particle system
4 ● and 4 🟩
→ 16 collision





In general: n • n = number collisions

Z = collision frequency = z • [A] [B]

STERIC FACTOR

- ***2. Orientation Factor - For collision to lead to products, the orientation of the molecules must be correct for bonds to break***

Before collision Collision After collision

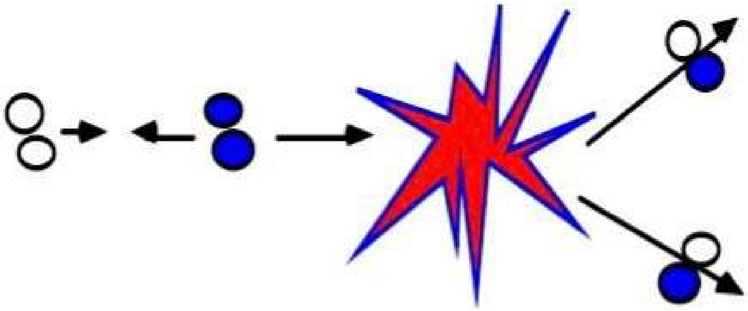
(a) Effective collision

Before collision Collision After collision

(b) Ineffective collision

ACTIVATION ENERGY

- ***KMT- According to the Kinetic Molecular Theory; any molecule in motion possesses kinetic energy (1/2 mv^2). Faster the motion, the more likely reactants will fragment upon collision.***
- ***Consider the Car Analogy:***
  - ***Cars will not disintegrate by itself. However at low speeds, collision between car will cause little to no damage. But at high speeds, there will be major damages.***

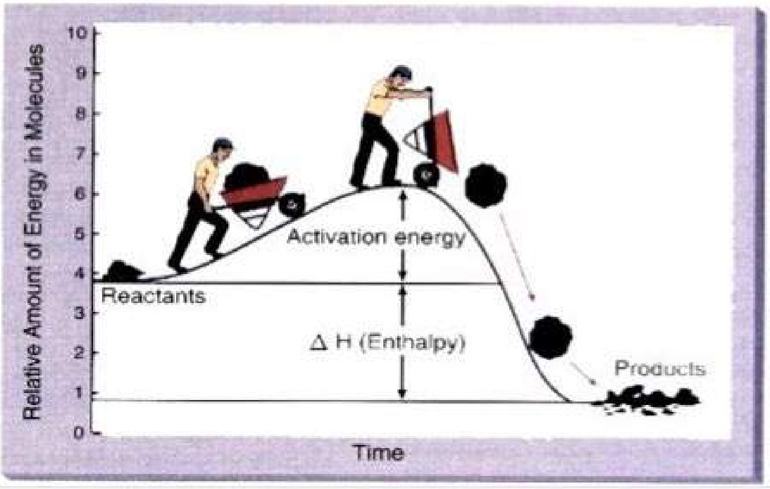


E_{act} - ACTIVATION ENERGY

•If the k.E. is large enough, then upon collision molecules will vibrate so vigorously as to break bonds which can lead to new products.

•Energetically, there must be some minimum collision energy that must be exceeded before a reaction occurs.

Arrhenius Suggested that molecules must possess a minimum amount of K.E. in order to react. In other words, energy must be available to the reactant for the reaction to occur

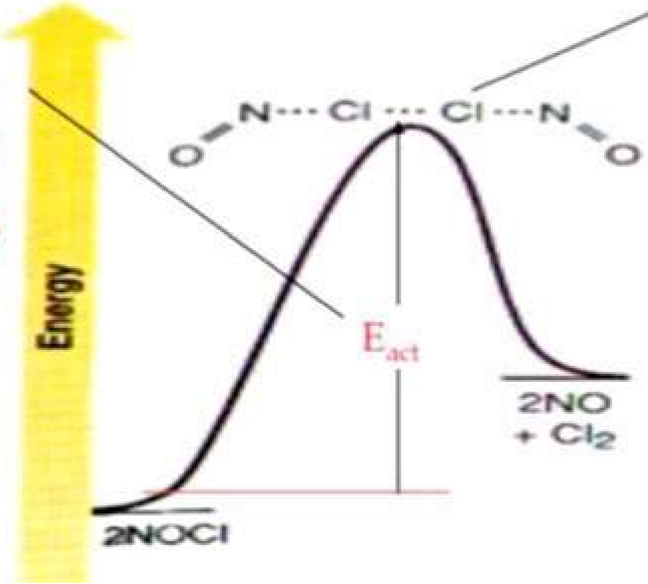


SVANTE AUGUST ARRHENIUS

REACTION COORDINATE DIAGRAM

Consider the following reaction coordinate diagram in which NOCl is decomposed to NO and Cl_2.

The reactant NOCl has a certain initial energy. In order for products to form, an activation barrier must be overcome, this activation barrier is a the energy of the transition state, or the activated complex.



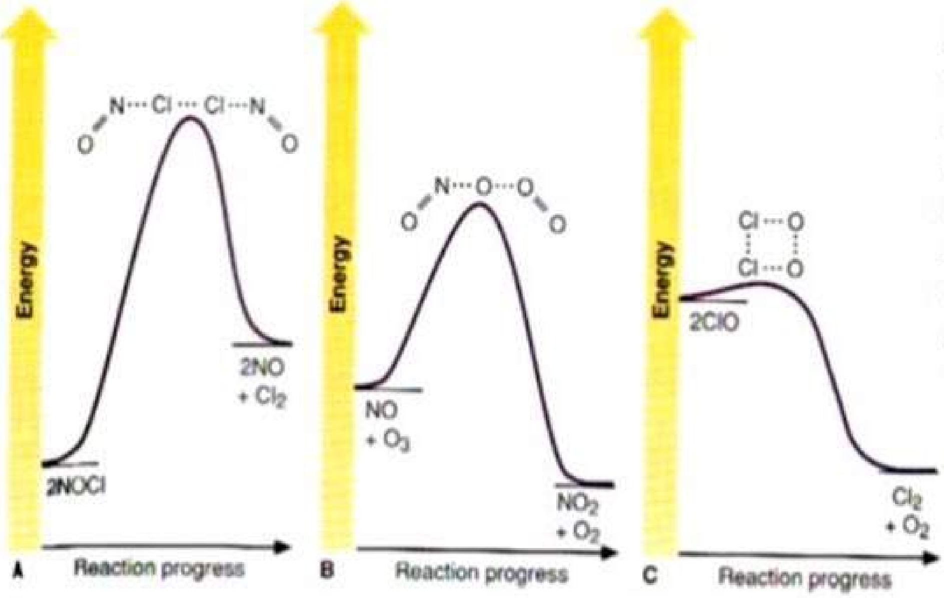
***E_a Activation Energy:* The minimum energy and conditions necessary for reactant to be converted to products.**

***Activated Complex:* The intermediate specie that is forms or produced [intermediate].**

In the end, the NO and Cl_2 products formed is more energetic than NOCl, the reaction is endothermic. □H (+)

REACTION RATE AND E_{act}

The rate of a reaction is directly correlated to the height of the activation barrier. The higher the E_{act}, the slower the reaction. Reactions with very low Eact, tend to go very fast

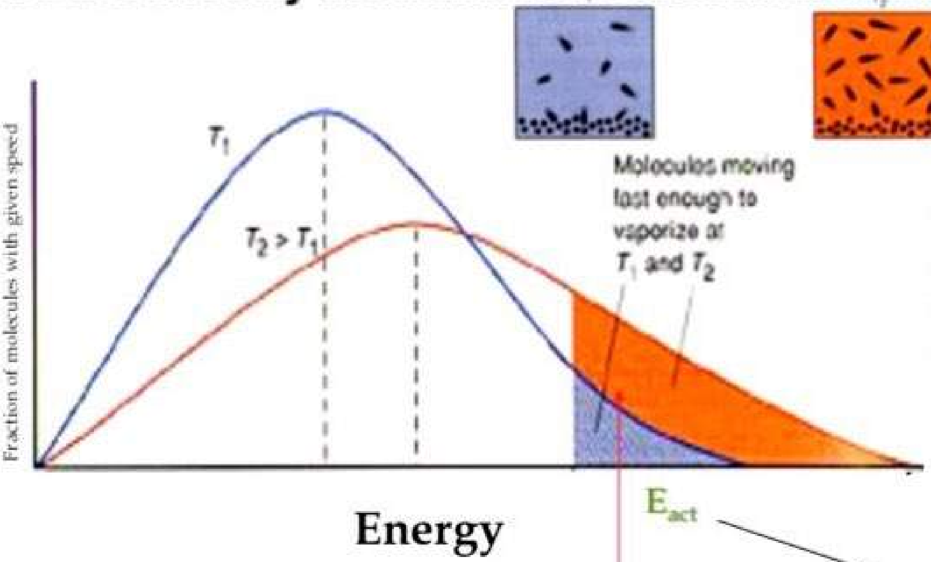


In the reaction coordinate diagram:
Rxn A is endothermic with a high E_{act}.
Rxn B is exothermic with a lower E_{act}, and
Rxn C is exothermic with a very low E_{act}.
This reaction is very fast.

