

CHEMICAL KINETICS & RADIOACTIVITY

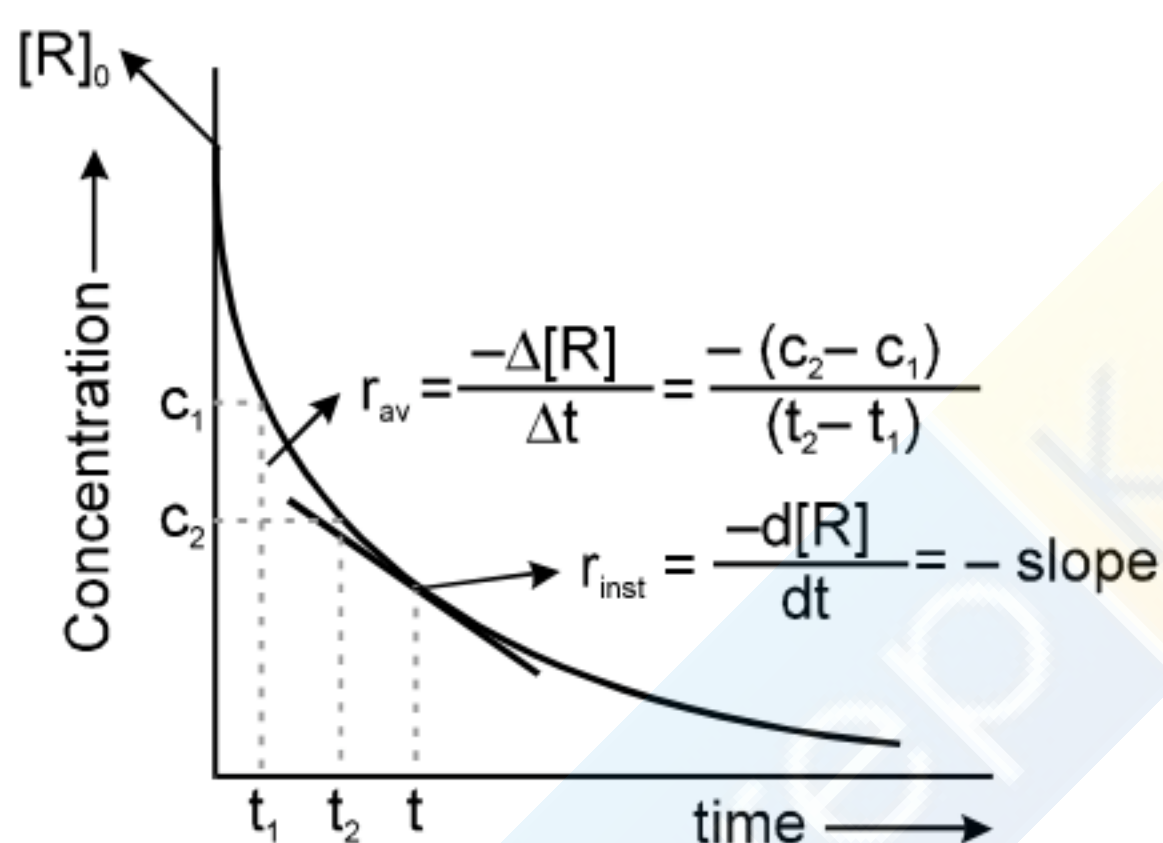
RATE/VELOCITY OF CHEMICAL REACTION :

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

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) :

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-order} 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 [conc.]⁰ = 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 = $\frac{C_0}{k}$

at $t_{1/2}$, $C_t = \frac{C_0}{2}$, 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, $A \longrightarrow \text{Products}$

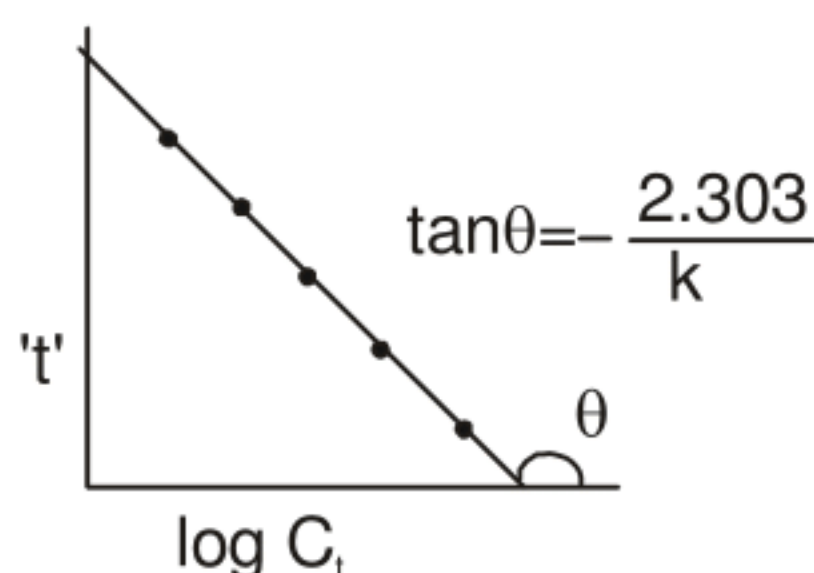
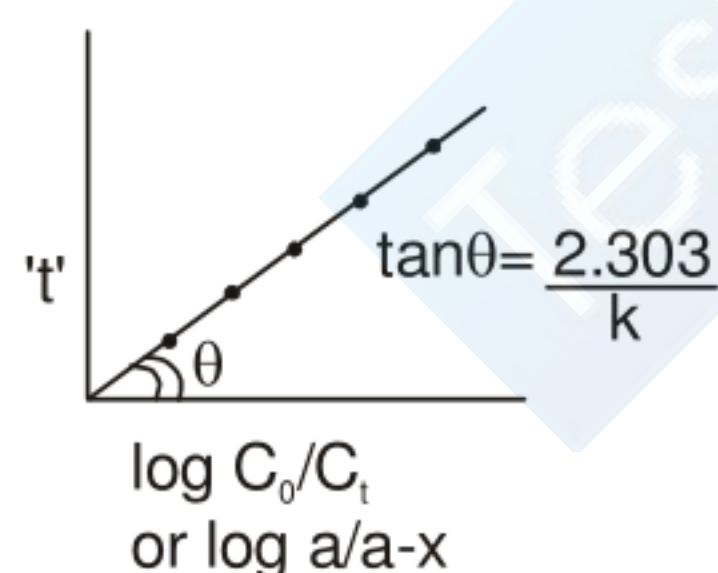
$$t = \frac{2.303}{k} \log \frac{a}{a-x} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

