

10. CHEMICAL KINETICS & RADIOACTIVITY

RATE/VELOCITY OF CHEMICAL REACTION :

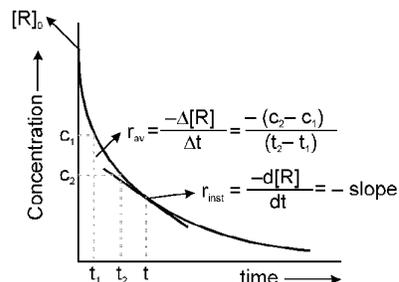
$$\text{Rate} = \frac{\Delta c}{\Delta t} = \frac{\text{mol/lit.}}{\text{sec}} = \text{mol lit}^{-1} \text{ time}^{-1} = \text{mol dm}^{-3} \text{ time}^{-1}$$

Types of Rates of chemical reaction :

For a reaction $R \longrightarrow P$

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

$$R_{\text{instantaneous}} = \lim_{t \rightarrow 0} \left[\frac{\Delta c}{\Delta t} \right] = \frac{dc}{dt} = - \frac{d[R]}{dt} = \frac{d[P]}{dt}$$



RATE LAW (DEPENDENCE OF RATE ON CONCENTRATION OF REACTANTS) :

$$\text{Rate} = K (\text{conc.})^{\text{order}} \quad \text{-- differential rate equation or rate expression}$$

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

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

Order of reaction :



$R \propto [A]^p [B]^q$ 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**.

INTEGRATED RATE LAWS :

C_0 or 'a' is initial concentration and C_t or $a - x$ is concentration at time 't'

(a) zero order reactions :

Rate = $k [\text{conc.}]^0 = \text{constant}$

$$\text{Rate} = k = \frac{C_0 - C_t}{t} \quad \text{or} \quad C_t = C_0 - kt$$

Unit of K = $\text{mol lit}^{-1} \text{sec}^{-1}$, Time for completion = $\frac{C_0}{k}$

$$\text{at } t_{1/2}, C_t = \frac{C_0}{2}, \text{ so } kt_{1/2} = \frac{C_0}{2} \Rightarrow t_{1/2} = \frac{C_0}{2k} \quad \therefore t_{1/2} \propto C_0$$

(b) First Order Reactions :

(i) Let a 1st order reaction is, $A \longrightarrow \text{Products}$

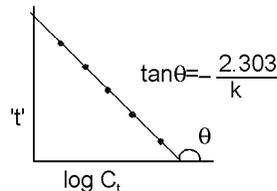
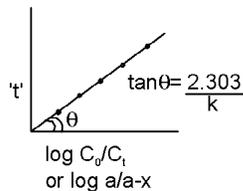
$$t = \frac{2.303}{k} \log \frac{a}{a-x} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

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

$$t_{\text{Avg.}} = \frac{1}{k} = 1.44 t_{1/2}$$

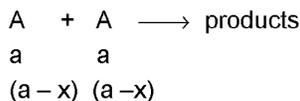
Graphical Representation :

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



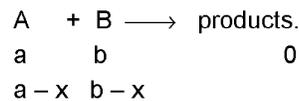
(c) Second order reaction :

2nd order Reactions
Two types



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

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



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

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

(d) Pseudo first order reaction :

\therefore For $A + B \longrightarrow \text{Products}$ [Rate = $K [A]^1 [B]^1$]

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

Now if 'B' is taken in large excess $b \gg a$.

$$\Rightarrow k = \frac{2.303}{bt} \log \frac{a}{a-x}$$

\therefore 'b' is very large can be taken as constant

$$\Rightarrow kb = \frac{2.303}{t} \log \frac{a}{a-x} \quad \Rightarrow \quad k' = \frac{2.303}{t} \log \frac{a}{a-x}, \quad k' \text{ is pseudo first order rate constant}$$

METHODS TO DETERMINE ORDER OF A REACTION

(a) Initial rate method :

$$r = k [A]^a [B]^b [C]^c \quad \text{if} \quad \begin{array}{l} [B] = \text{constant} \\ [C] = \text{constant} \end{array}$$

then for two different initial concentrations of A we have

$$r_{01} = k [A_0]_1^a, \quad r_{02} = k [A_0]_2^a \quad \Rightarrow \quad \frac{r_{01}}{r_{02}} = \left(\frac{[A_0]_1}{[A_0]_2} \right)^a$$

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

(c) Method of half lives :