The number of molecules with the minimum kinetic energy large enough to initiate a reaction is related to temperature.

MAXWELL-BOLTZMAN DISTRIBUTION

Recall from the gas laws that an energy profile for molecules can be describe by the Maxwell-Boltzman distribution diagram.



As the temperature goes up, the population of molecules with more energy also increases.

$E_{act} \propto e^{-Ea/RT}$

The increase of temperature yields to more molecules exceeding the E_{act}, the minimum energy required to overcome the activation barrier for a reaction to occur.

ARRHENIUS EQUATION

Savant Arrhenius (1889) - Expressed the three factors responsible for a reaction into an equation (Arrhenius Equation).

Factors influence reaction rate:

Rate → [Collision frequency • Orientation of molecules • Activation Energy]

A – pre-exponetial term

Eact = $e^{-\{Ea/RT\}}$

therefore, $\text{Rate} = A\,e^{-\{Ea/RT\}} \bullet [\text{Conc}_{(\text{react})}] = k\,[\text{Rct}]^{x}$

Where, K - rate constant = $A\,e^{-\{Ea/RT\}}$

$$K = A\,e^{-\{Ea/RT\}}$$

$$\ln K = \ln A - E_a/RT$$

$$\underset{y}{\ln K} = \underset{m}{-E_a/R}\ \underset{x}{(1/T)} + \underset{b}{\ln A}$$

GRAPHIC REPRESENTATION: ARRHENIUS EQUATION

$$\ln K = -\frac{Ea}{R} \bullet \frac{1}{T} + \ln A$$

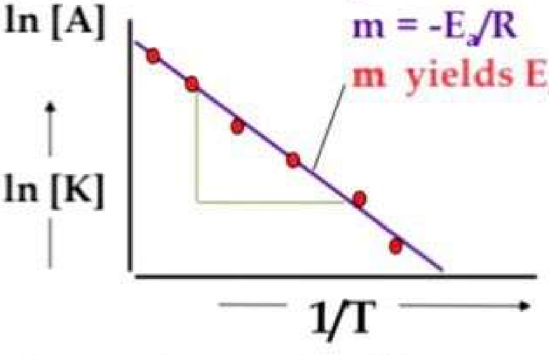
Where:

Ea - Activation Energy

R = 8.314 J/mol•K

T = Absolute Temp

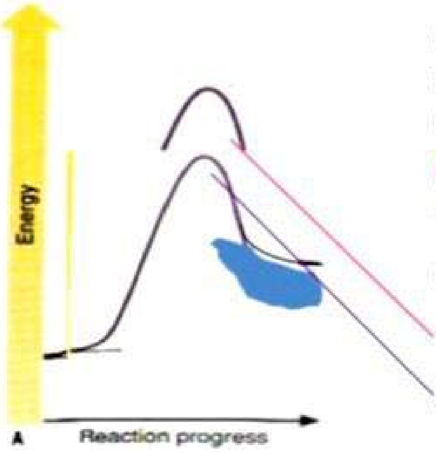
A = Collision freq. factor



plot of ln K vs 1/T yields

$m = -E_a/R$

m yields E_{act}



Note that as the magnitude of E_{act} (↑), the K becomes smaller, or the rate constant is smaller. *$\ln K \propto -E_a$ (minus E_a)*

The reaction rate decreases as the energy barrier increases

E_{act} large, K also large

E_{act} small, K also small

For the graph:

$$\ln \frac{K'}{K} = \frac{Ea}{R}\left[\frac{1}{T} - \frac{1}{T'}\right]$$

EFFECT OF TEMP.

① ~~co~~ Arrhenious Eqn ?

$$k = A\cdot e^{-Ea/RT}$$

where, k = Rate Constant.

A = Arrhenious factor or freq. ~~fre~~ factor or pure exponential factor. (It refers to binary collisions of molecules)

$e^{-Ea/RT}$ = exponential factor.

= It corresponds to those molecules which absorb energy (Ea) and gets activated.

Ea = Activation energy

R = gas constant

= ~~8.13~~ 8.314 J/k/mol. = 1.99 cal/k/mol

= 0.0821 L atm/k/mol.

T = Temperature.

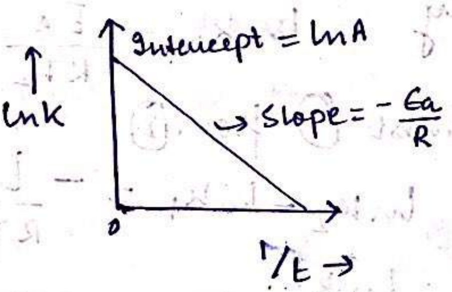
② Derive: $\log\frac{k_2}{k_1} = \frac{Ea}{2.303\,R}\left[\frac{T_2-T_1}{T_1T_2}\right]$.

from Arrhenious eqn,

$$k = A\cdot e^{-Ea/RT} \quad \text{— (i)}$$

taking ~~log~~ ln on b/s.

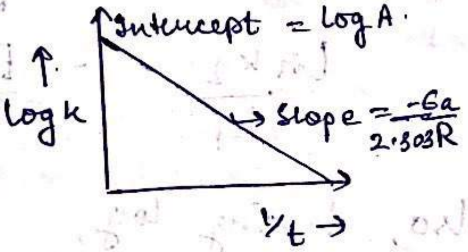
$$\ln k = \frac{-Ea}{RT} + \ln A$$



~~at Temp T:-~~

or, In terms of log

$$\log k = \frac{-Ea}{2.303\,RT} + \log A \quad \text{— ②}$$



when, time $t = t_1$, $k = k_1$

so eqn. 2 becomes,

$$\log k_1 = \frac{-Ea}{2.303\,RT_1} + \log A \quad Ⓐ$$

and

when $t = t_2$

$$\log k_2 = \frac{-Ea}{2.303\,RT_2} + \log A. \quad Ⓑ$$

Subt. Ⓑ from Ⓐ

$$\cancel{\log k_2 - \log k_1 = \frac{Ea}{R\times 2.303}\left[-\frac{1}{T_2} + \right.}$$

$$\log k_2 - \log k_1 = \frac{Ea}{2.303\,R\,T_2} + \log A - \left(\frac{Ea}{2.303RT_1} + \log A\right)$$

$$\log k_2 - \log k_1 = -\frac{Ea}{2.303\,RT_2} + \frac{Ea}{2.303\,RT_1}$$

$$\log \frac{k_2}{k_1} = \frac{Ea}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right].$$

$$\boxed{\log \frac{k_2}{k_1} = \frac{Ea}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right]}$$

X

When $t = t_1$, $k = k_1$

" $t = t_2$, $k = k_2$

Thus, $\ln k_1 = -\frac{Ea}{RT_1} + \ln A$ — ①

IIIly $\ln k_2 = -\frac{Ea}{RT_2} + \ln A$ — ②

Subt. ① from ②

$$\ln k_2 - \ln k_1 = -\frac{Ea}{RT_2} + \frac{Ea}{RT_1}$$

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

$$\ln \frac{k_2}{k_1} = \frac{Ea}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right].$$

Also, taking log,

$$\log \frac{k_2}{k_1} = \frac{Ea}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right].$$

Temp. Coefficient: (μ or γ)

It can be defined as the ratio of 2 rate constants which are separated from each other by a gap of 10 °C or 10K, normally the lower temp. taken is 25 °C and upper is 35 °C.

$$\gamma = \mu = \frac{k_{t+10}}{k_t} = \frac{k_{35}}{k_{25}}$$

γ possesses no units.

