

Handwritten Notes
On
Chemical Kinetics



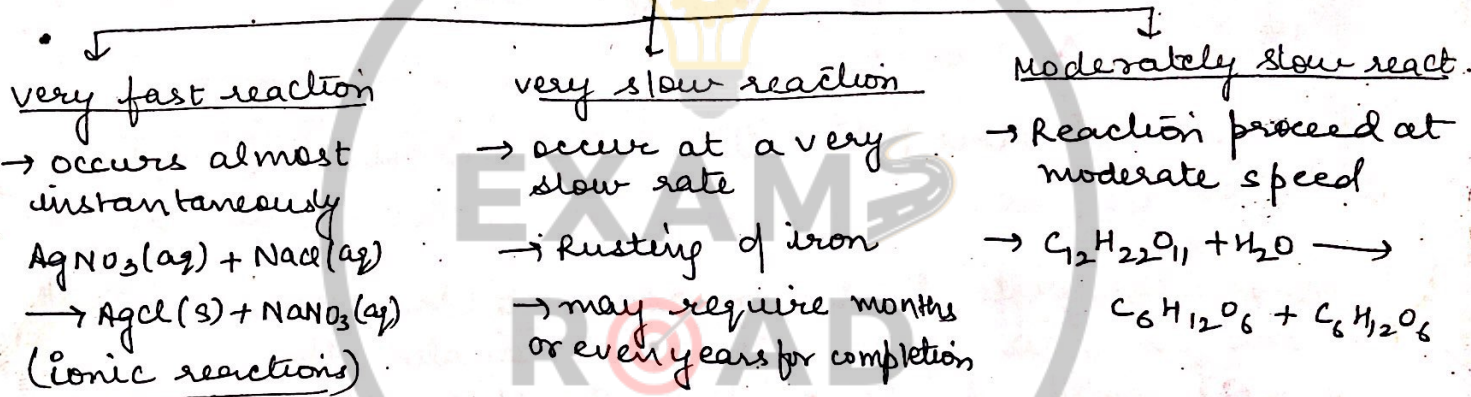
Chemical Kinetics

→ The branch of chemistry which deals with the study of rates of rxⁿs & their mechanism is called chemical kinetics.

→ While the thermodynamics tells us about the feasibility of the reaction and the chemical equilibrium tells us about the extent upto which a reaction may take place, the kinetic studies not only help us to determine the rate of reaction but also describe the conditions by which the reaction rates can be altered.

→

Type of chemical reaction



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Rate of reaction

→ The rate of reaction can be broadly defined as the rate at which reactants are converted into products.

→ Quantitatively, the rate of rxⁿ may be expressed in terms of change in conc of any of the reactants or products per unit time.



3) → consider a hypothetical reaction



Here,

$$\text{Rate of disappearance of A} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{Rate of appearance of B} = \frac{\Delta[B]}{\Delta t}$$

The rate of rxn may thus be represented as

$$\text{rate of rxn} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

$$\text{where } \Delta A = [A]_{\text{final}} - [A]_{\text{initial}}$$

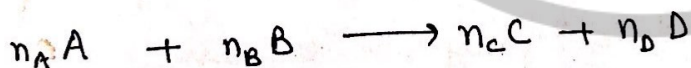
$$\Delta t = t_2 - t_1$$

The square bracket [] indicates the concentration expressed in mol L⁻¹.

→ Since the rate of reaction can not be -ve, the (-)ve sign in first expression indicates the ↓ in concentration of the reactant. In this case final conc - initial conc will have a negative value thus to get a +ve rate we put -ve sign in the rate expression.

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→ consider another reaction,



$$\text{rate of rxn} = -\frac{1}{n_A} \frac{d[A]}{dt} = -\frac{1}{n_B} \frac{d[B]}{dt} = \frac{1}{n_C} \frac{d[C]}{dt} = \frac{1}{n_D} \frac{d[D]}{dt}$$

but,

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

$$\text{" " " " B} = -\frac{d[B]}{dt}$$

$$\text{" " appearance " C} = \frac{d[C]}{dt}$$

$$\text{" " " " D} = \frac{d[D]}{dt}$$



units of rate of reaction

① For reactions in liquid phase,

$$\text{Rate} = \frac{\text{change in conc of reactant / product}}{\text{time taken}}$$

$$= \frac{\text{moles / litre}}{\text{sec}} = \text{mol l}^{-1} \text{sec}^{-1}$$

② For gaseous reactions,

→ The conc of reactants & products are given in terms of partial pressures.

$$\text{Rate} = \frac{\text{atm}}{\text{sec}} = \text{atm sec}^{-1} \text{ or atm min}^{-1} \text{ or atm hr}^{-1}$$

Average and instantaneous rate

Average rate: - rate of change of concentration per unit time.

$$\text{Average rate} = \frac{\text{change in concentration in given time}}{\text{time taken}} = \frac{\Delta x}{\Delta t}$$

Instantaneous rate: - change in concentration of ^{rate of} reactant or product ^{any one of} at a particular ^{instant of time} for a given ^{temperature}.

