

Unit 7: CHEMICAL KINETICS

Chemical Kinetics:

The branch of physical chemistry concerned with understanding of rates of chemical equation.

Rate of Reaction:

The change in concentration of the reactant or the product per unit time is called rate of reaction.

Let a general reaction,
 $A \rightarrow B$.

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

rate of A disappearance rate of B appearance.

(*) Equivalent Rate Expression:

For a general reaction,
 $aA + bB \rightarrow cC + dD$

Equivalent rate of reaction is,

$$-\frac{1}{a} \frac{\Delta [A]}{\Delta t} = -\frac{1}{b} \frac{\Delta [B]}{\Delta t} = \frac{1}{c} \frac{\Delta [C]}{\Delta t} = \frac{1}{d} \frac{\Delta [D]}{\Delta t}$$

The rate of reaction for one mole of reactant or product.

$$\# -\frac{\Delta [A]}{\Delta t} = \frac{d[A]}{dt} \quad \text{when } \Delta t \rightarrow 0.$$

(*) Types:

Rate of reaction are of two types:
 average rate and instantaneous rate.

(a) Average Rate:

The rate of change in concentration of reactants or products per unit interval of time.

Mathematically,

$$\text{Avg. rate} = \frac{[\text{change in conc of reactant/product}]}{\text{time taken}}$$

The average rate of reaction decreases as reaction moves forward.

(b) Instantaneous Rate:

The rate of reaction at a particular time instance is called instantaneous rate.

Mathematically,

$$\text{Instantaneous rate} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

$$\text{Avg rate} = -\frac{([A]_2 - [A]_1)}{t_2 - t_1}$$

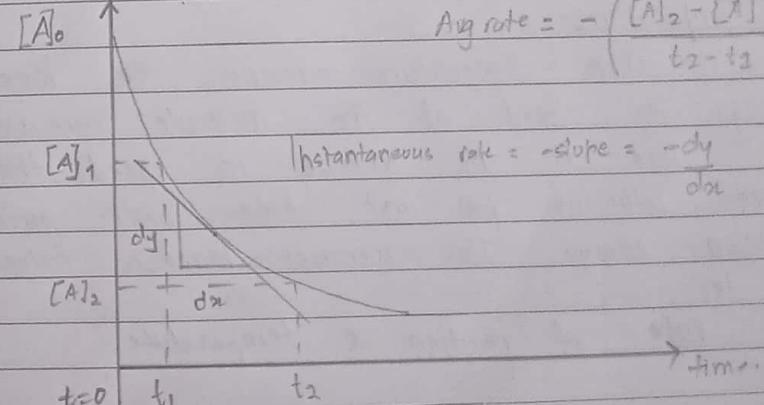


Fig: Concentration vs time.

Factors affecting Rate of Reaction:

a) Reactant concentration:

Increase in concentration of reactants increases the number of molecules per unit volume.

This increases the number of collisions per unit time, thus increasing reaction rate.
i.e.; reaction rate \propto concentration.

b) Physical State:

When reactions are in different phases, the finely divided solid or liquid reactant will have greater surface area increasing area of contact between reactants and thus, increasing the collision frequency and hence, rate.
i.e.

$$\text{rate of reaction} \propto \text{surface area.}$$

c) Temperature:

When temperature increases, the kinetic energy i.e. speed of the molecule increases.

Due to the increase in speed, this leads to more collisions per unit time with greater collision energy. This increases reaction rate
i.e.

$$\text{rate of reaction} \propto \text{temperature.}$$

(d): Catalyst:

Based upon their nature, they increase or decrease the rate of reaction by changing its mechanism.

Rate Equation / Rate of Law

An equation expressing relationship between rate of reaction and concentration of reactants present in given chemical equation is called rate equation.

for reaction, $aA + bB \rightarrow cC + dD$,

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

Here, k is proportionality constant called rate constant.

~~m~~ m = reaction order w.r.t A

n = reaction order w.r.t B

m and n are not related to a and b coefficients.

④ Order of reaction:

The number of moles of reactant whose concentration will determine the rate of reaction.

Here,

$$\text{order of reaction} = m+n.$$

i) If $m+n=0$, reaction is zero order.

Here, rate is independent of reactants concentration.

ii) If $m+n=1$, reaction is first order.

Here, one mole of reactant gives rate.

iii) If $m+n=2$, reaction is second order.

Here, 2 moles of reactant gives rate i.e., two reactant species.

iv) If $m+n=\text{fractional}$, reaction is fractional order.

Here, no. of moles reacting are in fractional value.

(*) Units of k :

Unit of $k = (\text{mol litre}^{-1})^{1-n} \text{ time}^{-1}$

Here, $n = \text{order of reaction}$:

Reaction order

Unit

0

$\text{mol litre}^{-1} \text{ sec}^{-1}$

1

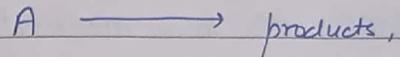
sec^{-1}

2

$\text{L mol}^{-1} \text{ sec}^{-1}$

Experimental Determination of Rate Law:

For reaction,



Rate law :

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

Here;

$m = \text{order of reaction}$:

If, concentration is doubled, then rates undergoes the following changes

rate doubles

rate quadruples

rate constant

rate depends on
 $[A]^1$,

→ first order.

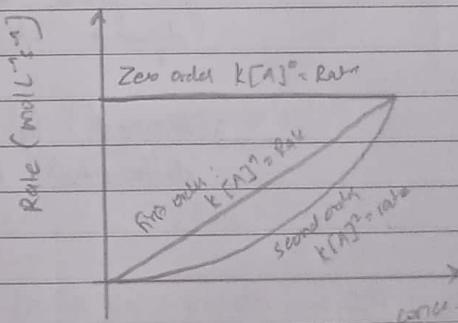
rate depends on
 $[A]^2$

→ second order

rate depends upon
 $[A]^0$ i.e., independent

→ zero order.