Also, $\frac{dx}{dt} = \gamma^{\frac{\Delta t}{10}}$

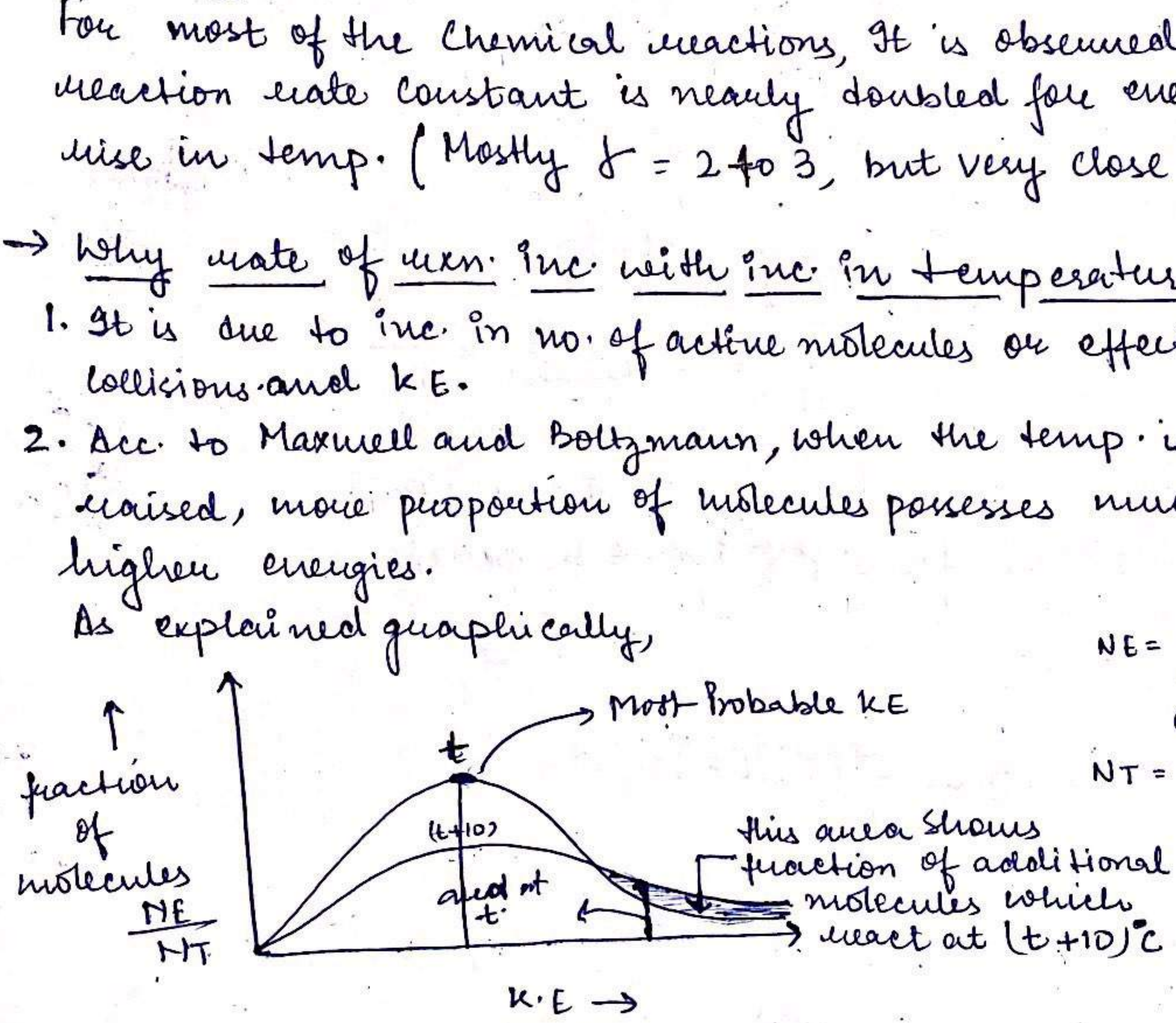
For most of the chemical reactions, it is observed that reaction rate constant is nearly doubled for every 10° rise in temp. (Mostly γ = 2 to 3, but very close to 2).

→ **Why rate of rxn. inc. with inc. in temperature:**

1. It is due to inc. in no. of active molecules or effective collisions and K.E.
2. Acc. to Maxwell and Boltzmann, when the temp. is raised, more proportion of molecules possesses much higher energies.

As explained graphically,

NE = no. of molecules with Energy E.
NT = Total no. of molecules.



When the temp. is raised from t to t+10, the max. of the curve moves to the higher energy value and the curve broadens out, i.e spreads to the right such that there is a greater proportion of molecules with much higher energies.

→ Effect of Catalyst:

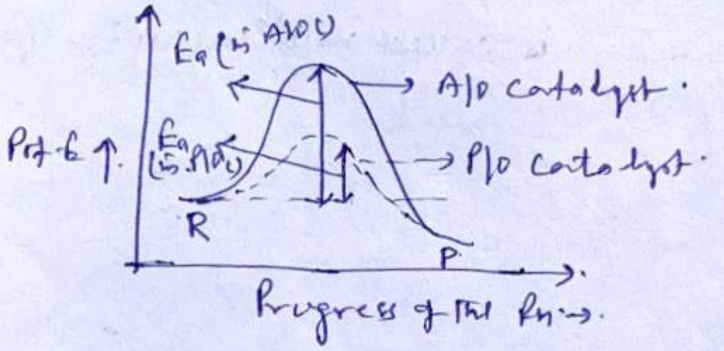
A catalyst is a substance which ↑es the rate of rxn. without undergoing any permanant chemical change.

Catalyst Participates in a chemical rxn., forms temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existance, and decomposes to yeild products and the catalyst.

i.e, $C + R \longrightarrow C\text{-----}R \longrightarrow P + C$

It is believed that catalyst provides an alt. path of lower E_a and hence lowering the P.E. barrier.

Graphically



* Catalyst does not alter gibbs free energy i.e ΔG.
It does not change the equilibrium constant of rxn., but helps to attain eq. earlier.

Let k_p = Rate Const. in P/o Catalyst.
k_a = Rate " " A/o Catalyst.
ΔE = Diff. in Activation energy.

$$\boxed{\log \frac{k_p}{k_a} = \frac{\Delta E}{2.303RT} = \text{Inc. in Rate.}}$$

The Substances which when added to the reactants and reduces the rate of rxn. are called inhibitor.

→ Rate Law:

It is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power which may or maynot be same as the stoichiometric coefficient of the reacting species in a balanced chemical eqn.

→ Order of a Rxn:

The sum of powers of the conc. of the reactants in the rate law expression is called the order of that chemical reaction.

→ Molecularity of a Rxn:

The no. of reacting species taking part in an elimentary reaction which must collide simultaneously in order to bring about a chemical rxn. is called molecularity of a rxn.

Order of Reaction

The order of a chemical reaction with respect to each reactant is defined as the exponent to which the concentration term of that reactant, in the rate law, is raised. The overall order of the reaction is defined as the sum of the exponents to which the concentration terms in the rate law are raised.

Molecularity of Reaction

The molecularity of a reaction is defined as the number of reacting molecules which collide simultaneously to bring about a chemical reaction. In other words, the molecularity of an elementary reaction is defined as the number of reactant molecules taking part in the reaction.

Difference between Molecularity and Order of Reaction

Molecularity	Order
It is the number of reacting species undergoing simultaneous collision in an elementary or simple reaction.	It is the sum of power of the concentrating terms on which the rate of reaction actually depends.
It can be calculated by simply adding the molecules of the slowest step.	It is determined experimentally only and cannot be calculated.
It is always a whole number, i.e. 1, 2, 3, etc.	It may be a whole number, zero, fractional, positive or negative.
It is applicable only for elementary reactions.	It is applicable for both elementary and complex reaction.
It is independent of pressure and temperature.	It depends on the pressure and temperature.
For simple reaction, it can be obtained from the stoichiometry of the equation.	Even the order of a simple reaction may not be equal to the number of molecules of the reactants.

Calculation of Order of Reaction

(*a*) **Integration Method.** In this method, known quantities of the reactants are mixed and the progress of the reaction is studied by analysing the portions of the reaction mixture withdrawn after regular intervals of time. The experimental data so obtained is substituted in the various *kinetic integrated equations for the reactions of first, second , third order, etc.*

As this method involves the trial of different equations, it is usually referred to as the *hit* and *trial method.*

The kinetic equation which gives the constant value of *k* (specific reaction rate) evidently will correspond to the *correct order of the reaction* under examination. The kinetic equations for the reactions of various orders are as under :

(*a*) *For the reactions of first order,*

$$k = \frac{2\cdot303}{t} \log \frac{a}{a-x}$$

(*b*) *For the reactions of second order,*

$$k = \frac{1}{t} \times \frac{x}{a(a-x)}$$

(*c*) *For the reactions of third order*

$$k = \frac{1}{2t} \times \frac{x(2a-x)}{a^2(a-x)^2}$$

The order of a reaction is given by the rate equation which gives constant value of *k*.

Fractional Change Method

(*b*) **Half-Life period Method.** In this method, the time ($T = t_{1/2}$) required to complete half of the reaction is determined and experiment is repeated with different but equal initial concentrations of the reactants.

