CHEMICAL KINETICS

10marks 7hr

1 Introduction
2 Rate of Reaction, Average and Instaneous reaction
3. Rate law and its expression
4. Rate Constant, its unit and significance
5. Order and molecularity
6. Integrated rate law
   a. Half law
   b. Collision Theory
   c. Factor of affecting rate of reaction
   d. Catalysis.

Chemical Kinetics

→ It is the branch of physical chemistry that deals with the study of rate of reaction called chemical Kinetics.

→ Some reactions complete within one to two seconds while some reaction takes to many years for its completion.

* Fast reaction *

$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + NaNO_3$
white ppt

$H_2SO_4 + BaCl_2 \longrightarrow 2HCl + BaSO_4\downarrow$

* Slow Reaction *

Iron + O_2 + moisture $\rightarrow$ Rusting of iron

∴ many years.

Rate of Reactions.

The change in concentrations of reactant or product with respect to time is called Rate of Reaction.

$$H_2 + I_2 \longrightarrow 2HI$$

Rate of Disappearance of hydrogen

$$-\frac{d[H_2]}{dt}$$

Rate of disappearance of iodine

$$-\frac{d[I_2]}{dt}$$

Rate of appearance of HI

$$+\frac{1}{2}\frac{d[HI]}{dt}$$

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

Rate of Disappearance N_2O_5

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt}$$

Rate of appearance of NO_2

$$+\frac{1}{4}\frac{d[NO_2]}{dt}$$

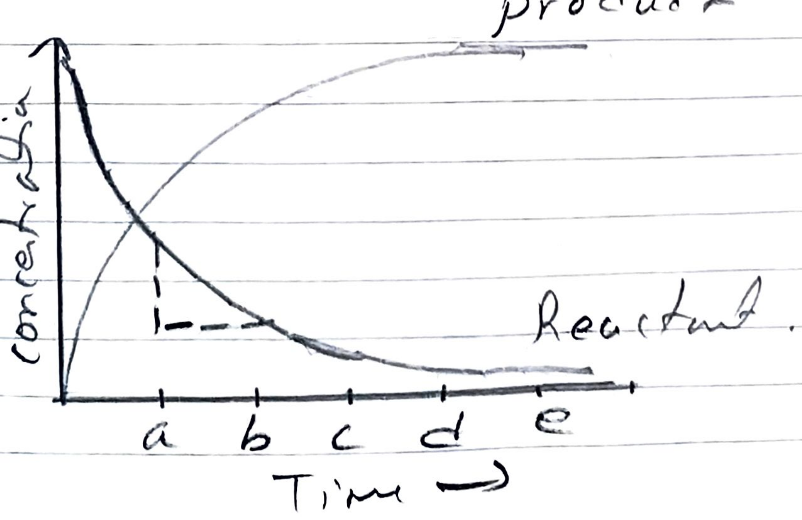
Rate of appearance of O_2

$$+\frac{d[O_2]}{dt}$$

Average Rate

The rate of reaction over a particular period of time is called Average Rate.

Reaction : $A \longrightarrow B$



Average rate = $\frac{\text{Change in concentration}}{\text{Time difference.}}$

$$= -\frac{[A]_b - [A]_a}{b-a}$$

$$= \frac{-\Delta A}{\Delta t}$$

Since, $[A]_a > [A]_b$ and $\Delta A = A_b - A_a$ is $-ve$

Instaneous Reaction.

The rate of reaction at small interval of time is called instaneous reaction.

$$2KClO_3 \xrightarrow[\Delta]{} 2KCl + 3O_2$$

Rate of disappearance of $KClO_3$

$$-\frac{1}{2}\frac{d[KClO_3]}{dt}$$

Rate of appearance of KCl

$$+\frac{1}{2}\frac{d[KCl]}{dt}$$

Rate of appearance of O_2

$$+\frac{1}{3}\frac{d[O_2]}{dt}$$

$$2H_2O_2 \xrightarrow[\Delta]{} 2H_2O + O_2$$

Rate of disappearance H_2O_2

$$-\frac{1}{2}\frac{d[H_2O_2]}{dt}$$

Rate of appearance of H_2O .

$$+\frac{1}{2}\frac{d[H_2O]}{dt}$$

Rate of appearance of O_2

$$+\frac{d[O_2]}{dt}$$

Date
Page

Factors affecting rate of chemical reaction. [4 marks]

$$A \longrightarrow B$$

Reactant Product

Some important factors that affect the rate of chemical reaction are given below.