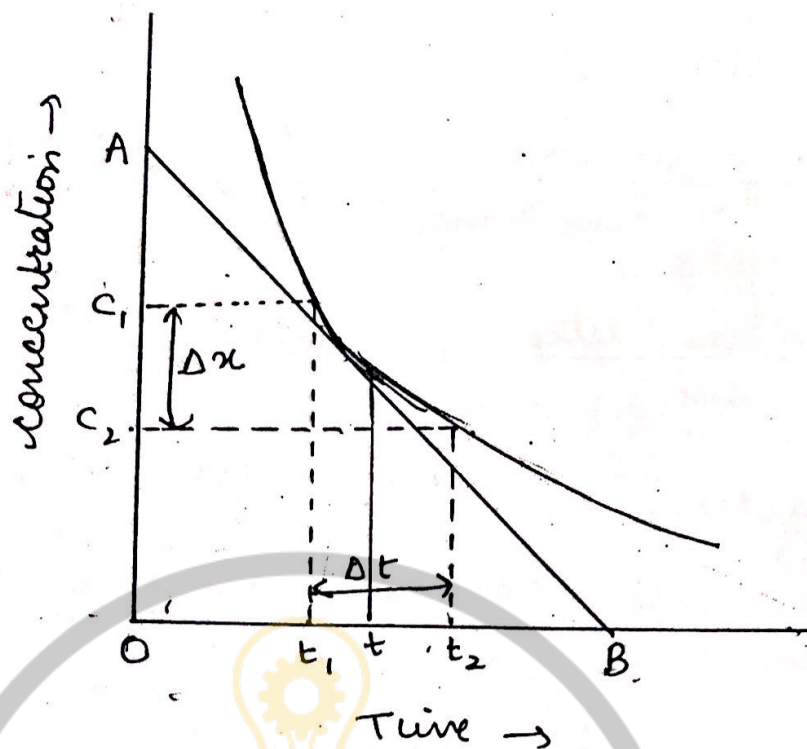
$$\left(\frac{\Delta x}{\Delta t} \right)_{\Delta t \rightarrow 0} = \frac{dx}{dt}$$

For a reaction,



$$\text{Average rate} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

$$\text{Instantaneous rate} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}$$



Average rate at time $t = \frac{C_2 - C_1}{t_2 - t_1} = \frac{\Delta x}{\Delta t}$

Instantaneous rate at time $t = \frac{OA}{OB}$

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Also,

$$\begin{aligned} \text{Rate}_{\text{inst}} &= -\frac{d[R]}{dt} = -\text{slope of tangent} \\ &= +\frac{d[P]}{dt} = \text{slope of tangent} \end{aligned}$$

FACTORS AFFECTING RATE OF REACTION

1. Concentration of the reactants :

The rate of a reaction is directly proportional to the concentration of the reactants.

2. Temperature of the system :

In general, an increase in the temperature increases the rate of almost all chemical reactions. A general approximate rule for the effect of temperature on reaction rates is that the reaction rate for most of the chemical reactions becomes almost double, for every 10°C rise in temperature.

3. Nature of reactants and products :

The reactivity of a substance can be related to the ease with which the specific bonds are broken or formed and the number of such bonds involved.

4. Presence of Catalyst :

A catalyst is a substance which influences the rate of a reaction without undergoing any chemical change itself. Many reactions are made to proceed at an increased rate by the presence of certain catalysts.

5. Surface area :

The larger the surface area of the reactants, the faster is rate of reaction. Finely divided solids reacts faster than massive substances.

because the total surface area of the smaller particles is greater than that of larger particles and this permits more molecules of the reactants to come in contact and form products.

6. Exposure to radiation -

On some cases, the rate of a chemical reaction is considerably increased by the use of certain radiations. The photons of these radiations having frequencies (ν) possess sufficient energies ($E = h\nu$) to break certain bonds in reactants.



Effect of concentration

1. Law of mass action

Accor. to this law, at a given temperature, the rate of a chemical reaction is directly proportional to the product of molar concentrations of reacting species with each conc. term raised to the power equal to numerical coefficient of that species in the chemical equation.

Thus for a hypothetical reaction;



The rate according to law of mass action is

$$r \propto [A][B] = k[A][B]$$

where $[A]$ & $[B]$ are molar conc of reactants A & B

k = rate constant / velocity constant / specific reaction rate

For any reaction,



Accor to law of mass action >

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

→ Law of mass action gives the rate on the basis of stoichiometry of the balanced equation.

2. Rate law expression

→ It represents the qualitative relationship b/w the rate of r_x^n & conc of reactants which actually influence the rate of reaction.

→ It is a mathematical expression which gives the actual rate of reaction observed experimentally.

→ For a hypothetical reaction:



Rate law expression may be written as:

$$\text{rate} = k[A]^m [B]^n$$

where m & n are determined experimentally and cannot be deduced from the balanced equation.

whereas Law of mass action may be written as

$$\text{rate} = k[A]^a [B]^b$$

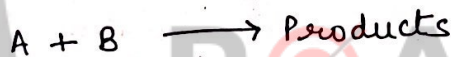
where a & b are the stoichiometric coeff. of the balanced chemical equation.

→ The const k is called rate constant / velocity constant / specific reaction rate

→ For a reaction $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$ Law of mass action $r = k [CHCl_3] [Cl_2]$
 Rate law expression $r = k [CHCl_3] [Cl_2]^{1/2}$

Rate constant (k)

For a reaction,



$$\text{rate} \propto [A][B] \quad \text{or} \quad \text{rate} = k[A][B]$$

If the concentration of all reacting species is taken as unity then

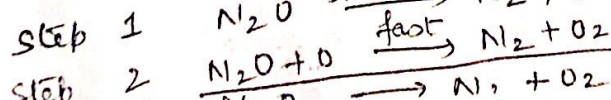
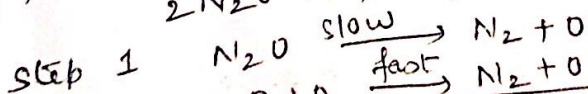
$$\text{rate} = k \quad [\because [A] = [B] = 1 \text{ mol l}^{-1}]$$

Thus, rate constant is defined as the rate of reaction when the concentration of each reactant is taken as unity.