If the time (T) required to complete half of the reaction is found :

(*i*) to be independent of initial concentration (a) *of the reactants, then the reaction is of first order.*

(*ii*) to be *inversely* proportional to the initial concentration (a) *of reactants, then the reaction is of second order.*

(*iii*) to be *inversely proportional to the square of the initial concentration* (a) of the reactants, then the reaction is of third order.

In general, the time (T) required to complete half of the nth order reaction may be written as :

$$T \propto \frac{1}{a^{n-1}}$$

Let us consider two experiments with initial concentrations a_1 and a_2. Let T_1 and T_2 be th times required to complete half of the change.

$$T_1 \propto \frac{1}{a_1^{\,n-1}} \qquad \text{and } T_2 \propto \frac{1}{a_2^{\,n-1}}$$

or
$$\frac{T_1}{T_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking logarithm, we have

$$\log \frac{T_1}{T_2} = (n-1) \log \frac{a_2}{a_1}$$

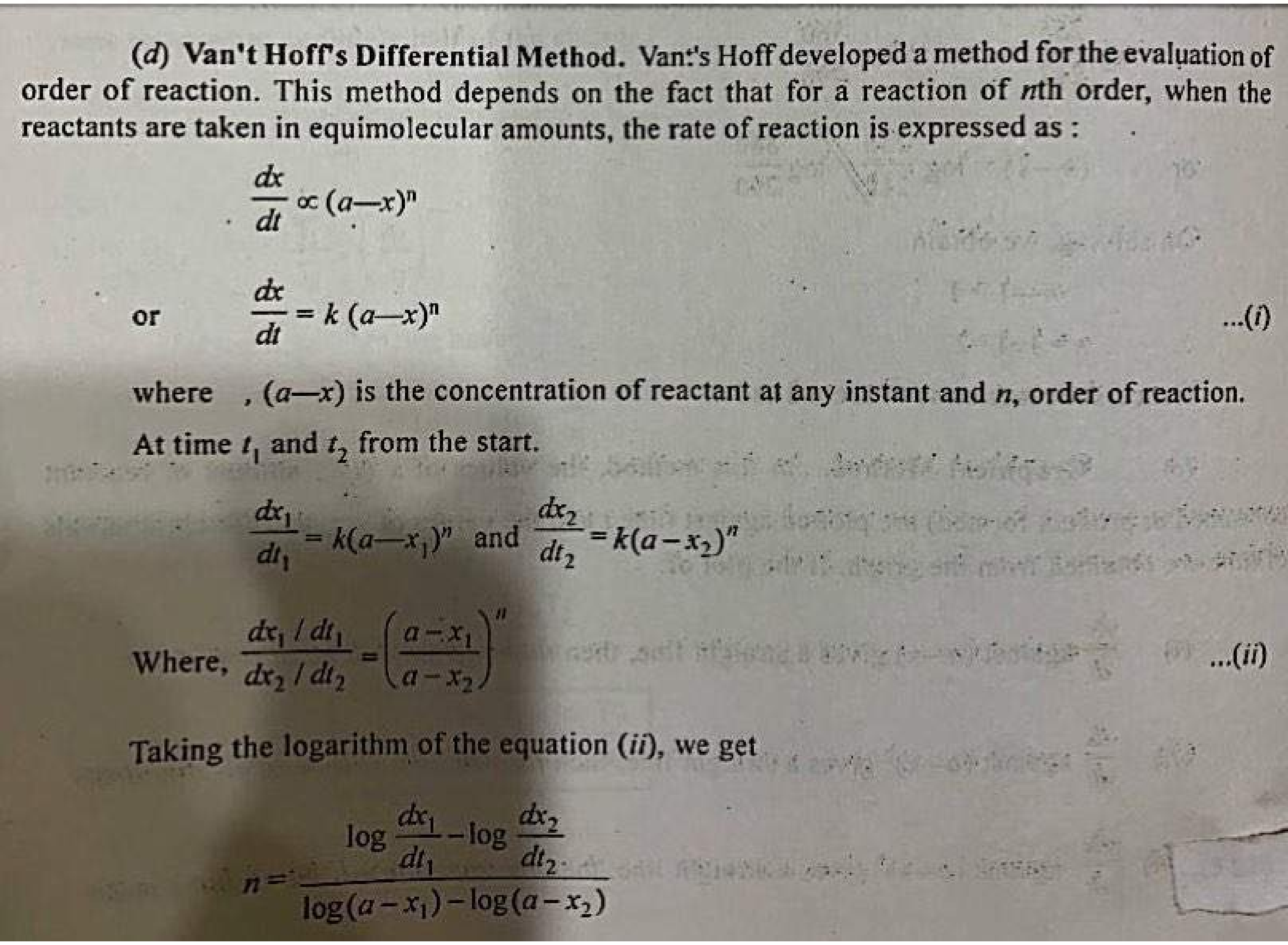
or
$$n-1 = \frac{\log T_1 / T_2}{\log a_2 / a_1}$$

$$= \frac{\log T_1 - \log T_2}{\log a_2 - \log a_1}$$

$$\therefore \quad \boxed{n = 1 + \frac{\log T_1 - \log T_2}{\log a_2 - \log a_1}}$$

where n is the order of reaction.

Differential Method



(*d*) **Van't Hoff's Differential Method.** Van's Hoff developed a method for the evaluation of order of reaction. This method depends on the fact that for a reaction of *n*th order, when the reactants are taken in equimolecular amounts, the rate of reaction is expressed as :

$$\frac{dx}{dt} \propto (a-x)^n$$

$$\text{or} \qquad \frac{dx}{dt} = k\,(a-x)^n \qquad \text{...}(i)$$

where , $(a-x)$ is the concentration of reactant at any instant and n, order of reaction.

At time t_1 and t_2 from the start.

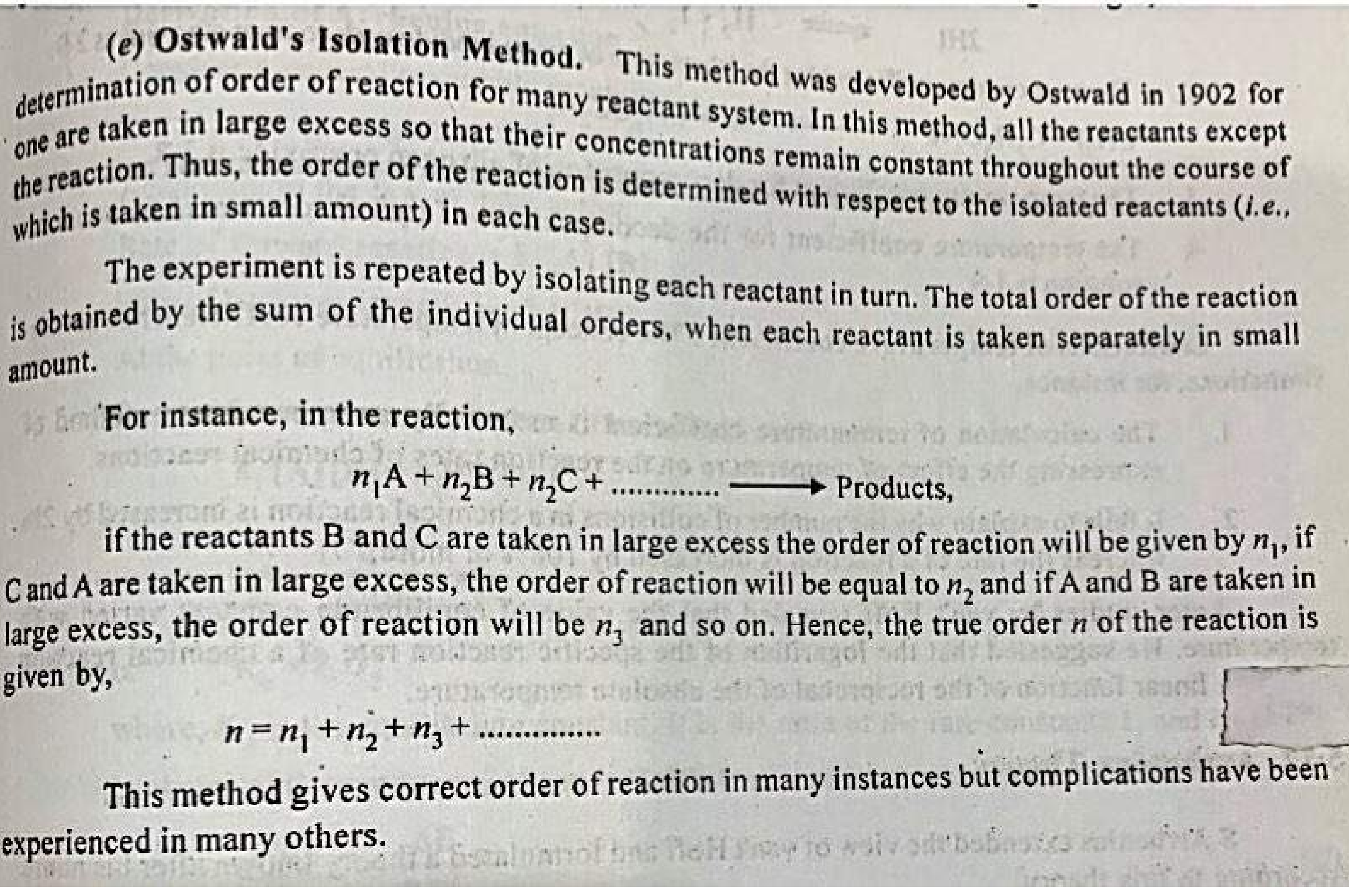
$$\frac{dx_1}{dt_1} = k(a-x_1)^n \text{ and } \frac{dx_2}{dt_2} = k(a-x_2)^n$$