1. Concentration

Higher the concentration of reactant molecules, more molecules can take part in chemical reaction which increase collision frequency and rate of reaction gets increase

2. Temperature

On increasing temperature the collision frequency of molecules get increase. Older bond between molecule get breakdown while new bonds are formed Scientists believe that on increasing the temperature by 10°C, the rate of reaction get double or triple.

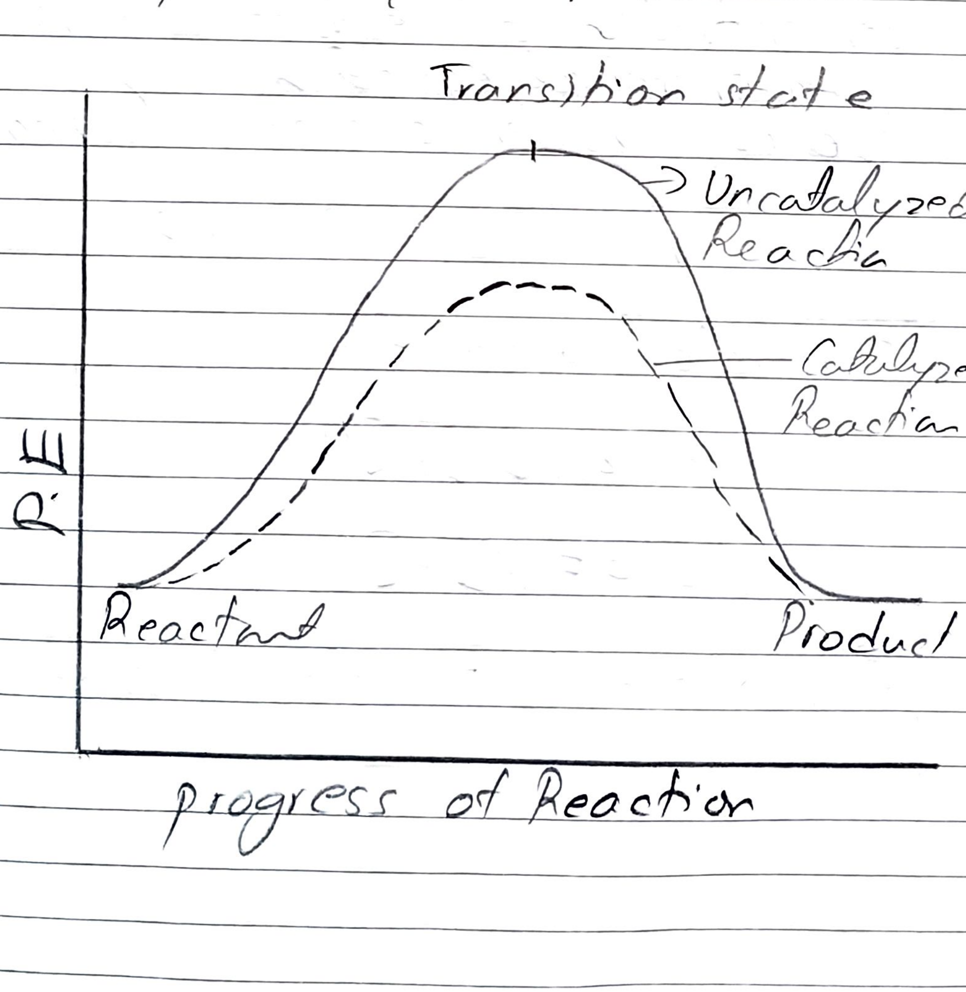
3. Pressure.

On increasing the external pressure it help to increase the collision between reactant molecules and ultimately rate of reaction get increase

4. Catalyst

Generally, catalyst are two types i.e positive and negative catalyst.
-> Positive catalyst accelerate rate of chemical reaction
-> while negative catalyst slow down the rate of chemical reaction

As we know, catalyst provide alternative pathway for reaction mechanism



5. Surface Area

On increasing the surface area of reactant molecules, rate of chemical reaction gets increase because more molecules can take part in chemical reaction

