Kinetics

RATE/VELOCITY OF CHEMICAL REACTION :

$$\text{Rate} = \frac{\Delta c}{\Delta t} = \frac{\text{mol}/\text{lit.}}{\text{sec}} = \text{mol lit}^{-1}\text{ time}^{-1} = \text{mol dm}^{-3}\text{ time}^{-1}$$
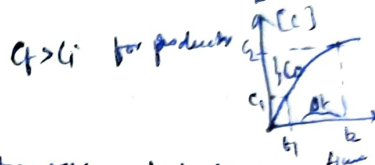
Rate of rxn $- \dfrac{\Delta C}{\Delta t}$

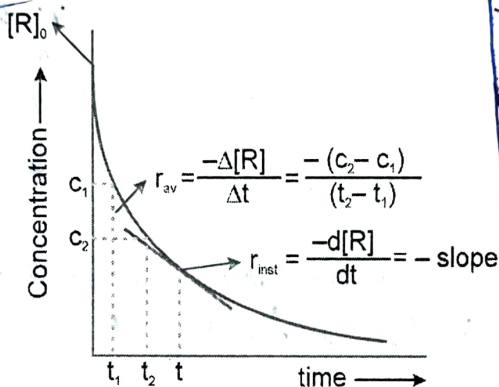units $- \dfrac{mol}{lts}$, atm s^{-1}

Types of Rates of chemical reaction :

For a reaction R $\longrightarrow$ P

$$\text{Average rate} = \frac{\text{Total change in concentration}}{\text{Total time taken}}$$

Case B

$\text{rate} = \dfrac{\Delta c}{\Delta t} = +\left(\dfrac{c_f - c_i}{\Delta t}\right)$

$c_f > c_i$ for products

Case I :

$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{-(c_2 - c_1)}{(t_2 - t_1)}$$

$$r_{inst} = \frac{-d[R]}{dt} = -\text{slope}$$

$\rightarrow$ for instantaneous rate of rxns.

i) for reactants $\quad r = \dfrac{-dc}{dt}$ [Re]

ii) for products $\quad r = \dfrac{+dc}{dt}$

$\dfrac{-d[A]}{dt}$, rate of disappearance of A

$\dfrac{+d[C]}{dt}$, rate of appearance of C.

⋆ Rate is same for all reactant & products

$$R_{\text{instantaneous}} = \lim_{t\to 0}\left[\frac{\Delta c}{\Delta t}\right] = \frac{dc}{dt} = -\frac{d[R]}{dt} = \frac{d[P]}{dt} = +\left(\frac{c_f - c_i}{\Delta t}\right)$$
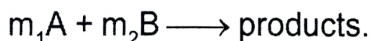
RATE LAW (DEPENDENCE OF RATE ON CONCENTRATION OF REACTANTS) :

Rate = K (conc.)^{order} – differential rate equation or rate expression

Where K = Rate constant = specific reaction rate = rate of reaction when concentration is unity

unit of K = (conc)$^{1-\text{order}}$ time^{-1}

$\rightarrow$ rate law is determined experimentally.

Order of reaction :

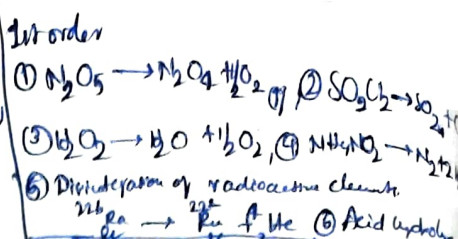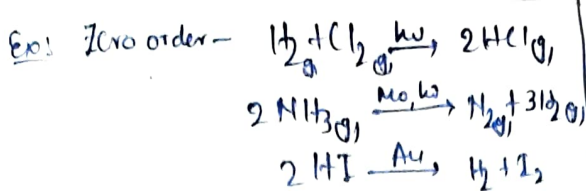$m_1 A + m_2 B \longrightarrow$ products.