$$\text{Where, } \frac{dx_1/dt_1}{dx_2/dt_2} = \left(\frac{a-x_1}{a-x_2}\right)^n \qquad \text{...}(ii)$$

Taking the logarithm of the equation (*ii*), we get

$$n = \frac{\log\dfrac{dx_1}{dt_1} - \log\dfrac{dx_2}{dt_2}}{\log(a-x_1) - \log(a-x_2)}$$

Dilution/Isolation Method



(e) Ostwald's Isolation Method. This method was developed by Ostwald in 1902 for determination of order of reaction for many reactant system. In this method, all the reactants except one are taken in large excess so that their concentrations remain constant throughout the course of the reaction. Thus, the order of the reaction is determined with respect to the isolated reactants (*i.e.*, which is taken in small amount) in each case.

The experiment is repeated by isolating each reactant in turn. The total order of the reaction is obtained by the sum of the individual orders, when each reactant is taken separately in small amount.

For instance, in the reaction,

$$n_1\mathrm{A} + n_2\mathrm{B} + n_2\mathrm{C} + \ldots\ldots\ldots\ldots \longrightarrow \text{Products,}$$

if the reactants B and C are taken in large excess the order of reaction will be given by n_1, if C and A are taken in large excess, the order of reaction will be equal to n_2 and if A and B are taken in large excess, the order of reaction will be n_3 and so on. Hence, the true order n of the reaction is given by,

$$n = n_1 + n_2 + n_3 + \ldots\ldots\ldots\ldots$$

This method gives correct order of reaction in many instances but complications have been experienced in many others.

Let us consider a zero order reaction of the type,

$$A \longrightarrow \text{Products}$$

For this reaction,

Thus, $$\frac{dx}{dt} = k(a-x)^{0} = k \qquad ...(5{\cdot}8)$$

where, a is the initial concentration of A and $(a-x)$ is the concentration after time 't' secs.

or $dx = k \times dt$ intigrating this equation

$$x = kt + I \qquad ...(5{\cdot}9)$$

where, I is the integration constant.

When $t = 0$, x is also equal to zero. Under these conditions,

$$0 = k \times 0 + I$$

or $I = 0$

Taking I = 0, the equation (5·9) becomes

$$x = kt$$

or $$k = \frac{x}{t} \qquad ...(5{\cdot}10)$$

This equation (5·10) is a general rate equation for the zero order reactions. As is evident from this equation, the rate constant for a zero order reaction is independent of the concentration of the reactant in the system.

Characteristics of reactions of zero order.

1. The concentration of the product increases linearly with time.
2. The units of the rate constant (k) are those of concentration x time^{-1}.

Examples of reactions of zero order. The typical examples of zero order reactions are as under :

(*i*) Photochemical interaction between H_2 and Cl_2 in presence of sunlight.

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{\text{Sunlight}} 2HCl(g)$$

(*ii*) Decomposition of HI on the surface of gold under high pressure.

$$2HI_{(g)} \xrightarrow{Au} H_{2(g)} + I_{2(g)}.$$

(*iii*) Decomposition of ammonia over the surface of tungsten.

$$2NH_{3(g)} \longrightarrow N_{2(g)} + 3H_{2(g)}$$

(*iv*) Decomposition of phosphine on the surface of molybdenum or tungsten at high pressure.

$$2PH_3 \longrightarrow 2P + 3H_2$$

(*v*) Reaction between acetone and iodine is found to be of zero order in respect of iodine.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + HI$$

(*vi*) Reaction between NO_2 and CO at 200° C is said to be of zero order with respect to CO.

$$NO_2 + CO \longrightarrow NO + CO_2.$$

5-9·2. Reactions of First Order

A reaction of first order is one in which the rate of reaction is determined by the variation of one concentration term only.

Consider a general reaction of first order,

$$A \rightarrow \text{Products}$$

Suppose a is the initial concentration of the reacting substance A in gm. moles per litre. Let x gm. moles/litre of A decompose in an interval of time t. Now remaining concentration of A is $(a-x)$ gm. moles per litre.

According to the law of mass action, the rate of the reaction at any time t is proportional to the concentration of A at that instant. Thus, we have ,

$$\frac{dx}{dt} \propto (a-x)$$

or

$$\frac{dx}{dt} = k(a-x) \qquad ...(5{\cdot}11)$$

where, $\frac{dx}{dt}$ is called the *reaction velocity* and k is generally known as *rate constant* or *specific reaction rate.*

The equation (*i*) is also referred to as **differential form of rate equation for the reactions of first order.**

Since, it is difficult to estimate the extremely small changes in concentration in infinitesimally small intervals of time, it is desirable to use integral calculus so as to obtain an equation involving measurable quantities.

Rearranging the equation (5·11) , we have

$$\frac{dx}{a-x} = kdt$$

On integrating it , we get

$$\int_{x=0}^{x=x} \frac{dx}{a-x} = \int_{t=0}^{t=t} kdt \qquad ...(5{\cdot}12)$$

$$[-ln(a-x)]_{x=0}^{x=x} = k\,[t]_{t=0}^{t=t}$$

or $-ln(a-x) + ln\, a = k\,(t-0)$

or $$ln \frac{a}{a-x} = kt$$

or $$k = \frac{1}{t}\, ln \frac{a}{a-x} \qquad \text{...(5·13)}$$

or $$k = \frac{2\cdot303}{t} \log_{10} \frac{a}{a-x} \quad \text{[because, } ln\, x = 2\cdot303 \log_{10} x\text{]}$$

or $$k = \frac{2\cdot303}{t} \log \frac{a}{a-x} \qquad \text{...(5·14)}$$

The equation (5·14) is referred to as **integrated from of rate equation for the reactions of first order.**

The equation (5·14) is also known as *kinetic equation for the reactions of first order* or simply *rate equation for the reactions of first order.* This is also, sometimes, referred to as the equation for the *unimolecular reactions.*

Second form of First order rate equation. In certain instances, the initial concentration is not known definitely due to the reason that the starting time of the reaction is uncertain. So the need arises to obtain an alternative expression by integrating within the limits as shown below :

$$\int_{x=x_1}^{x=x_2} \frac{dx}{a-x} = \int_{t=t_1}^{t=t_2} k\,dt \qquad \text{...(}i\text{)}$$

where, x_1 and x_2 are the moles of A decomposed in time t_1 and t_2, respectively.

On simplifying the equation.(*i*), we get,

$$ln \frac{(a-x_1)}{(a-x_2)} = k(t_2-t_1)$$

$$\text{...(5.15)}$$

or $$k = \frac{1}{(t_2-t_1)}\, ln \frac{(a-x_1)}{(a-x_2)} \qquad \text{...(5.16)}$$

or $$k = \frac{2\cdot303}{(t_2-t_1)} \log \frac{(a-x_1)}{(a-x_2)} \qquad \text{...(5.17)}$$

or $$k = \frac{2\cdot303}{(t_2-t_1)} \log \frac{C_1}{C_2}$$

where, C_1 and C_2 represent the molar concentrations of the reactant A at time t_1 and t_2, respectively.

Characteristics of reactions of first order.

1. *The value of k should remain the same all along the reaction of first order.* If the concentration of the reactant is determined at different intervals of time and these values (concentrations and times) are substituted in the rate equation (5·14), then value of k obtained should be the same.