So, the rate vs concentration graph for 0, 1st and 2nd order reactions.



Experimental Determination of Rate Constant.

If order of the reaction is determined, the rate constant can be measured as,

$$k = \frac{\text{initial or average rate}}{\text{concentration of reactant to the power of their order.}}$$

Since determination of rate constant accurately is difficult, 'k' is determined using integrated rate law.

Types of Rate law:

Rate law are of two types:
differential rate law or integrated rate law.

a) Differential rate law

- This shows how rate of reaction is dependent on concentration.

b) Integrated rate law:

- This shows how concentrations of species in reaction depends on time.

- Obtained by integrating of differential rate law.

Integrated Rate law for 1st Order Reaction

First order reaction is the chemical reaction in which the rate of reaction is dependent on the concentration of one reactant.

For first order reaction, $A \rightarrow \text{product}$,

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

So,

$$-\frac{d[A]}{dt} = k[A] \quad \text{--- (i)}$$

$\text{Eq } \text{(i)}$ is differential rate law for 1st order reaction.

So,

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

$$\text{on } \frac{d[A]}{[A]} = -k dt$$

Integrating both sides from t_0 to t ,

$$A_0 \int \frac{1}{[A_0]} d[A] = -k \int_{t_0}^t dt$$

$$\text{on } \ln \left[\frac{[A]}{A_0} \right] = -kt \Big|_{t_0}^t$$

$$\text{or } \ln [A] - \ln [A_0] = -kt$$

So,

$$\ln [A] = \ln [A_0] - kt \quad \text{--- (ii)}$$

Raising each side to power e,

$$e^{\ln[A]} = e^{\ln[A_0] - kt}$$

$$e^{\ln[A]} = \frac{e^{\ln[A_0]}}{e^{kt}}$$

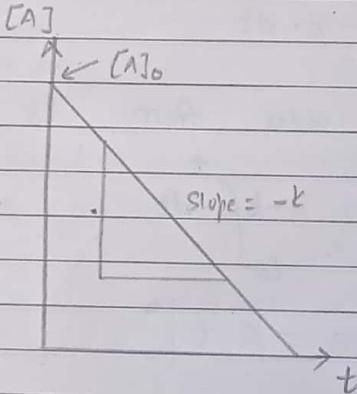
$$\text{or } \ln[A] = [A_0] e^{-kt} \quad \text{--- (iii).}$$

Eqn (iii) is the integrated rate law for 1st order reaction.

Graphically,

Here,

$\ln[A] = -kt + \ln[A_0]$ is similar to equation $y = mx + c$ with slope $-k$. Thus, the graph is plotted as,



(H) Integrated Rate law for second order

The second order reaction is the reaction in which the rate is dependent upon the concentration of two reactant species.

For second order reaction, $2A \rightarrow \text{product}$.

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

$$\text{or } -\frac{d[A]}{dt} = k[A]^2 \quad \text{--- (i)}$$

Eqn(i) is the differential equation for second order reaction.

$$\text{or } -\frac{d[A]}{[A]^2} = k dt$$

$$\text{or, } \frac{d[A]}{[A]^2} = -k dt \quad \text{--- (ii)}$$

Integrating both sides from t_0 to t ,

$$\int_{A_0}^A \frac{1}{[A]^2} d[A] = -k \int_{t_0}^t dt$$

$$\text{or, } -\frac{1}{[A]} \Big|_{A_0}^A = -k t \Big|_{t_0}^t$$

$$\text{or, } \frac{1}{[A]} - \frac{1}{[A_0]} = kt \quad \text{--- (iii)}$$

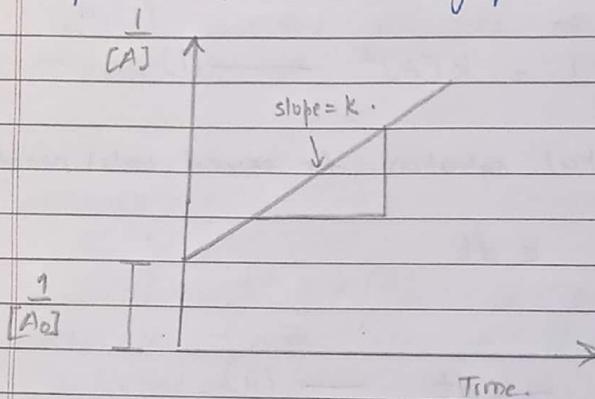
Eqn(iii) is the integrated rate law for 2nd order reaction.

Rearranging (iii),

$$\frac{1}{[A]} = \frac{kt}{[A_0]} + \frac{1}{[A_0]} \quad \text{--- (iv)}$$

Graphically,

eqn(iv) corresponds to $y = mx + c$ with slope k . Thus, the graph is plotted as,



Note:

(i): For 1st order, logarithm of reactant concentration decreases linearly as time increases

(ii): For 2nd order, reciprocal of reactant concentration is linear function of time.

Reaction half life:

The time taken by the reactant concentration to become half of its initial value is called reaction half life.

(x): Reaction half life for 1st order:

We know,

integrated rate law for 1st order reaction,

$$[A] = [A_0] e^{-kt} \quad \text{--- (i)}$$

For one half-life,

$$t = t_{1/2} \quad \text{and}$$

$$[A] = 0.5[A_0]$$

So, eqn(i) becomes

$$0.5[A_0] = [A_0] e^{-k t_{1/2}} \quad \text{--- (ii)}$$

$$\text{on } 0.5 = e^{-k t_{1/2}}$$

$$\text{or, } \frac{1}{0.5} = e^{k t_{1/2}}$$

$$\text{on } \ln 2 = k t_{1/2}$$

$$\text{or, } \frac{0.693}{k} = t_{1/2} \quad \text{--- (iii)}$$

Eqn(iii) gives the reaction half life for 1st order reaction.