* Rate controlling step: - The slowest step of the complex reaction is called Rate controlling step or Rate determining step

(eg) Thermal decomposition of nitrous oxide

$$\text{rate} = k [N_2O]$$



characteristics of rate constant

1. It gives an idea about the speed of a reaction, i.e. greater the value of rate const, faster is the reaction.
2. Each reaction has a definite value of rate const at a particular temperature.
3. Its value depends upon temp i.e. it changes with change in temperature.
4. It is independent of the conc. of reacting species.
5. The units of rate const depend on the order of reaction.

methods of calculating the value of Rate constant

(A) volumetric method

For 1st order reaction,

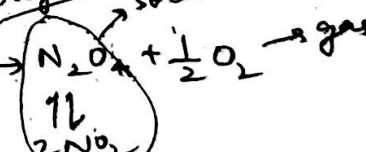
$$k = \frac{2.303 \log \frac{V_0}{V_t}}{t}$$

or $k = \frac{2.303 \log \frac{V_\infty}{V_\infty - V_t}}{t}$

where $V_0 \rightarrow$ initial volume

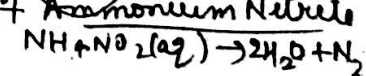
$V_t \rightarrow$ volume at time t

a) Decomposition of Nitrogen Pentoxide solution



for reaction such as N_2O_5

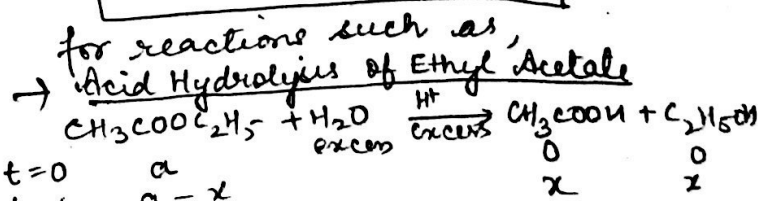
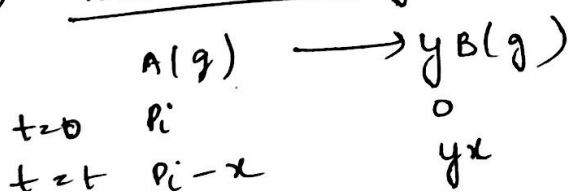
b) Decomposition of Ammonium Nitrite



$V_\infty =$ vol. of O_2 gas collected at infinite time $\propto a$
 $V_t =$ " " " " " any time $\propto x$

or $k = \frac{2.303 \log \frac{(V_\infty - V_0)}{(V_\infty - V_t)}}{t}$

(B) Pressure change method



ORDER OF REACTION

It may be defined as,

the sum of powers or exponents to which the concentration terms are raised in the rate law expression.

For a hypothetical reaction

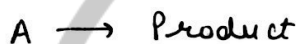


$$\text{Rate} = k[A]^m[B]^n$$

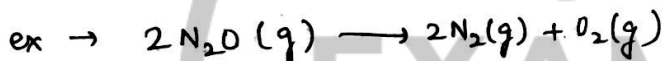
$$\text{order} = m + n$$

Example

① 1st order reaction

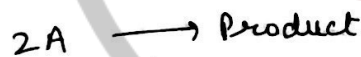


$$\text{Rate} = k_1[A]$$



$$\text{Rate} = k_1[N_2O]$$

② 2nd order reaction



$$\text{Rate} = k_2[A]^2$$

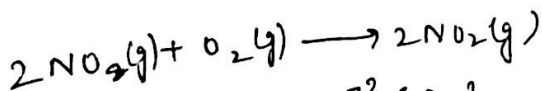
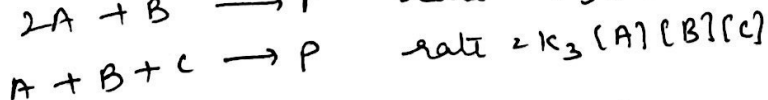
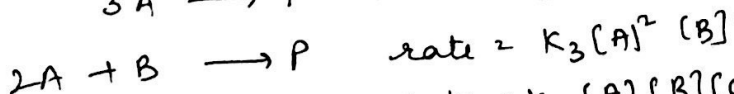
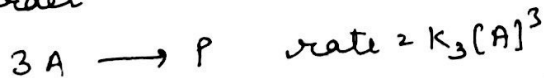


$$\text{Rate} = k_2[A][B]$$



$$\text{Rate} = k[H_2][I_2] \quad \text{order} = 1 + 1 = 2$$

③ 3rd order reaction

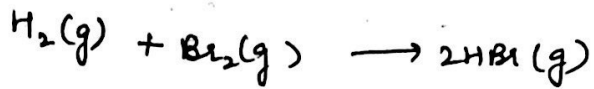


$$\text{Rate} = k[NO_2]^2[O_2]$$

$$\text{order} = 2 + 1 = 3$$

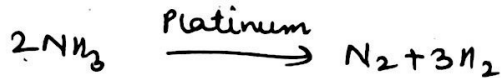


④ Fractional order reaction



$$\text{rate} = k[\text{H}_2][\text{Br}]^{1/2} \quad \text{order} = 1 + \frac{1}{2} = \frac{3}{2}$$

⑤ Zero order reaction



$$\text{Rate} = k[\text{NH}_3]^0 ; \text{order} = \text{Zero}$$

units of rate constants for different order reactions

→ The units of rate constant depends upon the order of the reaction.