2. *Effect of change in concentration units on the value of k.* Let the new unit be m times the first, then

$$k = \frac{2\cdot303}{t}\log\frac{ma}{m(a-x)} = \frac{2\cdot303}{t}\log\frac{a}{(a-x)}$$

This expression is the same as the original expression of reactions of first order. So a change in concentration unit will not alter the velocity coefficient.

3. *Time required to complete a definite fraction of the reaction of first order is independent of initial concentration.*

Consider the case when half the original amount of A has decomposed in the time $t_{1/2}$ *i.e.*, $x = \frac{a}{2} = 0\cdot5\ a$.

Then,

$$k = \frac{2\cdot303}{t}\log\frac{a}{a-x}$$

$$= \frac{2\cdot303}{t_{\frac{1}{2}}}\log\frac{a}{a-0\cdot5a}$$

$$\text{or } t_{1/2} = \frac{2\cdot303}{k}\log 2$$

$$\text{or } t_{1/2} = \frac{2\cdot303\times0\cdot301}{k}$$

$$= \frac{0\cdot693}{k} \qquad ...(5\cdot18)$$

In other words, $t_{1/2}$ is independent of initial concentration (a) and depends only on the specific reaction rate (k).

4. *Units of the first order rate constant* (k).

$$k = \frac{2\cdot303}{t}\log\frac{a}{a-x}$$

$$\text{Dimensionally, } k = \text{time}^{-1}\log\frac{\text{moles/litre}}{\text{moles/litre}} = \text{time}^{-1}. \qquad ...(5\cdot19)$$

Hence, k has the dimension of reciprocal of time or time^{-1}. When expressed in seconds, the units of k is sec^{-1}.

Problem 5·10. What is the half-life period of the radioactive element whose decay constant, $\lambda = 1{\cdot}5$ per hour.

(Chennai, 1997)

Solution. Half-life period, $t_{1/2} = \dfrac{0{\cdot}693}{\lambda}$

$$= \frac{0{\cdot}693}{1{\cdot}5}\text{ hr} = \frac{0{\cdot}693}{1{\cdot}5} \times 60\text{ min}$$

$$= 27{\cdot}72\text{ min.}$$

5·9·2. Reactions of Second Order

A reaction of second order is one in which the rate of reaction is determined by the change of two concentration terms. In the reactions of second order, the rate of the reaction is determined by the variation in the concentration of two reactants or the square of the concentration of a single reactant. The reactions of second order are of two types :

(1) *Reactions in which the rate of reaction is determined by the square of the concentration of the same reactant* (*i.e., single reactant*). Such a reaction is represented in the general way as :-

$$2\text{A} \longrightarrow \text{Products}$$

or $$\text{A} + \text{A} \longrightarrow \text{Products}$$

(2) *Reactions in which the rate of reaction is determined by the change of two concentration terms of different reactants.*

In general, such a reaction is represented as :

$$\text{A} + \text{B} \longrightarrow \text{Products}$$

Case I. Consider a general reaction,

$$2\text{A} \longrightarrow \text{Products}$$

or $$\text{A} + \text{A} \longrightarrow \text{Products}$$

Suppose a is the initial concentration of A in gm. moles/litre. Let x gm. moles/litre decompose in time t. Then, the concentration of A will be $(a—x)$ gm. moles/litre at time t.

According to the law of mass action, the rate of the reaction of second order is proportional to the concentrations of A at that instant , *i.e,* $(a—x)\,(a—x)$. This is expressed mathematically as under :

$$\frac{dx}{dt} \propto (a—x)\,(a—x)$$

or $$\frac{dx}{dt} \propto (a—x)^2 \qquad \text{...}(i)$$

or $$\frac{dx}{dt} = k(a—x)^2$$

where, $\frac{dx}{dt}$ is the reaction velocity and k is rate constant for reaction of second order.

This equation is known as *differential form of rate equation for reactions of second order.*

Rearranging the equation (*i*) and then integrating it, we have

$$\int_{x=0}^{x=x} \frac{dx}{(a-x)^2} = \int_{t=0}^{t=t} k\,dt \qquad \text{...}(ii)$$

$$\text{Thus,} \quad \left[\frac{1}{a-x}\right]_{x=0}^{x=x} = k\left[\,t\,\right]_{t=0}^{t=t}$$

$$\text{or} \quad \frac{1}{a-x} - \frac{1}{a} = kt$$

$$\text{or} \quad \frac{x}{a(a-x)} = kt$$

$$\text{or} \quad k = \frac{1}{t} \times \frac{x}{a(a-x)}$$

$$\boxed{k = \frac{1}{t} \times \frac{x}{a(a-x)}} \qquad \text{...}(5{\cdot}22)$$

This equation is called *integrated form of rate equation for reactions of second order.*

Case II. Consider a general reaction,

$$\mathrm{A + B \longrightarrow Products}$$

Suppose a and b are the initial concentrations in gm. moles/litre of the reactants A and B, respectively. Let x gm. moles/litre of A and B decompose in time t. Then, the remaining concentrations of A and B will be $(a-x)$ and $(b-x)$ gm. moles/litre, respectively.

According to the law of mass action, the rate of the reaction of second order is proportional to the concentrations of A and B at that instant, *i.e.*, $(a-x)\,(b-x)$. The rate is expressed mathematically as :

$$\frac{dx}{dt} \propto (a-x)\,(b-x) \qquad \text{or} \qquad \frac{dx}{dt} = k\,(a-x)\,(b-x) \qquad \text{...}(i)$$

where, $\frac{dx}{dt}$ is the reaction velocity and k is referred to as the *rate constant* for the second order.

This equation is known as *differential form of rate equation for reactions of second order.*

On separating the variables in the equation (*i*), we get

$$\frac{dx}{(a-x)(b-x)} = k\,dt \qquad \text{...}(ii)$$

By using partial fractions, the equation (*ii*) may be put as :

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

or

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

On integrating the equation (*iii*), we get

$$\frac{1}{(a-b)}[-ln(b-x) + ln(a-x)] = kt + \mathrm{I}$$

where, I is the constant of integration.

When $t = 0$, $x = 0$, and the equation (*iv*) is reduced to the form :

$$\frac{1}{(a-b)}[-ln\, b + ln\, a] = \mathrm{I}$$

or $$\frac{1}{(a-b)}\, ln\, \frac{a}{b} = \mathrm{I}$$

Substituting the value of I in the equation (*iv*), we get

$$\frac{1}{(a-b)}[-ln\,(b-x) + ln\,(a-x)] = kt + \frac{1}{a-b}\, ln\frac{a}{b}$$

or $$\frac{1}{(a-b)}\, ln\, \frac{(a-x)}{(b-x)} = kt + \frac{1}{(a-b)}\, ln\frac{a}{b}$$

or $$\frac{1}{(a-b)}[\, ln\, \frac{(a-x)}{(b-x)} - \frac{1}{(a-b)}\, ln\frac{a}{b}\,] = kt$$

or $$\frac{1}{(a-b)}[ln\frac{(a-x)}{(b-x)} - ln\frac{a}{b}\,] = kt$$

or $$\frac{1}{a-b}\, ln\, \frac{(a-x)b}{(b-x)a} = kt$$

or $$\frac{2\cdot 303}{a-b}\log\frac{(a-x)b}{(b-x)a} = kt$$

or $$k = \frac{2\cdot 303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}$$

$$\boxed{k = \frac{2\cdot 303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}}$$

This is called **integrated form of rate equation for reactions of second order.**

Characteristics of Reactions of Second order.

(1) *The value of k should remain the same all along the reaction of second order.* On substituting the values of $a, x,$ and t in the rate equation (5·22) or a, b, x and t in the rate equation (5·23), we obtain a constant value of k indicating that the reaction is of second order.

(2) *Effect of change in concentration units on the value of k.* Let the new unit be m times the initial unit. Then,

$$k = \frac{1}{t} \cdot \frac{mx}{ma \times m(a-x)} = \frac{1}{t} \frac{x}{a(a-x)} \cdot \frac{1}{m}$$

The new value of k is $\frac{1}{m}$ times the original value.