(Q): A first order reaction is 35% complete at 55 minutes. What is the value of k ?

Sol:

Let A_0 be initial concentration and A be concentration after 55 minutes.

So, according to question,
 $t = 55 \text{ minutes}$

$$[A] = \frac{[A_0]}{(100-35)} = \frac{[A_0]}{0.65}$$

We know,
integrated rate law for 1st order,

$$[A] = [A_0] e^{-kt}$$

$$\text{or, } \frac{[A]}{[A_0]} = e^{-k \cdot 55}$$

$$\text{on } \ln\left(\frac{1}{0.35}\right) \times \frac{1}{55} = k$$

$$\therefore k = 7.832 \times 10^{-3} \text{ min}^{-1}$$

Overview.

	Zero Order	1st Order	2nd Order
rate law	$\text{rate} = k$	$\text{rate} = k[A]$	$\text{rate} = k[A]^2$
units of k .	$\text{mol L}^{-1} \text{ sec}^{-1}$	sec^{-1}	$\text{L mol}^{-1} \text{ sec}^{-1}$
integrated rate law	-	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
plot for st. line	-	$\ln[A]_t \text{ vs } t$	$\frac{1}{[A]_t} \text{ vs } t$
slope	-	$-k$	k
y-intercept	-	$\ln[A]_0$	$\frac{1}{[A]_0}$
half-life	-	$0.693/k$	-
differential rate law	-	$\frac{-d[A]}{dt} = k[A]$	$\frac{-d[A]}{dt} = k[A]^2$

Reaction Mechanism

Reaction may occur due to one step or many discrete steps. Each process is an elementary process.

The sequence of events that describes the actual process by which reactant becomes products is called reaction mechanism.

Based on reaction mechanism, reactions are of two types: elementary and complex.

a) Elementary reactions

→ One step reactions.

→ No intermediate formation

→ Only one transition state.

- Divided into uni-, bi-, tri-molecular reaction based on molecularity.

b) Complex Reactions

→ Multi-step reactions

→ Intermediate formation.

→ Multiple transition state.

- Rate of overall complex reaction is the rate of its slowest step.

Elementary Reactions: 4 Molecularity

An elementary reaction is the chemical reaction in which one or more chemical species react directly to form product in a single reaction step.

Molecularity is the number of molecules coming together at a time to proceed with the reaction.

For elementary process,

Order of reaction = Molecularity of rxn

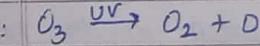
Depending upon the numbers of colliding species in elementary step, molecularity can be: unimolecular, bimolecular and trimolecular.

a) Unimolecular

E.P.

- involves only one molecule as reactant.

- reactant collides with walls or catalyst giving product.

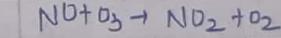


b) Bimolecular

E.P.

- involves two molecules as reactants.

- reactant collided with one another giving product.

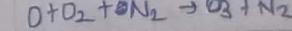


c) Trimolecular

E.P.

- involves three molecules as reactants.

- three reactant molecules combine to give product.



(X) Rate laws of Elementary steps:

The rate laws of various elementary process based on their molecularity is given below.

Molecularity	Reaction.	Rate law.
Uni	$A \rightarrow \text{product}$	$\text{Rate} = k[A]$
Bi	$A + A \rightarrow \text{product}$	$\text{Rate} = k[A]^2$
Bi	$A + B \rightarrow \text{product}$	$\text{Rate} = k[A][B]$
Tri	$A + A + A \rightarrow \text{product}$	$\text{Rate} = k[A]^3$
Tet	$A + A + B \rightarrow \text{product}$	$\text{Rate} = k[A]^2[B]$
Tet	$A + B + C \rightarrow \text{product}$	$\text{Rate} = k[A][B][C]$

Differences betn orders and Molecularity

Order of reaction	Molecularity of reaction.
The sum of the exponents of the concentrations of reactants in rate law equation.	- The number of reactant species present in the rate determining step of complex reaction.

Can't be calculated from stoichiometric coefficients. - coefficient of reactant.

- Experimentally determined. - Determined by simple calculation.
- May be whole numbers, 0 ^{or} fraction. - Has to be whole number.
- May change depending on given condition. - Always constant for a given reaction.
- Should be calculate for complex reactions. - for complex reaction, molecularity of slowest step is its molecularity.

(XQ7): Elementary process with molecularity greater than three are not known.

Ans:

In elementary process, all the species must undergo effective collision at the same instance to undergo product formation. The probability of collision of simultaneous collision of more than three species with proper orientation and sufficient energy is give effective collision is not favourable. Thus, the elementary process with molecularity greater than three are not known.

And also, the simultaneous collision of more than three species with proper orientation and sufficient energy for effective collision to give product is also favourable in very few cases.

These

Note: total order = no. of colliding particles

iff, the reaction must be first order w.r.t all individual species.

(Q7): The order of a reaction cannot, in general, be predicted from the stoichiometry of overall reaction. However, the order of an elementary process is predictable.

Soln:

In elementary process, the single step is itself the rate determining step.

The molecularity of elementary reaction is the number of molecules coming together to proceed with reaction.

i.e., molecularity = no. of molecules interacting — (ii)

According to definition,

the molecularity = orders of reaction — (ii)
for elementary step.

From (i) and (ii),
order of reaction = no. of molecules interacting to give effective collision.

Since, the molecularity of a elementary step is determinable, we can predict the order of elementary process.

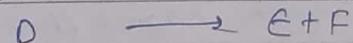
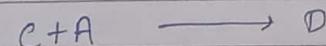
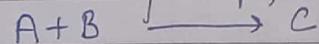
Reaction Mechanism & Rate Law :

The experimentally observed orders and rate of overall reaction are related to the order and rate of elementary process comprising the mechanism.