→ General expression (for nth order reaction)

$$\text{unit of rate const} = \frac{\text{mol}^{(1-n)} \text{ litre}^{(n-1)} \text{ sec}^{-1}}{\text{mol} \text{ litre}^{-1} \text{ sec}^{-1}}$$

① Zero order reaction

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

$$\frac{\text{moles litre}^{-1}}{\text{sec}} = k \cdot 1$$

$$k = \text{moles L}^{-1} \text{ sec}^{-1}$$

② 1st order reaction

$$\text{Rate} = \frac{dx}{dt} = k[A]^1$$

$$\frac{\text{moles L}^{-1}}{\text{sec}} = k \times \text{moles L}^{-1}$$

$$\text{or } k = \frac{\text{moles L}^{-1}}{\text{moles L}^{-1} \times \text{sec}}$$

$$k = \text{sec}^{-1}$$

③ 2nd order reaction

$$\text{Rate} = \frac{dx}{dt} = k[A]^2$$

$$\frac{\text{mol L}^{-1}}{\text{sec}} = k \cdot (\text{mol L}^{-1})^2$$

$$k = \frac{\text{mol L}^{-1}}{(\text{mol L}^{-1})^2 \cdot \text{sec}} = \text{mol}^{-1} \text{ litre sec}^{-1}$$

④ 3rd order reaction

$$\text{Rate} = \frac{dx}{dt} = k[A]^3$$

$$\frac{\text{moles L}^{-1}}{\text{sec}} = k (\text{moles L}^{-1})^3$$

$$k = \frac{\text{moles L}^{-1}}{\text{sec} \times (\text{moles L}^{-1})^3} = \text{moles}^{-2} \text{ lit}^2 \text{ sec}^{-1}$$

⑤ Half-order reaction

$$\text{mol}^{1/2} \text{ lit}^{-1/2} \text{ s}^{-1}$$

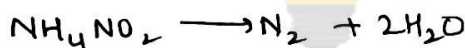
⑥ 3/2 order

$$\text{mol}^{-1/2} \text{ l}^{1/2} \text{ s}^{-1}$$

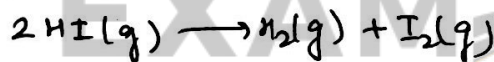
MOLECULARITY

- The number of reacting species which must collide simultaneously in order to bring about the chemical reaction is called molecularity.
- Molecularity of reaction can be 1, 2 or 3.
- Reaction may be classified as unimolecular, bimolecular, trimolecular on the basis of molecularity.
- Chemical reactions in which the molecularity is simply the sum of molecules of the different reactants as represented by the balanced chemical equation are called elementary reactions. Such reactions take place in one step only.

eg → unimolecular



Bimolecular



Trimolecular



- chemical reactions which proceed through more than one step are termed as complex reactions. Molecularity of overall reaction has no significance in such cases.

Difference between order and molecularity

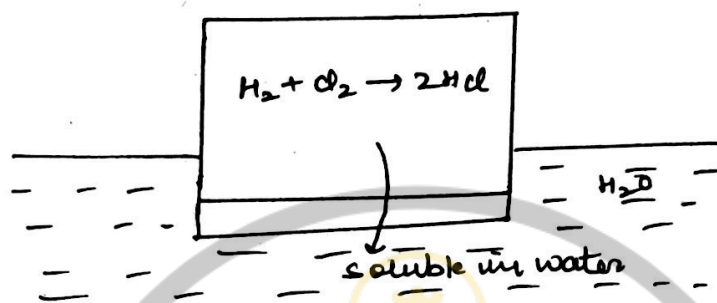
	ORDER	MOLECULARITY
1.	Sum of powers of concentration terms of reactants which are shown in rate law expression	Total number of species taking part in a particular step of the reaction
2.	Evaluated for overall reaction	Calculated separately for each step
3.	It is an experimental value	It is a theoretical value
4.	It may be zero	can never be zero
5.	May have fractional value	Always whole number
6.	Provide some idea about reaction mech.	does not provide any idea abt rxn mech.

Differential & integrated rate equations

1. ZERO-ORDER R_x^n

→ Those reactions whose rate does not depend upon the conc. of the reactants are called zero-order reactions.

eg→



→ Here the produced HCl is soluble in water. ∴ the pressure in the beaker is decreased as HCl is produced, thus water moves up. Due to this motion of water concentration of H_2 & Cl_2 in a unit volume remain constant. Thus rate of reaction is also constant.

Rate eqⁿ

	Reactant	Product
$t=0$	a	0
$t=t$	$a-x$	x

$$\frac{dx}{dt} = k_0(a-x)^0$$

$$\boxed{\frac{dx}{dt} = k_0} \rightarrow \text{differential rate eqⁿ}$$

$$\int dx = \int k_0 dt$$

$$x = k_0 t + C$$

$$\text{At } t=0 ; x=0 \therefore C=0$$

$$x = k_0 t$$

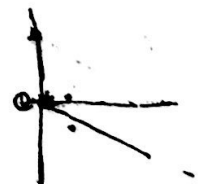
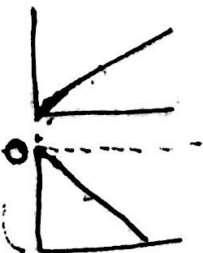
$$\boxed{k_0 = \frac{x}{t}} \rightarrow \text{Integrated rate eq}^n$$