(3) *Time required to complete a definite fraction of the reaction of second order is inversely proportional to the initial concentration.*

Let us consider the case when half of the reactants decompose in time $t_{1/2}$ *i.e.*, $x = 1/2\ a = 0{\cdot}5\ a$. Then, the equation (5·22) is reduced to the form,

$$k = \frac{1}{t_{1/2}} \times \frac{0{\cdot}5a}{a(a-0{\cdot}5a)} = \frac{1}{t_{1/2}} \times \frac{1}{a}$$

or $$t_{1/2} = \frac{1}{k} \times \frac{1}{a}$$

or $$t_{1/2} \propto \frac{1}{a}$$

(4) Units of the second order rate constant (k).

$$k = \frac{1}{at}\left[\frac{x}{a-x}\right]$$

$$\text{Dimensionally, } k = \frac{1}{\frac{\text{moles}}{\text{litre}}\text{sec.}} \cdot \frac{\text{moles / litre}}{\text{moles / litre}}$$

$$= \text{litre moles}^{-1}\ \text{sec}^{-1}.$$

Examples of reactions of Second order. Some typical instances of the reactions of the second order are :

1. Hydrolysis of Ethyl acetate by an alkali. This is also referred to as *saponification of ester.* The hydrolysis of ethyl acetate by an alkali is represented by the equation,

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

internal energy change.

5·14. Simple Collision Theory of Reaction Rates

The collision theory, as its name suggests, focuses attention on the idea that the mo (particularly in the gas phase) can react only if they come together or collide. This implies t rate of the reaction should be proportional to the number of collisions per unit time betwe reactant molecules.

However, it can be shown that if every collision were to result in a chemical interaction, then the rate of the chemical reaction would be much higher than expected on the basis of experimental observation. This anomaly can be removed by introducing the concept of activation energy and activated molecules given by Arrhenius.

The main postulates of collision theory of reaction rates may be given as under :

(*i*) For a chemical reaction to take place, the collisions between the reacting molecules must occur.

(*ii*) All the collisions between the reacting molecules do not lead to the formation of the products.

(*iii*) Only those collisions result in a chemical reaction (*i.e.*, product formation) in which the colliding molecules possess a certain minimum amount of energy known as *threshold energy*. **Threshold energy** *is defined as the minimum energy which must be associated with the molecules so that their mutual collisions result in product formation.* On the other hand, the **activation energy** *is defined as the excess energy that the reacting molecules acquire to attain the threshold energy in order to undergo chemical reaction.*

Activation energy (E or E_a) = [Threshold energy —Energy possessed by the molecules]

(*iv*) The colliding molecules must be properly oriented if the chemical reaction is to take place. Proper orientation is necessary for product formation.

5-14·1. Mathematical treatment of collision theory for a bimolecular reaction

The rate of a bimolecular reaction is given by :

$$\frac{dx}{dt} = z\, e^{-E/RT} \qquad ...(5{\cdot}38)$$

where, z is the number of binary collisions per second between two identical molecules in 1 ml of a gas and E is the energy of activation of the process.

According to the kinetic theory of gases, the reaction velocity is related to the concentration by the relation :

$$\frac{dx}{dt} \propto n^2$$

or $$\frac{dx}{dt} = k\, n^2 \qquad ...(5{\cdot}39)$$

where, k is the specific reaction rate and n is the concentration of the reactant.

From the equations (5·38) and (5·39), we have

$$kn^2 = ze^{-E/RT}$$

or $$k = \frac{z}{n^2} e^{-E/RT} \qquad ...(5{\cdot}40)$$

The value of z is known from the simple kinetic theory of gases. It is twice the number of collisions per ml. per sec. because two molecules are involved in each collision.

$$z = 4n^2 \sigma^2 \left(\frac{\pi RT}{M}\right)^{1/2} \qquad ...(5{\cdot}41)$$

where, σ is the molecular diameter and M is the gram molecular mass.

On substituting the equation (4) in the equation (3), we have

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

or $$k = Z\, e^{-E/RT}$$

where, $Z = 4\sigma^2 \left(\frac{\pi RT}{M}\right)^{1/2}$ referred to as *collision number, which is defined as the number of collisions per second when there is only one reactant molecule per ml. of the gas.* ...(5·42)

If the chemical reaction involves two different molecules, then the value of collision number Z is obtained by the relation :

$$Z = \sigma^2 \left[\frac{8\pi RT(M_1 + M_2)}{M_1 \cdot M_2}\right]^{1/2} \qquad ...(5·43)$$

where, M_1 and M_2 are the molecular masses and σ is the mean of the collision diameters of the two reactants.

The equation (5·42) is known *as the mathematical statement of simple collision theory of reaction rates.*

5-14.2. Comparison of Collision Theory Equation with Arrhenius Equation

Let us compare the collision theory relation with Arrhenius equation.

(*i*) Collision Theory relation :

$$k = Ze^{-E/RT} \qquad ..(Eq.\ 5·42)$$

(*ii*) Arrhenius equation :

$$k = A\, e^{-E/RT} \qquad ...(Eq.\ 5·34)$$

Form these two equations, we have

$$Z\, e^{-E/RT} = A\, e^{-E/RT} \qquad ...(5·44)$$

It implies that Z = A.

Thus, collision theory equation is identical with Arrhenius equation if A = Z.

5-14.3. Test of the Collision Theory of Reaction Rates

There are several ways of comparing the theoretical expression with the experimental values. We have three quantitites that are not known prior, specific reaction rate constant (k), the collision diameter (σ) and the activation energy (E). The following comparisons are made in order to test the simple collision theory of reaction rates.

(1) *Calculation of the rate constant* (k). From the known value of activation energy (E) obtained from Arrhenius equation for temperature coefficient and a value of collision diameter (σ) from kinetic theory (equation of viscosity), the value of the rate constant k can be calculated and hence, compared with the experimental value.

(2) *Calculation of energy of activation* (E). From the experimental value of rate constant (k) obtained at a temperature and the collision diameter (σ) obtained from kinetic theory, the value of energy of activation (E) can be evaluated and thus, compared with the value obtained from the temperature coefficient.

(3) *Calculation of collision diameter* (σ). From the experimental values of the activation energy (E) and rate constant (k), the value of collision diameter (σ) can be found and then compared with the value obtained from kinetic theory of electron diffraction diameter.

5-14.4. Failures of Collision Theory of Reaction Rates

Although the simple collision theory of reaction rates satisfactorily explains a number of chemical reactions, yet it conspicuously fails in a number of cases such as under :

(1) In case of very rapid reactions involving chain mechanism, there are numerous instances wherein the reaction rate is much less than expected from theoretical point of view.

(2) The bimolecular polymerisation of ethene occurs only once in about 2000 collisions between activated molecules. The rate of reaction is slower than the theoretical value calculated from simple collision theory of reaction rates.

(3) The polymerisation of 1 : 3-butadiene takes place only once in about 10,000 collisions between the activated molecules. The rate of such a reaction is slower by a factor of 10^4 than the value calculated from simple collision theory.

(4) The reaction between ethyl alcohol and acetic anhydride vapours takes place at a rate which is slower by a factor of 10^{-5} than the value calculated from the simple collision theory.

The failures of this theory are due to over simplification in assuming that the entire activation energy (E) is acquired by the molecules by utilising only their kinetic energy (*i.e.*, translational energy). *This is true in case of simple molecules which behave as rigid spheres*. The more complex molecules do not behave as rigid spheres and thus, possess vibrational and rotational energies in addition to translational energy. Large deviations have been observed as vibrational and rotational energies were neglected in the calculations based on the simple collision theory of reaction rates.

5-14.5. Modification of Collision Theory of Reaction Rates

In order to account for deviations from the simple colli- from it is modified as :

collisions between activated molecules but also a proper orientation. Under these conditions, all the collisions even between activated molecules will not be effective and hence, the rate of reaction calculated will be higher than the experimental value.

5·16. Transition State Theory

As learnt earlier, the simple collision theory of reaction rates was inadequate to explain the mechanism of most of reactions. Therefore, a more comprehensive theory known as *transition state theory* or *activated complex theory* was developed by H.Erying and Polanyi in the year 1935. This theory is also called the *theory of absolute reaction rates* because with its help it is possible to obtain the absolute value of the rate constant.

The postulates of transition state theory are as under :

(*i*) As the reactant molecules approach each other, there is a continuous series of changes in the bond distance. These changes are accompanied by corresponding energy changes.

(ii) The reactant molecules are transformed into an energy rich intermediate referred to as *activated complex* or *transition state.*

$$\text{Reactants} \rightleftharpoons \text{Activated complex}$$

(iii) The activated complex may be formed by some loose association or bonding of reactant molecules with necessary rearrangement of valence bonds and energy. Or if it be a unimolecular reaction, the reactant molecule may produce the activated complex by the rearrangement of atoms and redistribution of energy.

(iv) The activated complex, though unstable, has a transient existence. It is treated formally as a definite molecule with an independent entity. The activated complex is in equilibrium with the reactants. The potential energy of activated complex is maximum.

(v) The activated complex decomposes to give the products. It is schematically represented as :

$$\text{Reactants} \rightleftharpoons \text{Activated complex} \longrightarrow \text{Products}$$

(vi) The activation energy of reaction, on the basis of transition state theory, is defined as the additional energy which the reactant molecules must acquire to form the activated complex.