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2 marks-

Rate Equation / Rate law

An equation which express the ~~reaction~~ relation between rate of reaction and concentration of reatant present in the given chemical equation.
Let us consider a chemical reaction

$$nA \longrightarrow \text{Product}$$

Thus rate law equation

$$\text{Rate} \propto [A]^n$$

$$\text{Rate} = K[A]^n$$

$\therefore$, where $K \rightarrow$ rate constant

* For Zero Order [n = 0]

$$mol\,L^{-1}\,sec^{-1} = k\,[mol\,L^{-1}]^0$$

$$mol\,L^{-1}\,sec^{-1} = k$$

* For first Order [n = 1]

$$mol\,L^{-1}\,sec^{-1} = k\,[mol\,L^{-1}]^1$$

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

* For second order [n = 2]

$$mol\,L^{-1}\,sec^{-1} = k\,[mol\,L^{-1}]^2$$

$$mol\,L^{-1}\,sec^{-1} = k \times mol^2\,L^{-2}$$

$$\frac{sec^{-1}}{mol\,L^{-1}} = k$$

$$k = mol^{-1}\,L\,sec^{-1}$$

ORDER of REACTION

* Define Order of Reaction [2marks]

$$xA + yB \longrightarrow \text{product}$$

Rate of reaction $= k[A]^x[B]^y$
Order of reaction $= x+y$

Order of Reaction is the sum of power of reactant molecules in give chemical equation.

Molecularity of reaction

Molecularity of reaction is the sum of number of molecules present in rate determing step of balanced chemical reaction.

Order of reaction	Molecularity of reaction
1. It is the sum of power of concentration of reactant in rate law equation	1. It is the sum of number of molecule present in rate determining step of balanced chemical equation
2 It can be determined experimentally.	2. It is only theoretical concept
3. It's value can be fraction, zero or whole number	3. It's value is always whole number.

Date
Page

4. It can be change with external condition	4. It is invarient.
5. It has certain unit	5. It has no unit.

Moleculartity of Reaction

1. Elementary reaction

→ The reaction that occurs only in single steps is called elementary reaction.

Single Steps

→ a. Unimolecular Reaction

→ A ~~balance~~ reaction involving only one molecule in balance chemical reactions. Its molecularity is one

→ b. Bimolecular Reaction

→ A reaction involving two molecule in balance chemical equation is called bimolecular reaction. Its molecularity is two

→ c. Trimolecular Reaction

→ A reaction involving three molecule in balance chemical equation is called trimolecular reaction. Its molecularity is three.

Integrated Equation for Zero Order reaction

Those reaction whose rate of reaction is independent to the concentration of reactant.

Let us consider a reaction

$$A \longrightarrow \text{Product}$$

at time = 0	a	0
at time = t	$(a-x)$	x

For Zero Order Reaction

At time (t)

Rate of Reaction $\propto [A]^0$

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

$$\frac{dx}{dt} = k_0$$

$$dx = k_0 dt$$

on integration on both sides

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

$$x = k_0 t + c \quad \text{.....} \quad eq\ (i)$$

At time $(t) = 0$ $x = 0$

$$0 = k_0 \times 0 + c$$

$$\therefore c = 0$$

Putting value of (c) in eq (i)

$$x = k_0 t$$

$$\frac{x}{t} = k_0 \quad \text{.......} \quad eq\ (ii)$$

At time $(t) = t_{1/2}$ $\quad x = a/2$

$$\frac{a/2}{t_{1/2}} = k_0$$

$$\frac{a}{2} = k_0 t_{1/2}$$

$$\frac{a}{2k_0} = t_{1/2} \quad \text{...} \quad eq\ (iii)$$

Integrated equation for first Order Reaction

Those reaction in which rate of reaction depend upon concentration of only one reactant.

Let us consider a reaction

$$A \longrightarrow Product$$

at time = 0	a	0
at time = t	$(a-x)$	x

Rate of equation $\propto (a-x)^1$

$$\frac{dx}{dt} = k_1 (a-x)^1$$

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

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

at time $t = 0$ $\quad x = 0$

$$-\ln a = k_1 \times 0 + c$$

$$-\ln a = c$$

Putting value of c in eq (1)

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

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

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

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

At time $(t) = t_{1/2}$ $\quad x = a/2$

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

$$\frac{2.303}{t_{1/2}} \log \frac{1}{0.5} = k$$

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

* 2nd Order of Reaction

Those reaction in which rate of reaction depend upon concentration of two reactant is called second order of reaction.

Pseudo Order of Reaction - 2 marks

→ Those reactions which seems to follow higher order but actually follow lower order of reactant.

For e.g:-

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{22}O_6 + C_6H_{12}O_6$$

Sucrose — Glucose — Fructose

Enzymes.

Ezymes are the protein molecule that are used as catalyst in many biochemical reaction.