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

(d) Ostwald Isolation Method :

$$\text{rate} = k [A]^a [B]^b [C]^c = k_0 [A]^a$$

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. $\therefore k = \frac{2.303}{t} \log$

$$\frac{P_0(n-1)}{nP_0 - P_t} \quad \{\text{Formula is not applicable when } n = 1, \text{ the value of } n \text{ can be fractional also.}\}$$

(b) By titration method :

$$1. \quad \therefore a \propto V_0 \quad a - x \propto V_t \quad \Rightarrow \quad k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

2. Study of acid hydrolysis of an ester.

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

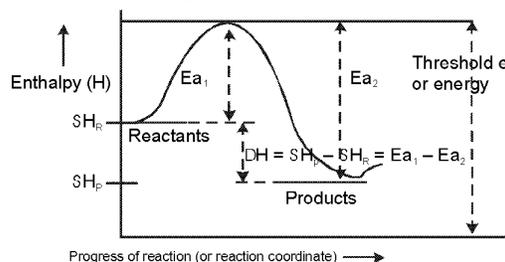
(c) By measuring optical rotation produced by the reaction mixture :

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

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 thery of reaction rate.



SH_R = Summation of enthalpies of reactants
 SH_P = Summation of enthalpies of products
 ΔH = Enthalpy change during the reaction
 E_{a_1} = Energy of activation of the forward reaction
 E_{a_2} = Energy of activation of the backward reaction

$E_p > E_r \rightarrow$ endothermic
 $E_p < E_r \rightarrow$ exothermic

$$\Delta H = (E_p - E_r) = \text{enthalpy change}$$

$$\Delta H = E_{af} - E_{ab}$$

$$E_{\text{threshold}} = E_{af} + E_r = E_b + E_p$$

Arhenius equation

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

$$r = k [\text{conc.}]^{\text{order}}$$

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

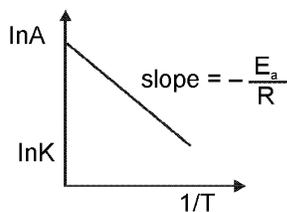
$$\log k = \left(-\frac{E_a}{2.303 R} \right) \frac{1}{T} + \log A$$

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

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

❖ $\ln k = \ln A - \frac{E_a}{RT}$

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



$$E_a \geq 0$$

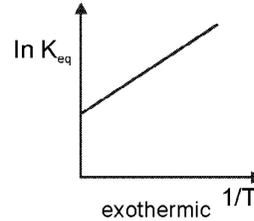
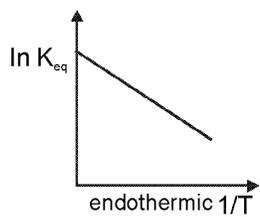
REVERSIBLE REACTIONS

$$k_f = A_f e^{-E_{af}/RT}$$

$$k_b = A_b e^{-E_{ab}/RT}$$

$$K_{eq} = \frac{K_f}{K_b} = \left(\frac{A_f}{A_b} \right) e^{-(E_{af} - E_{ab})/RT}$$

$$\ln K_{eq} = -\frac{\Delta H}{RT} + \ln \left(\frac{A_f}{A_b} \right)$$



$$\frac{[B]}{[C]} = \frac{K_1}{K_2} \Rightarrow E_a = \frac{E_{a_1}k_1 + E_{a_2}k_2}{k_1 + k_2}$$

(ii) **REVERSIBLE 1ST ORDER REACTION (both forward and backward)**

$$x = \frac{K_f a}{K_f + K_b} (1 - e^{-(k_f + k_b)t})$$

$$K_f + K_b = \frac{1}{t} \ln \left(\frac{x_{eq.}}{x_{eq.} - x} \right)$$

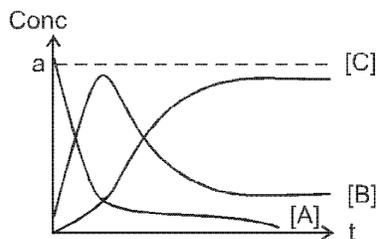
(iii) **SEQUENTIAL 1ST ORDER REACTION**

$$[A] = [A] e^{-k_1 t}$$

$$x = a(1 - e^{-k_1 t})$$

$$y = \frac{K_1 a}{K_2 - K_1} \{ e^{-k_1 t} - e^{-k_2 t} \} \quad t_{B(max.)} = \frac{1}{(K_1 - K_2)} \ln \frac{K_1}{K_2}$$

CASE-I $K_1 \gg K_2$



CASE II : $K_2 \gg K_1$