5-16.1. Mathematical (Thermodynamic) Treatment of Transition State Theory

Consider a bimolecular reaction between the reactants A and B.

According to transition state theory, we have

$$\underset{\text{(Reactants)}}{A+B} \rightleftharpoons \underset{\text{(Activated complex)}}{Z^{\neq}} \longrightarrow \text{Products}$$

The equilibrium constant ($K^{\neq}$) for the formation of activated complex is expressed as :

$$K^{\neq}=\frac{Z^{\neq}}{[A][B]} \quad \text{...}(i)$$

or

$$Z^{\neq}=K^{\neq}[A][B] \quad \text{...}(ii)$$

In accordance with transition state theory, the rate of reaction is the number of activated complexes, which pass over the potential barrier in a unit time. This, in turn, is equal to the concentration of activated complex multiplied by the frequency at which the activated complex would decompose to give products.

It is expressed mathematically as :

$$\frac{dx}{dt}=[Z^{\neq}] \times \text{Rate or frequency of dissociation of activated complex} \quad \text{...}(iii)$$

From the equations *(ii)* and *(iii)*, we get

$$\frac{dx}{dt}=K^{\neq}[A]\,[B] \times \text{Rate or frequency of dissociation of activated complex} \quad \text{...}(iv)$$

The activated complex undergoes decomposition only if enough vibrational energy (E_{vib}) is supplied to the system as as to cause the atoms to vibrate with certain critical frequency, leading to bond rupture. This frequency is given by the relation :

$$\text{Frequency of dissociation of activated complex} = \frac{E_{vib}}{h} \quad ...(v)$$

where, E_{vib} = Average vibrational energy at temperature T and h = Planck's constant

But $E_{vib} = k_B T$ (k_B is the Baltzmann constant)

Since $k_B = R/N$

$\therefore \quad E_{vib} = RT/N$ ...(vi)

where, N = Avogadro's number

R = Gas constant

T = Absolute temperature.

From the equations (v) and (vi), we obtain

Frequency of dissociation = RT/Nh ...(vii)

$$\therefore \quad \frac{dx}{dt} = K^{\neq}[A][B]\,RT/Nh \quad ...(5{\cdot}47)$$

We know that :

Rate for conversion of reactants into products is expressed by the relation,

$$\frac{dx}{dt} = k[A][B]$$

Substituting for $\frac{dx}{dt}$ in the equation (5·47), we have

$$k[A][B] = K^{\neq}[A][B]\,RT/Nh$$

$$\text{or} \quad k = K^{\neq}RT/Nh \quad ...(5{\cdot}48)$$

The relation (5·48) is the mathematical statement of transition state theory.

From chemical thermodynamics, it is possible to correlate the equilibrium constant ($K^{\neq}$) with free energy $\Delta G^{\neq}$ using the relation,

$$\Delta G^{\neq} = -RT \log K^{\neq} \quad ...(5{\cdot}49)$$

where, $\Delta G^{\neq}$ = Free energy of activated complex

$$\text{or} \quad \log K^{\neq} = -\frac{\Delta G^{\neq}}{RT} \quad ...(5{\cdot}50)$$

But $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$.

$$\therefore \qquad \log K^{\neq} = -\frac{(\Delta H^{\neq} - T\Delta S^{\neq})}{RT}$$

or $$K^{\neq} = e^{-(\Delta H^{\neq} - T\Delta S^{\neq})/RT} \qquad ...(5\cdot51)$$

From the equations (5·48) and (5·51)

$$k = \frac{RT}{Nh}\, e^{-\Delta H^{\neq}/RT} \cdot e^{\Delta S^{\neq}/R} \qquad ...(5\cdot52)$$

or $$k = \frac{k_B T}{h}\, e^{-\Delta H^{\neq}/RT} \cdot e^{\Delta S^{\neq}/R} \qquad ...(5\cdot53)$$

where $\Delta H^{\neq}$ = Standard enthalpy change (*i.e.*, standard heat of activation).

$\Delta S^{\neq}$ = Standard entropy change (*i.e*, standard entropy of activation)

This equation (5.52 or 5.53) is known as **Eyring equation.**

Log Properties !-

1) $\log m \times n = \log m + \log n$
$\log m/n = \log m - \log n$

2) $\log m^n = n \log m$

$\log 2 = 0.3040 \simeq 0.30$
$\log 3 = 0.4771 \simeq 0.48$
$\log 7 = 0.8451 \simeq 0.85$

* without using log books or log tables, one can calculate any log using just point 1) & 2)

Eg:- $\log 4 = \log 2 \times 2 = \log 2 + \log 2$
$= 0.30 + 0.30 = 0.60.$

$\log 5 = \log 10/2 = \log 10 - \log 2$
$= 1 - 0.30 = 0.70$

$\log 6 = \log 2 \times 3 = \log 2 + \log 3$

$$= \begin{array}{r} 0.30 \\ +\,0.48 \\ \hline 0.78 \end{array}$$

$\log 8 = \log 2^3 = 3 \log 2 = 3 \times 0.30$
$= 0.90$

$\log 9 = \log 3^2 = 2 \log 3$
$= 2 \times 0.48$
$= 0.96$

and so on.

3) Also, In General,
$\log 10 = 1$ [No. of zeros = 1]
$\log 100 = 2$ [" " " = 2]
$\log 1000 = 3$ [" " " = 3]
& so on.

Scanned with CamScanner

Explaination

1) $$n = \frac{\log R_1 - \log R_2}{\log a_1 - \log a_2} = \frac{\cancel{(\log 1 - \log 10)}}{\cancel{(\log 1 - \log 10)}} = 1$$

2) $$n = \frac{\log 1 - \log 1.2}{\log 1 - \log (1.2)^2} = \frac{\cancel{\log 1.2}}{2 . \cancel{\log 1.2}}$$
$$= \frac{1}{2}$$

3) $$n = \frac{\log 1 - \log 8}{\log 1 - \log 4} = \frac{\log 2^3}{\log 2^2}$$
$$= \frac{3 \cancel{\log 2}}{2 \cancel{\log 2}}$$
$$= 3/2$$

Note:-
when initial Conc.
and Rate are not
given, we can select
them as one for mathematical
simplicity.

Numericals:-

A) Related to concentration effect:

1) $A \rightarrow B$

conc. of Reactant A is doubled, New Rate = ?

Sol:- $R_1 = k[A]^1$

$R_2 = k[2A]^1 = 2k[A]^1 = 2R_1$

2) $2X \rightarrow Y$

Conc. of Reactant X is increased to 3 times, New Rate=?

Sol:- $R_1 = k[x]^2$

$\therefore R_2 = k[3x]^2 = 9k[x]^2 = 9R_1$.

3) $X + 2Y \rightarrow$ Products.

conc. of X is doubled & that of Y is reduced to half, New Rate = ?

Sol:- $R_1 = k[X]^1[Y]^2$

$\therefore R_2 = k[2X]^1\left[\frac{Y}{2}\right]^2 = \frac{1}{2}k[X]^1[Y]^2$

$= \frac{1}{2}R_1$

4) $2X \rightarrow Y$.

If volume of Reaction vessel is doubled, What will be the change in New Rate. ?

Sol:- If volume is doubled, Concentration becomes half $\left[\text{vol.} \propto \frac{1}{\text{conc.}}\right]$

$\therefore R_1 = k[x]^2$

$\therefore R_2 = k\left[\frac{x}{2}\right]^2 = \frac{1}{4}k[x]^2 = \frac{1}{4}R_1$

——— x ———

Solutions to Numericals:-

Basic key:-

100 —— 50 —— 25 —— 12.5 ...... & so on.

$1\,t_{1/2} = 50\%$ completion

$2\,t_{1/2} = 75\%$ completion

$3\,t_{1/2} = 87.5\%$ completion.

OR

$1\,t_{1/2} = 50\%$.
$2\,t_{1/2} = 75\%$.
$3\,t_{1/2} = 87.5\%$.

Q.A

1) $50\% = 1\,t_{1/2} = 10$ minutes.
a) $\therefore 75\% = 2\,t_{1/2} = 2 \times 10 = 20$ minutes.
b) $\therefore 87.5\% = 3\,t_{1/2} = 3 \times 10 = 30$ mintes.

2) $75\% = 2\,t_{1/2} = 16$ minutes
a) $\therefore 50\% = 1\,t_{1/2} = 16/2 = 8$ minutes.
b) $\therefore 875\% = 3\,t_{1/2} = 8 \times 3 = 24$ mintes.

—— x ——