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Plots

(i) $y = mx$

(ii) $y = -mx$



2. FIRST ORDER REACTION

$$\text{Rate} = k[A]$$

	Reactants	Products
$t=0$	a	0
$t=t$	$a-x$	x

$$\boxed{\frac{dx}{dt} = k_1(a-x)} \rightarrow \text{differential rate eq}^n$$

$$\frac{dx}{dt} = k_1(a-x)$$

$$\int \frac{dx}{(a-x)} = \int k_1 dt$$

$$-\log_e(a-x) = k_1 t + c \quad \text{--- (1)}$$

at $t=0$ $x=0$

$$-\log_e a = c$$

Putting the value of c in the 1st eqⁿ

$$-\log_e(a-x) = k_1 t - \log_e a$$

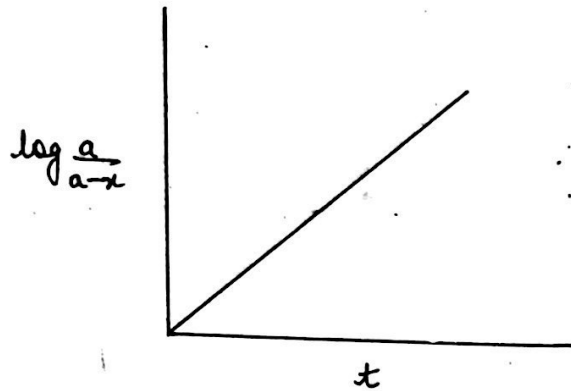
$$k_1 t = \log_e a - \log_e(a-x)$$

$$k_1 t = \log_e \left(\frac{a}{a-x} \right)$$

$$k_1 = \frac{1}{t} \log_e \left(\frac{a}{a-x} \right)$$

$$\boxed{k_1 = \frac{2.303}{t} \log \frac{a}{a-x}} \rightarrow \text{integrated rate eq}^n$$

i) Graph b/w $\log\left(\frac{a}{a-x}\right)$ & t



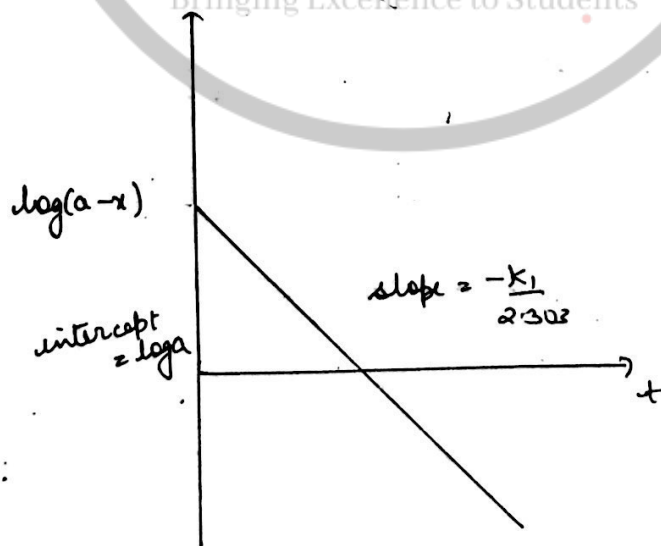
$$\text{slope} = \frac{k_1}{2.303}$$

ii) Graph b/w $\log(a-x)$ & t

$$k_1 t = \ln a - \ln(a-x)$$

$$\ln \log(a-x) = \ln a - k_1 t$$

$$\log(a-x) = \left(\frac{-k_1}{2.303}\right) t + \log a$$



3. SECOND ORDER REACTION

Case - I

$$\text{Rate} = k[A]^2$$

	Reactant conc	Product conc
$t=0$	a	0
$t=t$	$a-x$	x

$$\boxed{\frac{dx}{dt} = k_2(a-x)^2} \rightarrow \text{Differential rate eq}^n$$

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

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

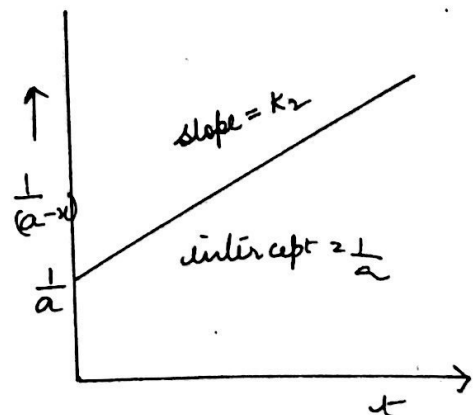
at $t=0, x=0 \quad C = \frac{1}{a}$

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

$$\boxed{k_2 = \frac{1}{t} \frac{x}{a(a-x)}} \rightarrow \text{Integrated rate eq}^n$$

(i) Graph b/w $\left(\frac{1}{a-x}\right)$ & t

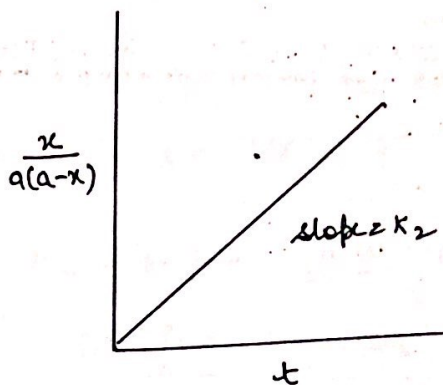
$$\frac{1}{a-x} = k_2 t + \frac{1}{a}$$



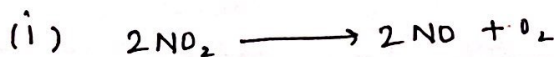
(ii) Graph between $\frac{x}{a(a-x)}$ & t