The phenomenon of enzymes catalyst is called enzyme catalysis

For e.g:-

Amylasis, Invertase, Zymase, lactose, pepsin, maltase

Characteristics of Enzyme

- Remain unchanged after the completion of biochemical reaction
- Enzymes are very sensitive to catalytic poison in block catalytic activities of enzyme

- The enzymes are very specific in nature they only catalysis particular bio-chemical enzyme

→ There are two types of Catalyst and they are :-
  - Homogenous Catalyst
  - Heterogerous Catalyst

Homogenous Catalyst

→ They are those catalyst which are in same phase with reactant and the product
For. eg.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$SO_2 + O_2 \xrightarrow{NO} SO_3$$

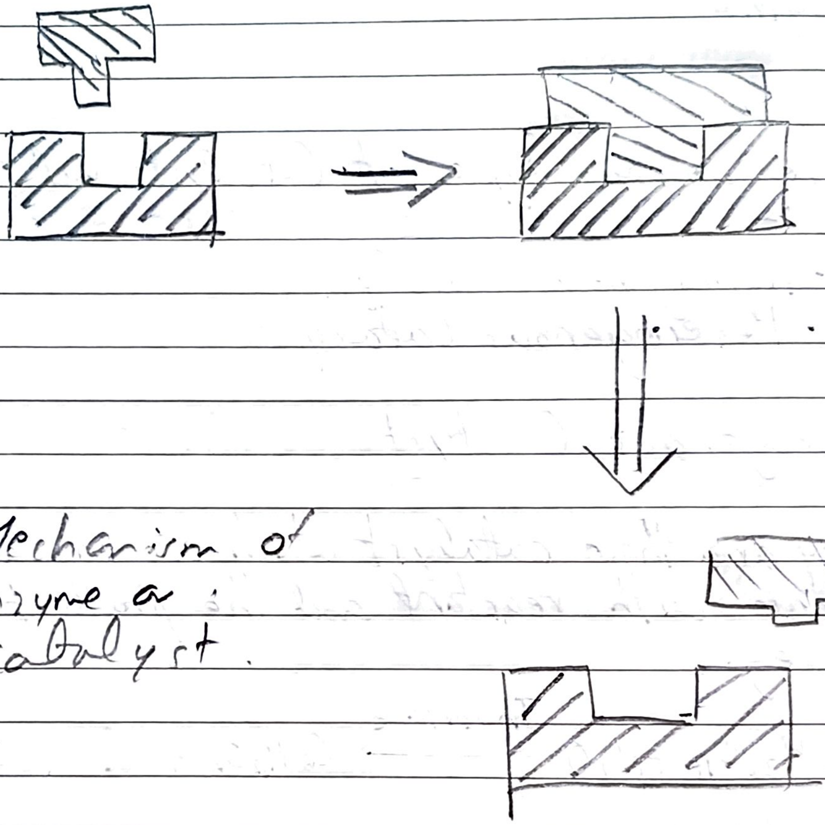
Heterogenous Catalyst

They are those catalyst which are in different phase with reactant and the product
For e.g

$$SO_2 + O_2 \xrightarrow{V_2O_5} SO_3$$

$$N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$$

Mechanism of Enzyme or Catalyst.



Mechanism of enzyme a catalyst.

Step : I

$E + S \longrightarrow ES$

Step II

$ES \longrightarrow EP$

Step III

$EP \longrightarrow E + P$

Short notes on collision theory

For any chemical reaction there must be collision between reactant molecule which convert reactant into product During collision older bond between molecules get breakdown while new bond between molecules form

The total number of collision in 1 second is called collision frequency

Only those collision which convert reactant into product are called effective collision

Those collision which do not convert reactant into product are ineffective collision.

Collision must be greater then the threshold energy to cross the energy barrier. Effective collision in proper orientation gives product in chemical reaction

For any chemical reactio

$A - B + B - B \longrightarrow$ no reactio

The reaction do not occur due to improper orientation of reactant molecule

$$\begin{array}{c} A \\ | \\ A \end{array} + \begin{array}{c} B \\ | \\ B \end{array} \longrightarrow \begin{array}{ccc} A & \cdots & B \\ \vdots & & \vdots \\ A & \cdots & B \end{array} \longrightarrow A - B + A - B$$

Date
Page

Factors affecting Ratee of Collision.

1 Temperature

→ Higher temperature Higher the rate of collision between reactant mollicule due to increase in K.E

2. Pressure

→ Higher the Pressure Higher the rate of collision between reactant mollicule ~~betwe~~ due to increase in K.E

Q The following rate data, are obtained at 303K for the reaction [4 marks]

$$2A + B \longrightarrow \text{Product}$$

Expt	[A] mol L^{-1}	[B] mol L^{-1}	Initial rate mol L^{-1} min^{-1}
1	0.1	0.1	6.0×10^{3}
2	0.3	0.2	7.2×10^{-2}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.4×10^{-2}

1. Find the rate of law.
2. Find the order of each and overall order.
3. Calculate rate constant
4. Find the rate of reaction when initial concentration of A and B are 0.5m and 0.1m?