$R \propto [A]^p [B]^q$ Where p may or may not be equal to m_1 & similarly q may or may not be equal to m_2.

p is order of reaction with respect to reactant A and q is order of reaction with respect to reactant B and (p + q) is **overall order of the reaction.**

Order may be +ve, –ve, 0, fractional values.

Units of rate const $(K) = \left(\dfrac{mol}{lt}\right)^{1-n} sec^{-1}$ (n= order)

Ex: Zero order — $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl_{(g)}$ | **1st order**

$2NH_{3(g)} \xrightarrow{Mo,W} N_{2(g)} + 3H_{2(g)}$ | ① $N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$ (g) ② $SO_2Cl_2 \to SO_2+...$

$2HI \xrightarrow{Au} H_2 + I_2$ | ③ $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$ ④ $NH_4NO_2 \to N_2+...$

⑤ Disintegration of radioactive elements

$^{226}Ra \longrightarrow \,^{222}Rn + \frac{4}{2}He$ ⑥ Acid hydrolysis

INTEGRATED RATE LAWS :

C_0 or 'a' is initial concentration and C_t or $a-x$ is concentration at time

(a) **zero order reactions :**

Rate = k [conc.]⁰ = constant   differential equ. $\dfrac{-d[A]}{dt}, \dfrac{+d[B]}{dt} = k$

$r \propto k$

Rate $= k = \dfrac{C_0 - C_t}{'t'}$ or $\boxed{C_t = C_0 - kt}$
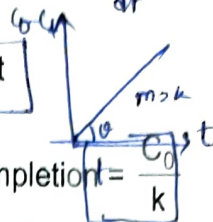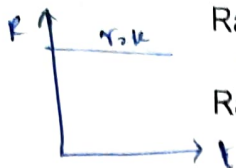
i) $t_{3r\%} = \dfrac{1}{4} \dfrac{C_0}{k} = \dfrac{1}{4}$ Unit of K = mol lit⁻¹ sec⁻¹, Time for completion $= \dfrac{C_0}{k}$

$t_{90\%} = \dfrac{0.9\,C_0}{k}$

$t_{90\%} = 1.8 \times t_{50\%}$. at $t_{1/2}$, $C_t = \dfrac{C_0}{2}$, so $kt_{1/2} = \dfrac{C_0}{2} \Rightarrow \boxed{t_{1/2} = \dfrac{C_0}{2k}}$ $\therefore t_{1/2} \propto C$
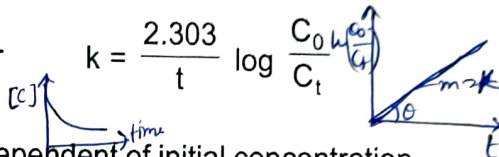
(b) **First Order Reactions :**

$t_{90\%} = \dfrac{10}{3} t_{50\%}$.

$t_{99\%} = 2 \times \dfrac{10}{3} t_{50\%}$.

$t_{99.9\%} = 10\, t_{50\%}$.

$t_{99.99\%} = 4 \times 10\, t_{50\%}$.

(i) Let a 1st order reaction is, A $\longrightarrow$ Products $r = k[A]^1$

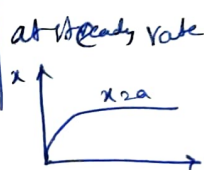$t = \dfrac{2.303}{k} \log \dfrac{a}{a-x}$ or $k = \dfrac{2.303}{t} \log \dfrac{C_0}{C_t}$

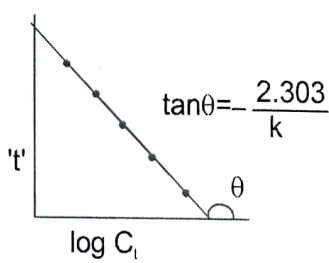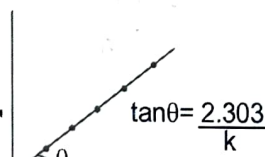$t_{1/2} = \dfrac{\ln 2}{k} = \dfrac{0.693}{k}$ = Independent of initial concentration.