Let us consider a reaction,



Possible elementary steps;



Here, C and D are intermediates.

Here, E and F are the result of three elementary steps and with which can't be formed faster than the slowest step.

That slower step is called rate determining step and overall order is same as the order of that step.

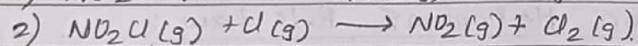
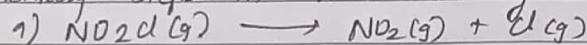
If 1st step is the slowest step,

$$\text{Rate} = -\frac{1}{2} \frac{d[A]}{dt} = k_1 [A][B]$$

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

$\downarrow_{\text{w.r.t. A}}$ $\uparrow_{\text{w.r.t. B}}$

(Q7): The following two reactions are proposed as elementary steps in mechanism of an overall reaction.



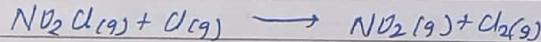
a) Write overall balanced equation.

b) Determine molecularity of each step.

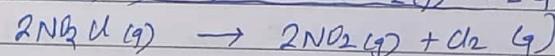
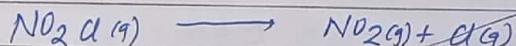
c) Write rate law for each step.

Soln:

Given steps,



a) For overall balanced equation,



b): Here,

step 1 is unimolecular

step 2 is bimolecular.

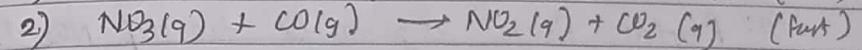
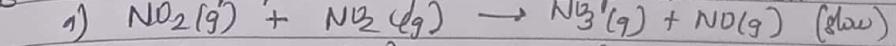
c): Rate law for each step.

$$\text{Rate}_1 = k_1 [\text{NO}_2\text{Cl}]$$

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

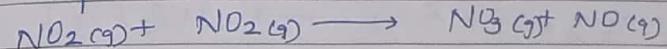
(Q7): The reaction $\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$

has been proposed by two step mechanism:



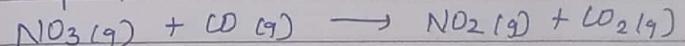
So 10.

For step 1,



$$\text{Rate} = k_1 [\text{NO}_2]^2 \quad \text{--- (i)}$$

For step 2;



$$\text{Rate} = k_2 [\text{NO}_3][\text{CO}] \quad \text{--- (ii)}$$

Here,

→ NO_3 is intermediate.

→ Eqn (i) is the experimental rate law.

→ Step 1 is the rate determining step.

→ Overall order = 2

→ Molecularity = 2.

∴ Rate law of rate determining step is the rate law for overall reaction.

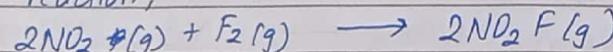
Valid Mechanism:

A mechanism fulfilling the following three criteria are called valid mechanism.

- (i) Elementary step must add up to overall equation
- (ii) Elementary steps must be physically reasonable.
- (iii) Mechanism must correlate with observed rate law.

(iv): Reaction Energy diagram for two-step $\text{NO}_2 - \text{F}_2$ reaction;

Overall reaction,



and

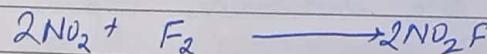
experimental rate law: Rate = $k[\text{NO}_2][\text{F}_2]$

The accepted mechanism is

- i) $\text{NO}_2 + \text{F} \longrightarrow \text{NO}_2\text{F} + \text{F}$ & slow?
- ii) $\text{NO}_2 + \text{F} \longrightarrow \text{NO}_2\text{F}$ & fast?

Step 1 corresponds to observed rate law — (a)

Adding (i) + (ii), we get

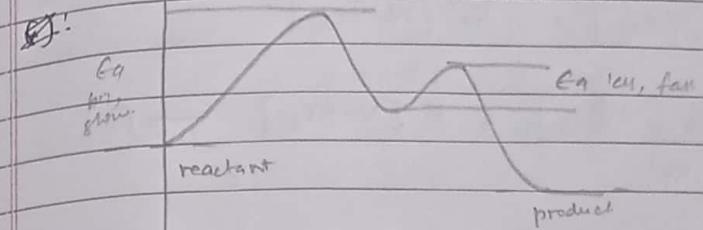


The elementary steps sum to overall balanced equation.
— (b).

Both steps are ~~not~~ bimolecular hence physically reasonable — (c).

From A, B, C,

the given mechanism is valid.



(v): Given eq^o is: $2\text{NO}(g) + \text{Br}_2(g) \rightarrow 2\text{NOBr}(g)$
and experimental rate law is,
rate = $k[\text{NO}]^2[\text{Br}_2]$.

So I.D:

Here,
proposed mechanism,

- (1): $\text{NO} + \text{Br}_2 \xrightleftharpoons[k_1]{k_1} \text{NOBr}_2$ (fast)
- (2): $\text{NOBr}_2 + \text{NO} \xrightleftharpoons[k_2]{k_2} 2\text{NOBr}$ (slow).

Since step 1 is equilibrium, step 2 gives rate.

So,
rate = $k_2 [\text{NOBr}_2][\text{NO}]$ — (i)

For step 1,
rate = $k_1 [NO][Br_2]$ — (a)

for forward

rate for backward = $k_1' [NOBr_2]$ — (b).

Equating (a) and (b),

$$k_1 [NO][Br_2] = k_1' [NOBr_2]$$

$$\therefore \frac{k_1}{k_1'} [NO][Br_2] = [NOBr_2] \quad \text{--- (ii)}$$

Putting in eqn (i), we get.

$$\text{rate} = \frac{k_1 k_2}{k_1'} [NO][NO][Br_2]$$

$$\text{or rate} = k [NO]^2 [Br_2]$$

Here, the mechanism is valid because, experimental rate law and rate law for rate determining step are same.