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

$$k_2 t = \frac{x}{a(a-x)}$$



example :



$$\text{Rate} = k_2 [\text{NO}_2]^2$$



$$\text{Rate} = k_2 [\text{NO}]^2$$

Case II

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

	Reactant		Product
$t=0$	a	b	0
$t=t$	$a-x$	$b-x$	x

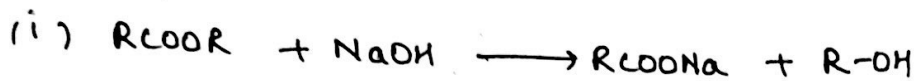
$$\boxed{\frac{dx}{dt} = k_2 (a-x)(b-x)} \rightarrow \text{Differential rate eq}^n$$

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

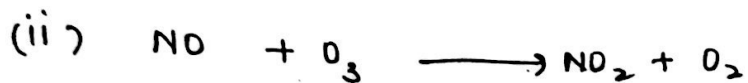
$$\frac{1}{(a-b)} \int \left[\frac{1}{b-x} - \frac{1}{a-x} \right] dx = \int k_2 dt$$

$$\boxed{k_2 = \frac{2.303}{(a-b)t} \log \frac{b(a-x)}{a(b-x)}} \rightarrow \text{Integrated rate eq}^n$$

example :



$$\text{Rate} = k_2 [\text{RCOOR}] [\text{OH}^-]$$



$$\text{Rate} = k [\text{NO}] [\text{O}_3]$$

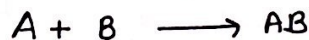
Rate law Expressions & their integrated form for diff reactions .

Reaction	order	Rate law expression	Integrated form
$A \longrightarrow \text{Product}$	0	$\text{rate} = k[A]^0$	$k_0 = \frac{x}{t}$
$A \longrightarrow \text{Product}$	1	$\text{rate} = k[A]$	$k = \frac{2.303}{t} \log \frac{[A]}{[A-x]}$
$2A \longrightarrow \text{Product}$	2	$\text{rate} = k[A]^2$	$k = \frac{1}{t} \frac{x}{A(A-x)}$
$A+B \longrightarrow \text{Product}$	2	$\text{rate} = k[A][B]$	$k = \frac{2.303}{(A-B)t} \log \frac{B(A-x)}{A(B-x)}$
$3A \longrightarrow \text{Product}$	3	$\text{rate} = k[A]^3$	$k = \frac{1}{2t} \left[\frac{1}{[A-x]^2} - \frac{1}{[A]^2} \right]$

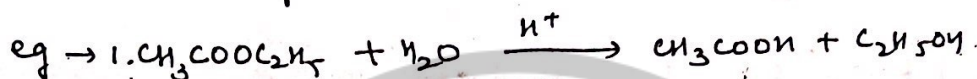
PSEUDO FIRST ORDER REACTIONS

→ When a reaction of higher order under special conditions follows 1st order kinetics then such reactions are called Pseudo first order reactions.

→ For a reaction

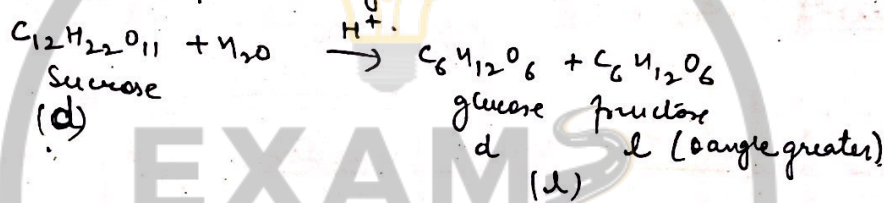


if conc. of B is large enough so that it does not change appreciably during the reaction, then the rate will depend only upon the conc. of A & it will follow the kinetics of 1st order

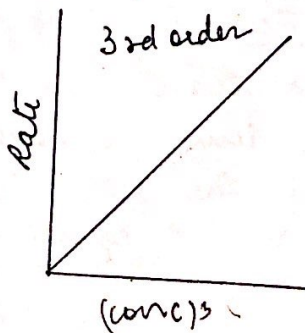
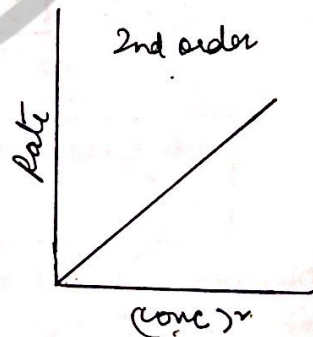
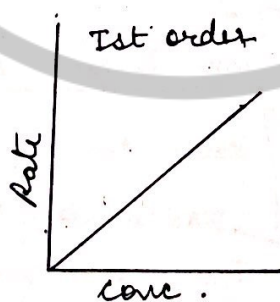


$$\text{rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5]$$

2. Inversion of cane sugar



Plot of Rate vs concentration for reactions of diff orders



Half-life

→ The definite time ~~inter~~ period in which the conc of the reactant is decreased to 50% (half) of the initial value is called half-life for that rxⁿ

$$\text{when } t = t_{1/2} = \text{half life } x = \frac{a}{2}$$

I Half-life for zero-order reaction

$$k_0 = \frac{x}{t}$$

$$t_{1/2} = \frac{a}{2k_0} \quad \left(\because \text{At } t = t_{1/2} \quad x = \frac{a}{2} \right)$$

Conclusion: For ZOR $t_{1/2} \propto a$

II Half-life for 1st-order reaction

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{a/2}$$

$$t_{1/2} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{0.693}{k}$$

radioactive decay

→ Nuclear reactions are 1st order reactions.

Conclusion: $t_{1/2}$ for FOR does not depend on a . $\therefore t_{1/2}$ for a particular FOR is always const. (initial conc)

That is, whether we start with 100 kg of a reagent, or 0.1 g of it, the same time is taken to reduce the former to 50 kg, and the latter to 0.05 g provided the change follows a FOR equation.