Generation time

$t_g = \ln 2/k$

$t_{Avg.} = \dfrac{1}{k} = 1.44\, t_{1/2}$.   First order for gaseous phase   at already rate

1st order for bacterial growth

$k = \dfrac{1}{t} \ln\left(\dfrac{C_t}{C_0}\right)$

$\to$ for homogeneous rxn $A \to 2B + C$ $P_∞$ at t

$k = \dfrac{2.303}{t} \log\left(\dfrac{2P_∞}{3(P_∞ - P_t)}\right)$

$k = \dfrac{2.303}{t} \log\left(\dfrac{P_i}{2P_i - P_t}\right)$

Graphical Representation :

$t = -\dfrac{2.303}{k} \log C_t + \dfrac{2.303}{k} \log C_0$

tanθ $= \dfrac{2.303}{k}$

log C_0/C_t or log a/a-x

tanθ $= -\dfrac{2.303}{k}$

log C_t

(c) **Second order reaction :**

2nd order Reactions

Two types
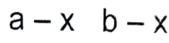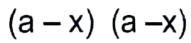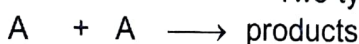
A + A $\longrightarrow$ products	A + B $\longrightarrow$ products.
a a	a b 0
(a−x) (a−x)	a−x b−x

$t_{1/2} \propto \dfrac{1}{|c|^{n-1}}$

$\therefore \dfrac{dx}{dt} = k(a-x)^2$ m=constant

$\Rightarrow \dfrac{1}{(a-x)} - \dfrac{1}{a} = kt$

$\dfrac{dx}{dt} = k(a-x)(b-x)$

$k = \dfrac{2.303}{t(a-b)} \log \dfrac{b(a-x)}{a(b-x)}$

Ex: ① $2N_2O \to 2N_2 + O_2$
② $2Cl_2O \to 2Cl_2 + O_2$
③ $2HI \to H_2 + I_2$
④ $2HO_2 \to 2NO_2O$
⑤ Basic hydrolysis of ester

$t_{90\%} = 9 \times t_{50\%}$, $t_{99\%} = 99 \times t_{50\%}$

nth order rxn

$r = k[A]^n$

$kt = \dfrac{1}{n-1}\left[\dfrac{1}{c_t^{n-1}} - \dfrac{1}{c_0^{n-1}}\right]$

$n \neq 1$

① 3rd order $r = k[A]^3$

Ex: $2NO + O_2 \to 2NO_2$

$2NO + Cl_2 \to 2NOCl$
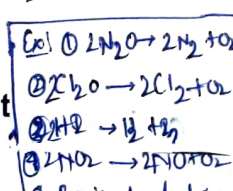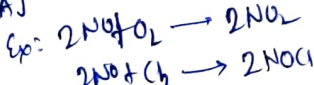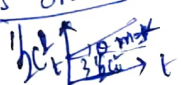
Molecularity – No. of atoms or ions known 1 the rxn mechanism.

Ex:- → Max from (1 to 3) only,

$NH_4NO_2 \rightarrow N_2 + 2H_2O$ — (1)

$H_2 + Cl_2 \rightarrow 2HCl$ — (2)

$2NO + O_2 \rightarrow 2NO_2$ — (3)

Pseudounimolecular

Hydrolysis of ester

$(C_{12}O_6C_2)H + H_2O \rightarrow CH_3COOH + C_2H_5OH$

0.01 ml   10 ml   0   0

0.01-0.01   10-0.1   0.01   0.01

= 0   = 9.9

actual order

$r = k [CH_3COOC_2H_5]^1$

because conc. of H_2O is very large due to high than orders — less conumed

METHODS TO DETERMINE ORDER OF A REACTION

(a)   **Initial rate method :**

$r = k [A]^a [B]^b [C]^c$ if   [B] = constant
                                          [C] = constant

then for two different initial concentrations of A we have

$r_{0_1} = k [A_0]_1^a$, $r_{0_2} = k [A_0]_2^a$

$\Rightarrow \quad \dfrac{r_{0_1}}{r_{0_2}} = \left(\dfrac{[A_0]_1}{[A_0]_2}\right)^a$

(b)   **Using integrated rate law :**   It is method of trial and error.