The two steps giving overall reaction when added.

Both steps have same molecularity.

Steady State Approximation:

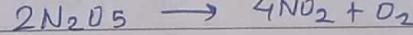
Q7: Define SSA. Apply SSA for determination of overall rate of the decomposition of N_2O_5 with support of reaction mechanism.

Complex reaction proceeds using the involvement of successive step with comparable rate. So, it is difficult to facilitate the rate law for such complex reaction.

To facilitate rate law for such complex reaction, we use steady state approximation.

Steady state approximation states that, "the rate of formation of intermediate is equal to the rate of destruction of intermediate."

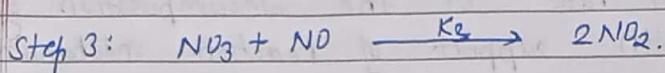
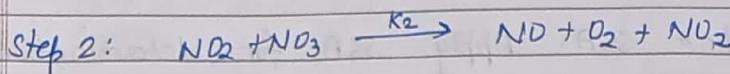
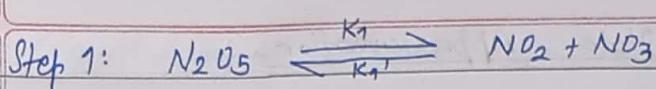
Consider the decomposition of N_2O_5 is represented as,



The proposed rate law for above reaction is,

$$\frac{d[O_2]}{dt} = k [N_2O_5]$$

The proposed mechanism for decomposition of N_2O_5 is,



Here, NO and NO₃ are intermediates.

Using SSA to find concentration of reaction intermediate

For NO,

$$\text{rate of formation of } NO = \text{rate of decomposition of } NO \\ \text{or, } k_2 [NO_2] [NO_3] = k_3 [NO_3] [NO]$$

So,

$$[NO] = \frac{k_2 [NO_2]}{k_3} \quad \text{--- (i)}$$

For NO₃,

$$\text{rate of formation of } NO_3 = \text{rate of decomposition of } NO_3, \\ \text{or, } k_1 [N_2O_5]$$

$$k_1 [N_2O_5] = k_1' [NO_2][NO_3] + k_2 [NO_2][NO_3] \\ + k_3 [NO_3][NO]$$

$$\text{or, } k_1 [N_2O_5] = (k_1' [NO_2] + k_2 [NO_2] + k_3 [NO]) [NO_3] \quad \text{--- (ii)}$$

Substituting k₃[NO],

$$k_1 [N_2O_5] = (k_1' [NO_2] + k_2 [NO_2] + k_2 [NO_2]) [NO_3]$$

$$[NO_3] = \frac{k_1 [N_2O_5]}{k_1' [NO_2] + 2k_2 [NO_2]} \quad \text{--- (iii)}$$

Here,

rate of reaction is also the rate of oxygen formation,

$$\frac{d[O_2]}{dt} = k_2 [NO_2] [NO_3] \quad \text{--- (iv)}$$

Putting eqn (iii) in (iv),

$$\frac{d[O_2]}{dt} = k_2 [NO_2] \times \frac{k_1 [N_2O_5]}{[NO_2] (k_1' + 2k_2)}$$

$$\text{or, } \frac{d[O_2]}{dt} = \frac{k_2 k_1}{k_1' + 2k_2} [N_2O_5] \quad \text{--- (v)}$$

From eqn (i) and (v), we get.

$$k = \frac{k_2 k_1}{k_1' + 2k_2}$$

is the experimental rate constant.

Chain Reaction:

The reactions proceeding in a series of successive steps once initiated by suitable primary process is called chain reaction.

(*) Steps of chain Reaction:

(i) Chain initiation step:

- first step in which reactive intermediate species are produced.
- slow step so rate determining step.
- mostly catalyzed by ~~the~~ light and heat.

(ii) Chain propagation step:

- second step in which reactive intermediate reacts to give product and another intermediate.

(*) Branching: If two intermediates are produced by the loss of one intermediate, it is called branching.

(iii) Chain termination step:

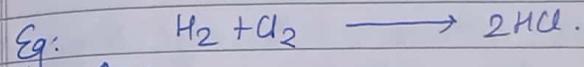
- third step in which two intermediate react to give product and ends the reaction.

(iv) Retardation:

The step in which the carrier strikes the product reducing the rate of formation of product is retardation step.

(v) Chain inhibition step:

The step in which the reacting radicals are removed by away chain termination.

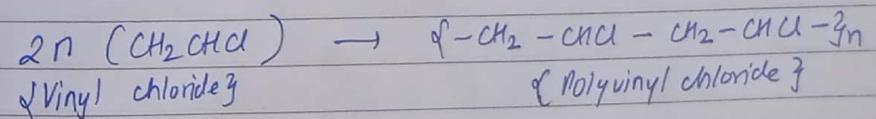


Ans:

- $Cl_2 \xrightarrow{\text{Light}} 2\dot{Cl}$ (Chain initiation)
- $\dot{Cl} + H_2 \longrightarrow HCl + \dot{H}$ (chain propagation)
- $\dot{H} + Cl_2 \longrightarrow HCl + \dot{Cl}$ (propagation)
- $2\dot{Cl} + H \longrightarrow Cl_2 + H$ (Chain inhibition)
- $\dot{H} + \dot{Cl} \longrightarrow HCl$ (Chain termination)
- $\dot{H} + HCl \longrightarrow H_2 + \dot{Cl}$ (Chain retardation)

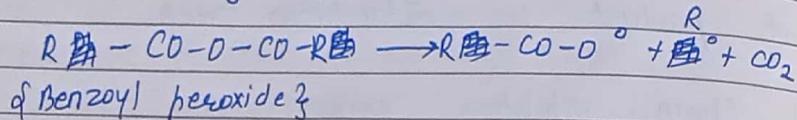
Polymerization of Ethylene / Vinyl chloride:

Polymerization is the process by which monomers {small compounds} combine to give long chain compounds.
For vinyl chloride,



(i): Chain initiation step:

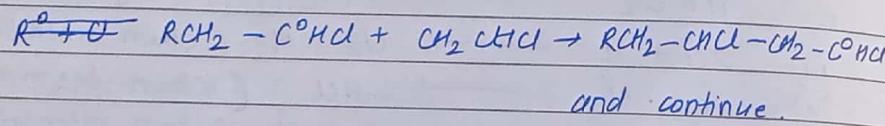
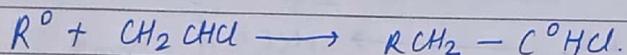
Organic peroxides are easily split into free radicals by light.