III 2nd order reaction

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

$$t_{1/2} = \frac{a/2}{k_2 a(a-a/2)} = \frac{a/2}{k_2 a(a/2)}$$

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

Conclusion: For SOR, $t_{1/2} \propto \frac{1}{a}$

GENERAL EXPRESSION FOR $t_{1/2}$

for n th order (where $n \geq 2$)

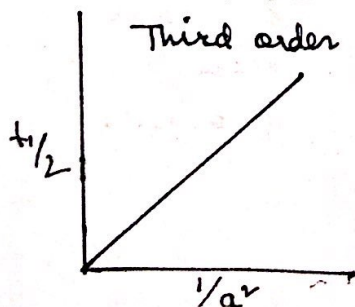
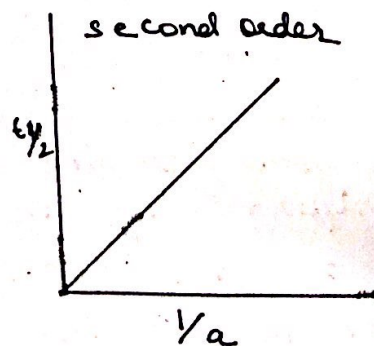
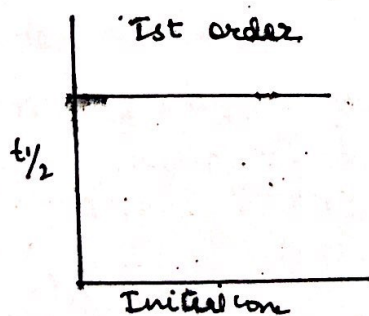
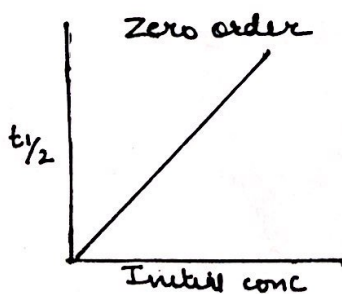
$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k_n a^{n-1}}$$

ie $t_{1/2} \propto \frac{1}{a^{n-1}}$

Amount of substance after N half lives.

$$[A] = \frac{[A_0]}{2^N} \quad (\text{Here } n \rightarrow \text{no of half lives})$$

Plots of Half lives vs initial conc or diff orders



Effect of temperature on reaction rates

→ The increase in temperature generally increases the rate of reaction due to increase in number of effective collisions (collisions which bring abt the che. reaction).

For example

- (i) The spoilage of food takes place more rapidly on warm day than on cold ones.
- (ii) Due to fever the body weight decreases rapidly, because at a higher temperature, the metabolic reactions in the cells take place at increased rate which results in burning of body fats.

→ For most of the chemical reactions there is a two fold increase in the rate for each 10°C rise in temperature. It is expressed in terms of temperature coefficient.

$$\text{Temp. coefficient} = \frac{k_{t+10}}{k_t} \approx 2-3$$

→ Temp. coefficient is the ratio of rate const of same reactions at 2 diff. temperatures differing by 10°C .

ACTIVATION ENERGY

→ The min. energy which is required to bring about a chemical change is called E_a .

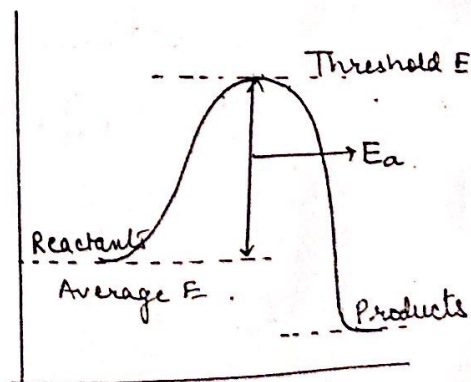
or

→ The additional energy which a molecule must possess above its average value is called E_a .

→ It is always +ve and never depends on Temp.

→ $E_a = \text{Threshold E} - \text{Average E of reactants}$

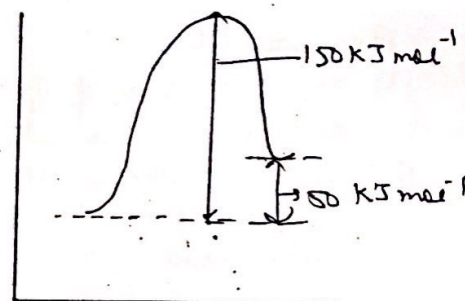
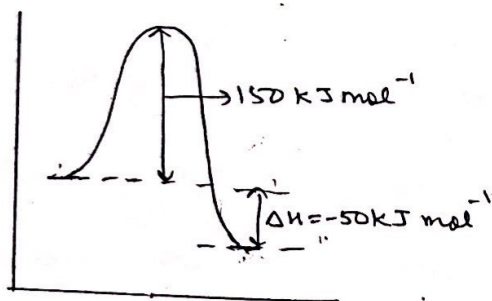
→ Threshold E is the E of activated complex i.e. it is the min. E possessed by the molecules for effective collisions.