(c)   **Method of half lives :**

for n^{th} order reaction $t_{1/2} \propto \dfrac{1}{[R_0]^{n-1}}$

(d)   **Ostwald Isolation Method :**
      rate = $k [A]^a [B]^b [C]^c = k_0 [A]^a$

METHODS TO MONITOR THE PROGRESS OF THE REACTION :

(a)   *Progress of gaseous reaction can be monitored by measuring total pressure at a fixed volume & temperature or by measuring total volume of mixture under constant pressure and temperature.*

$$\therefore \quad k = \frac{2.303}{t} \log \frac{P_0(n-1)}{nP_0 - P_t}$$

{Formula is not applicable when n = 1, the value of n can be fractional also.}

(b)   *By titration method :*

1. $\therefore \ a \propto V_0$ $a - x \propto V_t$ $\Rightarrow$ $k = \dfrac{2.303}{t} \log \dfrac{V_0}{V_t}$
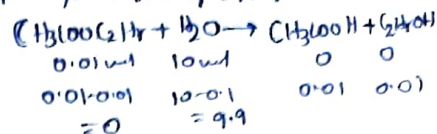
2.   Study of acid hydrolysis of an easter.

$k = \dfrac{2.303}{t} \log \dfrac{V_\infty - V_0}{V_\infty - V_t}$

(c)   *By measuring optical rotation produced by the reaction mixture :*

$k = \dfrac{2.303}{t} \log \left(\dfrac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}\right)$

EFFECT OF TEMPERATURE ON RATE OF REACTION.

$$\text{T.C.} = \frac{K_{t+10}}{K_t} \approx 2 \text{ to } 3 \text{ (for most of the reactions)}$$

Arhenius theroy of reaction rate.
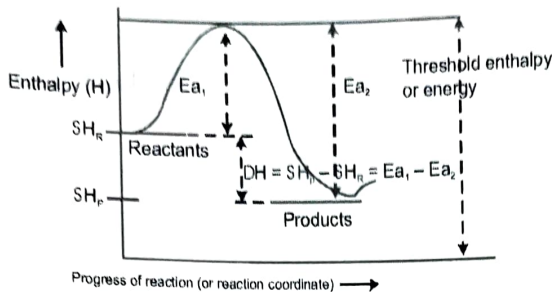
SH_R = Summation of enthalpies of reactants
SH_p = Summation of enthalpies of reactants
DH = Enthalpy change during the reaction
Ea_1 = Energy of activation of the forward reaction
Ea_2 = Energy of activation of the backward reaction

$$E_p > E_r \qquad \rightarrow \text{endothermic}$$
$$E_p < E_r \qquad \rightarrow \text{exothermic}$$

$$\Delta H = (E_p - E_r) = \text{enthalpy change}$$
$$\Delta H = E_{af} - E_{ab}$$
$$E_{threshold} = E_{af} + E_r = E_b + E_p$$

Arhenius equation

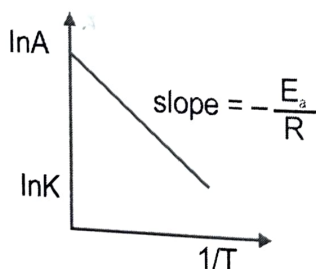$$k = Ae^{-E_a/RT} \qquad\qquad r = k\,[\text{conc.}]^{order}$$

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2} \qquad\qquad \log k = \left(-\frac{Ea}{2.303\ R} \right)\frac{1}{T} + \log A$$

If k_1 and k_2 be the rate constant of a reaction at two different temperature T_1 and T_2 respectively, then we have

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\cdot\left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

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

$$\text{slope} = -\frac{E_a}{R} \qquad\qquad E_a \geq 0$$

$$T \rightarrow \infty, K \rightarrow A.$$