Let R^{\bullet} = free radical.

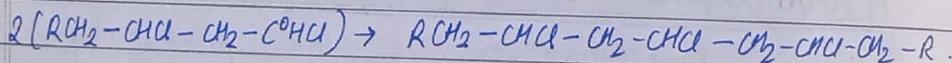
(ii): Chain propagation:

Free radicals combine with vinyl chloride to give long chain free radical.



(iii) Chain termination:

It can occur in any step.



and more.

Collision Theory of Gaseous Reaction:

According to collision theory of gaseous reaction, "the reactant molecules must undergo effective collision to give product and the rate of reaction depends upon the rate of collision."

*) Conditions for Effective Collision:

i) The colliding molecules must have kinetic energy greater than the activation energy.

ii) The colliding molecules must collide with proper orientation.

x) Reaction Rate Expression:

For elementary process, $A + B \longrightarrow C + D$,

taking into account the two postulates of collision theory,

the reaction rate is given by,

$$\text{rate} = f \times p \times z$$

Here,

f = fraction of molecules possessing sufficient energy to react

z = collision frequency

p = probable fraction of collisions.

(*) Note: Increase of temperature by 10°C , doubles the reaction rates.

Dependence of Rate Constant on Temperature

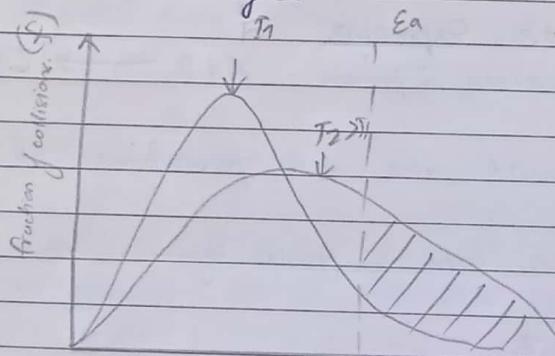
From Arrhenius eq²,

$$k = Ae^{-E_a/RT}$$

Here,

A = frequency factor = $z \times p$.

(*) Effect of Temperature on Distribution of Collision Energies



The shaded area shows greater fraction of molecules at T_2 have enough energy to react. Thus,

rate of reaction \propto temperature.

(*) Activation Energy

The minimum energy needed by reactant species to undergo effective collision.

We know, Arrhenius equation: is $k = Ae^{-E_a/RT}$. L(i)

Here,

k = rate constant of reaction A = frequency factor

E_a = activation energy

R = gas constant

T = temperature.

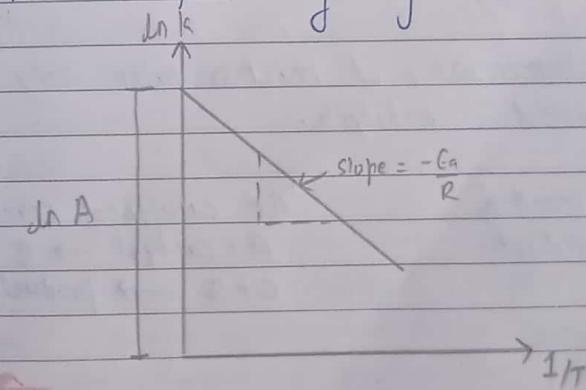
Taking ln on both sides,

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

$$\text{or } \ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$$

$$\text{or } \ln k = \left(-\frac{E_a}{R} \right) \frac{1}{T} + \ln A \quad \text{--- (ii)}$$

This in form of $y = mx + c$.



If reaction occurs at two different temperatures,

$$\ln k_1 = \ln A - \frac{E_a}{R} \left(\frac{1}{T_1} \right) \quad (\text{iii})$$

$$\ln k_2 = \ln A - \frac{E_a}{R} \left(\frac{1}{T_2} \right) \quad (\text{iv}).$$

Subtracting (iii) from (iv),

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (\text{v})$$

E_a^{v} is Arrhenius E_a^{v} for gas at two different temperatures.

Catalyst and Catalysis:

Catalyst are the substances that speed up the reaction without being consumed itself is called catalyst.

The enhancement of reaction rates using catalysts is called catalysis.

For uncatalyzed reaction,
 $A + B \rightarrow \text{product}$

For catalyzed reaction,
 $A + \text{catalyst} \rightarrow C$
 $C + B \rightarrow \text{product} + \text{catalyst}$.