(i) Finding the rate law

Rate of reaction $\propto [A]^m [B]^n$

Rate of reaction $= k [A]^m [B]^n$

So,

$$6.0 \times 10^{3} = k [0.1]^m [0.1]^n \ldots \text{eq (i)}$$

$$7.2 \times 10^{-2} = k [0.3]^m [0.2]^n \ldots \text{eq (ii)}$$

$$2.88 \times 10^{-1} = k [0.3]^m [0.4]^n \ldots \text{eq (iii)}$$

$$2.4\times10^{-2} = k[0.4]^m[0.1]^n \quad \text{..... eq iv.}$$

Dividing eq (i) by eq iv

$$\frac{6.0\times10^{-3}}{2.4\times10^{-2}} = \frac{k[0.1]^m[0.1]^n}{k[0.4]^m[0.1]^n}$$

$$\left[\frac{1}{4}\right]^1 = \left[\frac{1}{4}\right]^m$$

$\therefore m = 1$

Dividing eq (ii) by eq (iii)

$$\frac{7.2\times10^{-2}}{2.88\times10^{-1}} = \frac{\cancel{k[0.3]^m}[0.2]^n}{\cancel{k[0.3]^m}[0.4]^n}$$

$$\left[\frac{1}{4}\right]^2 = \left[\frac{1}{2}\right]^n$$

$\cancel{n = 2}$,, $\left[\frac{1}{2}\right]^2 = \left[\frac{1}{2}\right]^n$

$\therefore n = 2$

Rate law $= k[A]^1[B]^2$

ii. Finding the order ~~of~~ for each and overall order.

Order of reaction with respect to A is 1 and with respect to B is 2.

Overall order = 1+2 = 3

iii. Calculating Rate constant
Taking ~~eq~~ (I) equation

$$\frac{6.0\times10^{-3}}{[0.1]^1[0.1]^2} = k$$

$$k = 6$$

iv. Finding the initial rate of reaction when initial of A and B are 0.5 and 0.1
Now,
Rate of Reaction $= 6\times[0.5]^1\times[0.1]^2$
$= 0.03\ mol\ L^{-1}\ min^{-1}$

The following rate data are obtained at 303K for the reaction

$$2A + B \longrightarrow 2AB$$

Expt	$[A] mol L^{-1}$	$[B] mol L^{-1}$	Inital rate $mol L^{-1} min^{-1}$
1	0.5	0.5	1.6×10^{-4}
2	0.5	1	3.2×10^{-4}
3	1	1	3.2×10^{-4}
4			

1. Find the rate law

Rate of reaction $\propto [A]^m [B]^n$

Rate of reaction $= k [A]^m [B]^n$

So,

$$1.6 \times 10^{-4} = k [0.5]^m [0.5]^n$$

$$3.2 \times 10^{-4} = k [0.5]^m [1]^n$$

$$3.2 \times 10^{-4} = k [1]^m [1]^n$$

ii. ~~Find the order for each and overall order~~

~~Order of reaction with respect to A is ?~~
~~with respect to B is ?~~

Dividing eq (i) & (ii)

$$\frac{1.6\times10^{-4}}{3.2\times10^{-4}} = \frac{k[0.5]^m[0.5]^n}{k[0.5]^m[1]^n}$$

$$\left[\frac{1}{2}\right]^1 = \left[\frac{1}{2}\right]^n$$

$$n = 1$$

Dividing eq (ii) & eq (iii)

$$\frac{3.2\times10^{-4}}{3.2\times10^{-4}} = \frac{k[0.5]^m \cancel{[1]^n}}{k[1]^m \cancel{[1]^n}}$$

$$1 = \left(\frac{1}{2}\right)^m$$

$$\left(\frac{1}{2}\right)^0 = \left(\frac{1}{2}\right)^m$$

$$m = 0$$

Rate law $= k[A]^0[B]^1$

(i) Order of reaction with respect A is 0
with respect to B is 1

Overall order $= 0 + 1$
$= 1$

Date
Page

iii. Calculating Rate Constant

$$\frac{1.6 \times 10^{-4}}{[0.5]^0 [0.5]^1} = k$$

$$k = 3.2 \times 10^{-4}$$

iv. Rate of Reaction $= 3.2 \times 10^{-4} [0.5]^0 [0.1]$

$= 3.2 \times 10^{-5}$