CHEMICAL KINETICS & REDIOACTIVITY

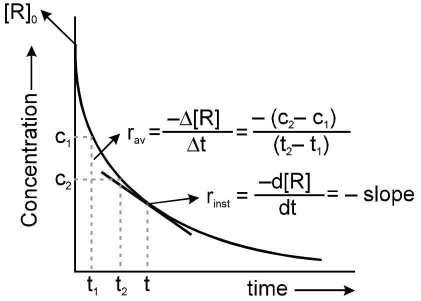
RATE/VELOCITY OF CHEMICAL REACTION :

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

Types of Rates of chemical reaction :

For a reaction $R \longrightarrow P$

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



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

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

Order of reaction :

$m_1A + m_2B \longrightarrow$ 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.**

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 [conc.]° = constant

$$\text{Rate} = k = \frac{C_0 - C_t}{'t'} \qquad \text{or} \qquad C_t = C_0 - kt$$

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

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

(b) **First Order Reactions :**

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

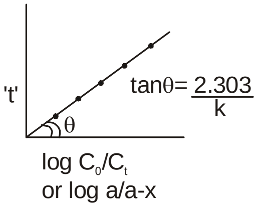
$$\mathbf{t = \frac{2.303}{k} \log \frac{a}{a-x}} \qquad \text{or} \qquad k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

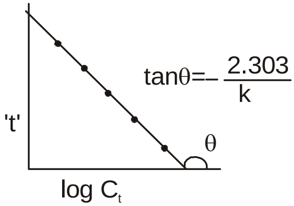
$$\Rightarrow \quad t_{1/2} = \frac{\ell n 2}{\mathbf{k}} \mathbf{=} \frac{0.693}{\mathbf{k}} = \text{Independent of initial concentration.}$$

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

Graphical Representation :

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





(c) **Second order reaction :**

2nd order Reactions

Two types

$$A + A \longrightarrow \text{products}$$

$a \qquad a$

$(a - x) \quad (a - x)$

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

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

$$A + B \longrightarrow \text{products.}$$

$a \qquad b \qquad\qquad 0$

$a - x \quad b - x$

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

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

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

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

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

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

(c) Method of half lives :

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

(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*.**

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

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

(b) By titration method :

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

2. Study of acid hydrolysis of an easter.

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

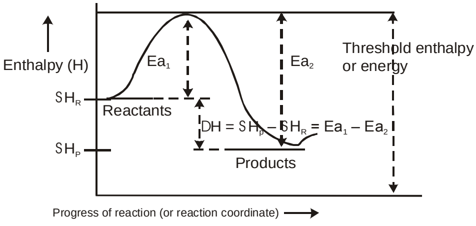
(c) By measuring optical rotation produced by the reaction mixture :

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

EFFECT OF TEMPERATURE ON RATE OF REACTION.

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

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

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

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

Arhenius equation

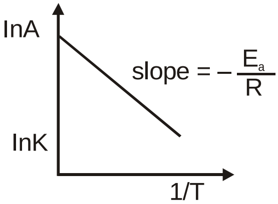
$k = Ae^{-E_aRT}$ $\qquad$ $r = k\,[conc.]^{order}$

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

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

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

❖ $\ln k = \ln A - \frac{E_a}{RT}$



$E_a \geq O$

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