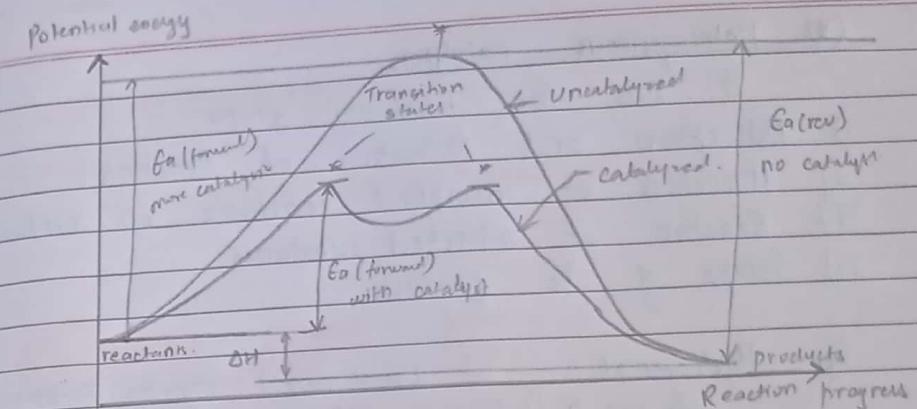


fig: Energy diagram.

ΔH and overall yield is not affected by catalyst.

Catalyst are of two types: Homogeneous and Heterogeneous.

(a): Homogeneous catalyst

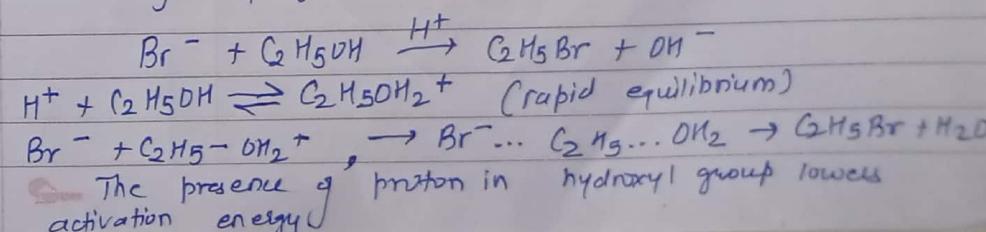
→ The catalyst exists in the same phase as the reacting molecules.

b) Heterogeneous catalyst.

→ The catalysts exists in the different phase as the reacting molecules.

(x): Homogeneous catalysis:

Catalysts act by modifying electronic structure of reactants. Eg: conversion of an alcohol into organic halide by hydrogen ion.

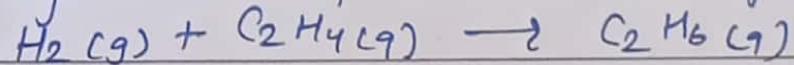


(*) Heterogeneous catalysis:

It has the following steps:

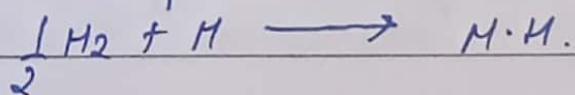
- i) Adsorption and Activation of Reactants.
- ii) Migration of adsorbed reactants on surface.
- iii) Reaction of adsorbed substance
- iv) Escape of the products.

Eg: Hydrogenation of Unsaturated organic compound.



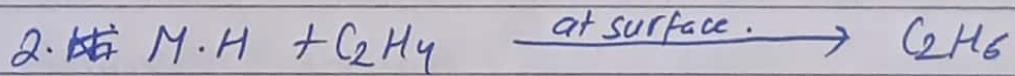
Here, the reaction is quicker if it occurs on the surface of metal. mostly Nickel.

Metal Nickel adsorbs large quantity of hydrogen and incorporates it as hydrogen atoms.



Here, $\text{M}\cdot\text{H}$ is pool of atomic hydrogen in metal lattice.

So, hydrogenation,



Here, metal provides a new path which lowers the activation energy.

Enzymes:

Enzymes are the biological catalysts i.e., proteins that are folded into complex shapes allowing smaller molecules to fit into them.

The places where these molecules fit into are called active sites.

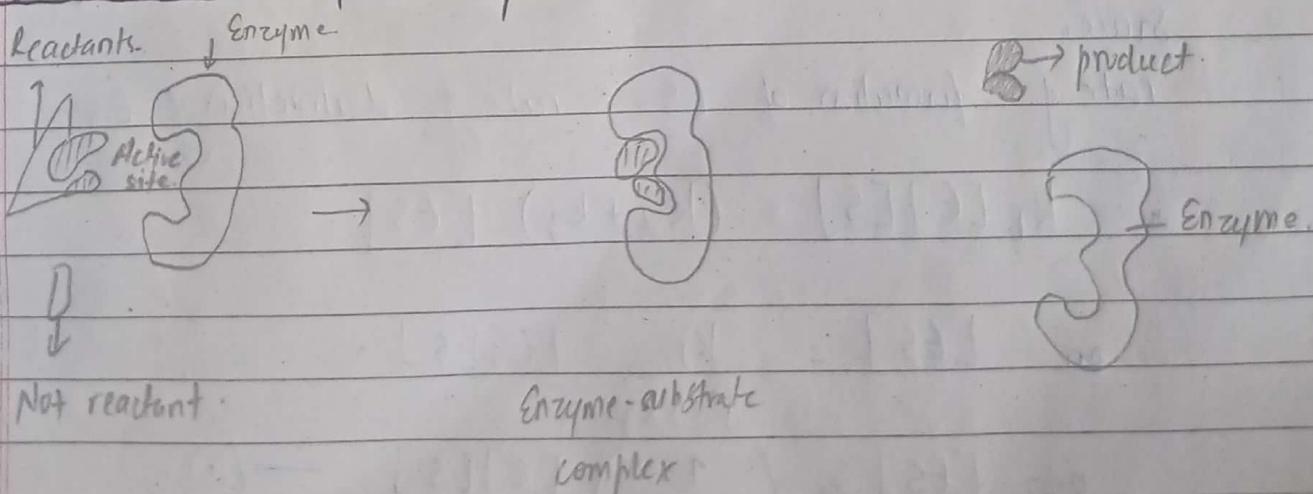
(*) Characteristics:

- i) Have great catalytic power
- ii) Highly specific and show varying degree of specificities.
- iii) Enzymes catalyze chemical reactions by binding the substrates on the active site.
- iv) Substrates fit into the active site of enzymes.