Calculate the E_a for the backward reaction in following cases if E_a for forward reaction is 150 kJ mol^{-1}

Case-I $\Delta H = -50 \text{ kJ mol}^{-1}$

Case-II $\Delta H = +50 \text{ kJ mol}^{-1}$



E_a for back reⁿ = 200 kJ/mol

E_a for back reⁿ = 100 kJ mol^{-1}

*

Determination of activation Energy (Arrhenius Eqⁿ)

From Arr eqⁿ

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

where

K = rate constant

A = Arr. pre exponential factor (unitless)

E_a = Activation E

R = Gas constant

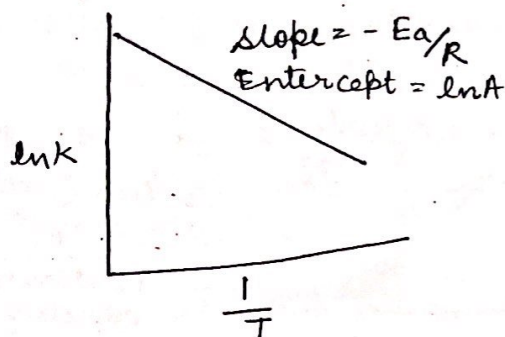
T = Temperature in K

on taking log

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

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

Plot a graph b/w $\ln k$ v/s $\frac{1}{T}$ to evaluate the value of E_a



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

$$y = +c - mx$$

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

Alternative method for the determination of E_a

Given rxn is carried at two different temp

Suppose at T_1 temp rate constant = k_1

at T_2 " " " " = k_2

$$\therefore \ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \ln k_2 = \ln A - \frac{E_a}{RT_2}$$

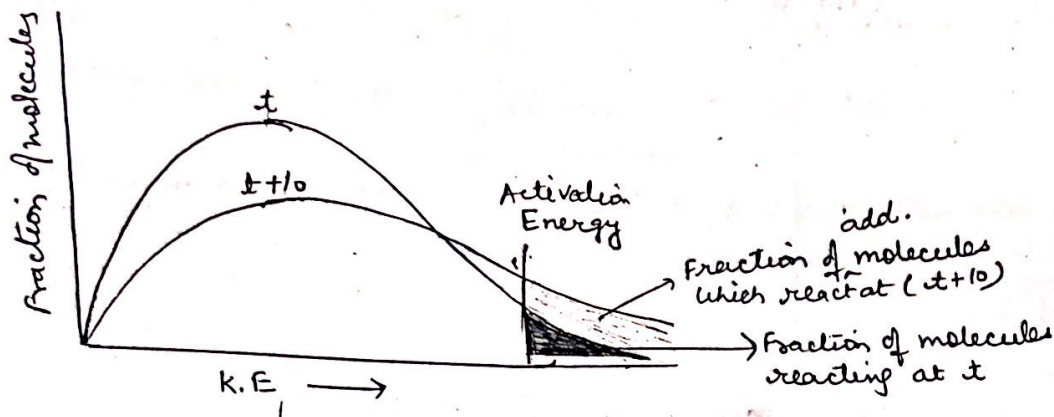
$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

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

$$\ln = 2.303 \log$$

$$\text{or } \log \frac{k_2}{k_1} = \frac{E_a}{2303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$T_2 > T_1$$



Distribution curve showing temp dependence of rate of reaction

Effect of Catalyst

- Lower the value of activation energy, faster will be the rate of the reaction.
- So, catalyst provides an alternate pathway or reaction mech. by reducing the A-E b/w reactants and products & hence lowering the energy barrier.
- Catalyst does not change eq^m constant of a reaction rather, it helps in attaining the eq^m faster.
- It catalyses the forward as well as backward reactions to the same extent.
- Catalyst does not alter Gibbs energy, ΔG of a reaction.

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

$$\log K_1 = \log A - \frac{E_{a1}}{2.303RT} \quad (\text{absence of catalyst})$$

$$\log K_2 = \log A - \frac{E_{a2}}{2.303RT} \quad (\text{presence of catalyst})$$

$$\log K_2 - \log K_1 = \left(\log A - \frac{E_{a2}}{2.303RT} \right) - \left(\log A - \frac{E_{a1}}{2.303RT} \right)$$

$$= \cancel{\log A} - \frac{E_{a2}}{2.303RT} - \cancel{\log A} + \frac{E_{a1}}{2.303RT}$$

$$\log \frac{K_2}{K_1} = \frac{E_1}{2.303RT} - \frac{E_{a2}}{2.303RT} = \frac{1}{2.303RT} (E_{a1} - E_{a2})$$

$$\log \frac{K_2}{K_1} = \frac{1}{2.303RT} (E_{a1} - E_{a2})$$

COLLISION THEORY

- A chemical reaction occurs only as a result of collisions between the reacting molecules.
- The total number of collisions which occur among the reacting species per second per unit volume is called collision frequency (Z)
- All collisions do not result in chemical reaction. The collisions which bring about the chemical reaction are called effective collisions.
- There are 2 imp barriers to a reaction, namely energy barrier & orientation barrier.

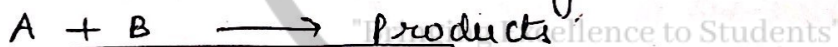
1) Energy barrier

The min amount of energy which the colliding particles must possess in order to bring about chemical reaction is called threshold energy.

2) orientation barrier

In a chemical reaction the colliding species must have proper orientation at the time of collision so that the old bond break & new bonds are formed.

For a bimolecular elementary reaction



$$\text{Rate} = Z_{AB} e^{-E_a/RT}$$

Z_{AB} → collision freq of reactants A & B

$e^{-E_a/RT}$ → fraction of molecules with energies equal to or greater than E_a .

Comparing $\bar{A} \cdot e^{-E_a/RT}$, we can say that A is related to collision freq.

To account for effective collisions, another factor P called probability factor / steric factor is introduced. It takes into account the fact that in a collision molecules must be properly oriented; i.e.

$$\text{Rate} = P Z_{AB} e^{-E_a/RT}$$