(*) Absolute Specificity:

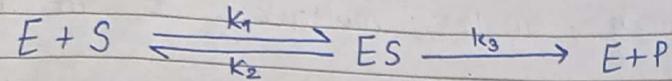
Absolute specificity is the phenomenon when enzymes react specifically with only one substrate.

(*) Model of Enzyme Action:



Michaelis - Menten Equation

Michaelis - Menten Equation model:



Here, enzyme E binds to substrate S to form complex ES which releases product P regenerating original enzyme. The binding of ES surface is reversible.

Let V be the rate at which product appears,

$$V = k_3 [ES] \quad \text{--- (i)}$$

for intermediate $[ES]$, we use SSA.

Now,

$$\text{rate of formation of } ES = k_1 [E][S]$$

$$\begin{aligned} \text{rate of destruction of } ES &= k_2 [ES] + k_3 [ES] \\ &= (k_2 + k_3) [ES] \end{aligned}$$

Since,

rate of formation of ES = rate of destruction of ES

$$\text{or, } k_1 [E][S] = (k_2 + k_3) [ES]$$

$$\text{or, } [ES] = \frac{k_1}{k_2 + k_3} [E][S]$$

$$\text{or, } [ES] = \left(\frac{1}{\frac{k_2 + k_3}{k_1}} \right) [E][S] \quad \text{--- (ii)}$$

$$\text{Let } km = \frac{k_2 + k_3}{k_1} \quad \text{--- (iii)}$$

So,

$$[ES] = \frac{1}{km} [E][S] \quad \text{--- (iv)}$$

We know, the total amount of enzyme equals the free and that bounded to substrate.

$$[E]_T = [E] + [ES]$$

$$\text{or, } [E]_T - [ES] = [E] \quad \text{--- (v)}$$

Substituting in eqⁿ (iv),

$$[ES] = \frac{1}{km} ([E]_T - [E]) [S] \quad \text{--- (vi)}$$

Solving for $[ES]$,

$$[ES] = \frac{[E]_T [S] - [E] [S]}{km}$$

$$\text{or, } km [ES] + [E] [S] = [E]_T [S]$$

$$\text{or, } [ES] (\frac{1}{[S]} + km) = [E]_T [S]$$

$$\text{or, } [ES] = \frac{[E]_T [S]}{\frac{1}{[S]} + km} \quad \text{--- (vii)}$$

Multiplying both sides by k_3 , in eqⁿ (vii),

$$k_3 \times [ES] = k_3 \times [E_T] \times \left(\frac{[S]}{[S] + K_m} \right)$$

We know,
velocity of reaction = $k_3 \times [ES]$

So,

$$V = V_{max} \times \left(\frac{[S]}{[S] + K_m} \right) \quad \text{--- (viii)}$$

Eqn (viii) gives Michaelis-Menten Equation.

Now,

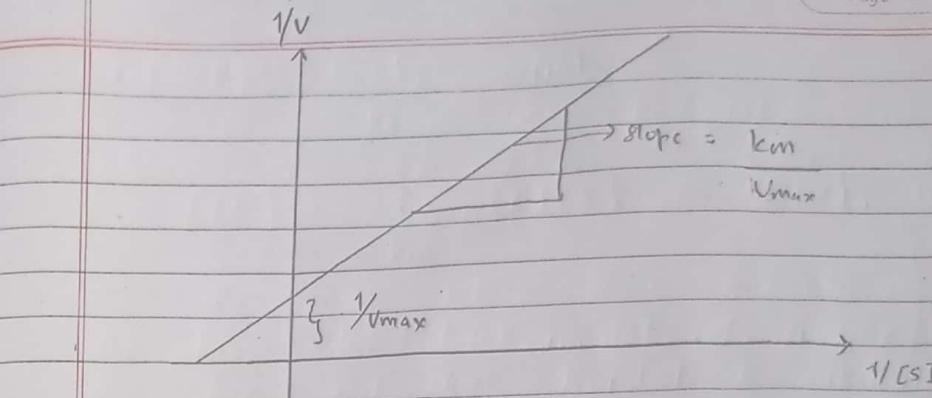
$$\frac{1}{V} = \frac{[S]}{[S] V_{max}} + \frac{K_m}{V_{max} \times [S]}$$

$$\text{or } \frac{1}{V} = \frac{1}{V_{max}} + \frac{K_m}{V_{max} \times [S]}$$

$$\text{or } \frac{1}{V} = \frac{1}{k_3 [E_T]} + \frac{K_m}{k_3 [E_T] [S]} \quad \text{--- (ix)}$$

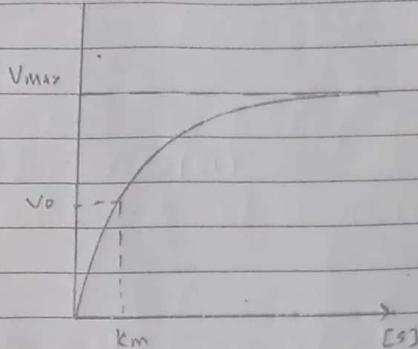
Eqn (ix) is another form of Michaelis-Menten rate law.

Thus, linear reciprocal of reaction rate is linear function of the reciprocal of substrate concentration when total amount of enzyme is held constant.



d) Understanding K_m

K_m is numerically equal to concentration of substrate required to drive reaction at half of maximum velocity.



(x) Condition (1):

If $[S] \ll K_m$
eqn (viii) becomes

$$V = V_{max} \times \left(\frac{[S]}{K_m} \right)$$

(x) Condition (2):

If $[S] \gg K_m$,
eqn (vii) becomes

$$V = V_{max}$$

This shows rate is 1st order w.r.t substrate concentration.

This shows that rate is 0 order w.r.t substrate concentration.