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

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

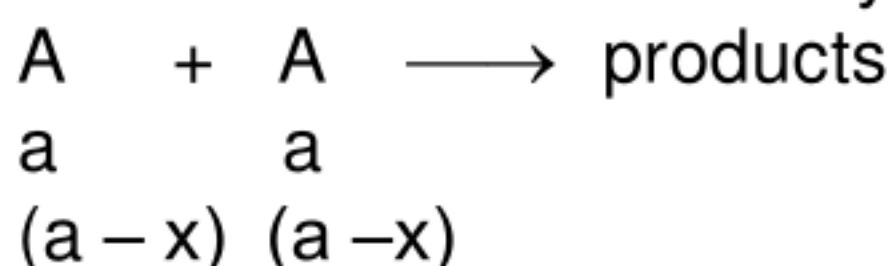
Graphical Representation :

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



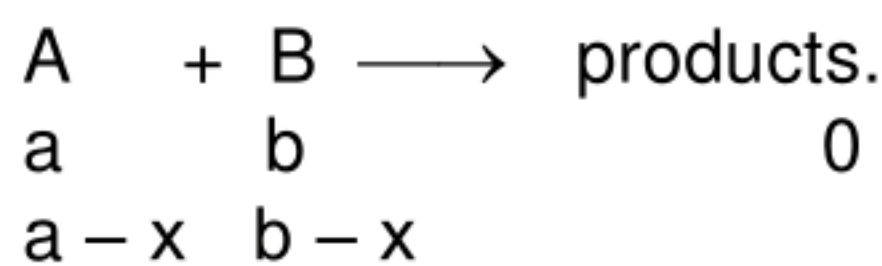
(c) Second order reaction :

2nd order Reactions
Two types



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

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



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

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

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

$$r_{01} = k [A_0]_1^a, \quad r_{02} = k [A_0]_2^a$$

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

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

(c) Method of half lives :

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

(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.*

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

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

(b) *By titration method :*

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

2. Study of acid hydrolysis of an ester.

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

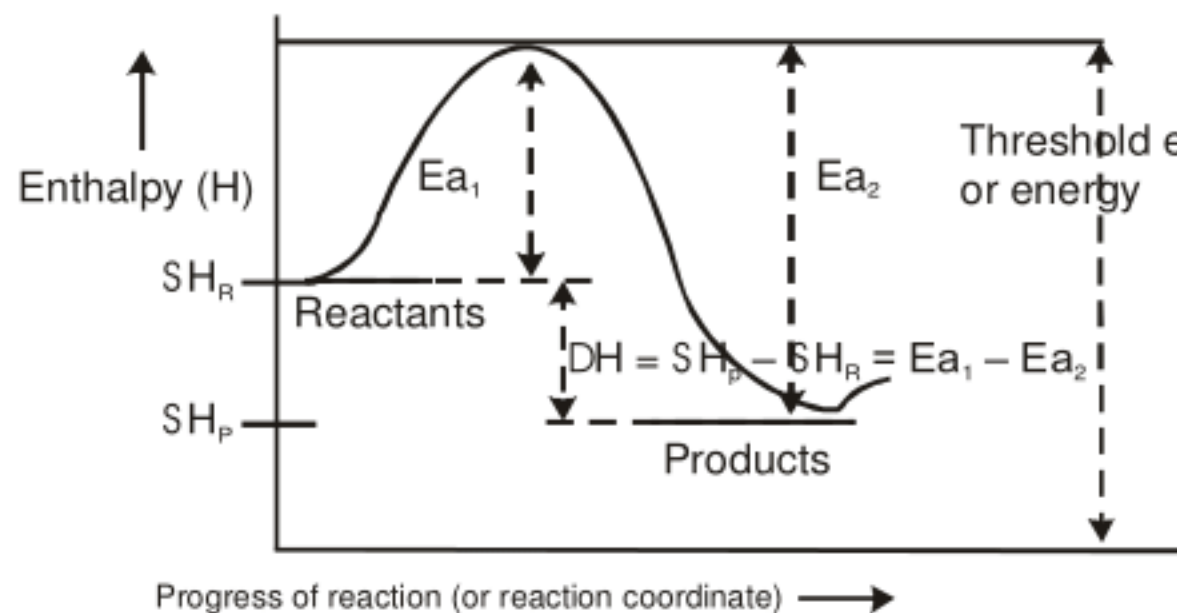
(c) *By measuring optical rotation produced by the reaction mixture :*

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

EFFECT OF TEMPERATURE ON RATE OF REACTION.

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

Arhenius theroy of reaction rate.



SH_R = Summation of enthalpies of reactants
 SH_P = Summation of enthalpies of products
 DH = 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

$$E_p > E_r \quad \rightarrow \text{endothermic}$$

$$E_p < E_r \quad \rightarrow \text{exothermic}$$

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

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

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

Arhenius equation

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

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

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

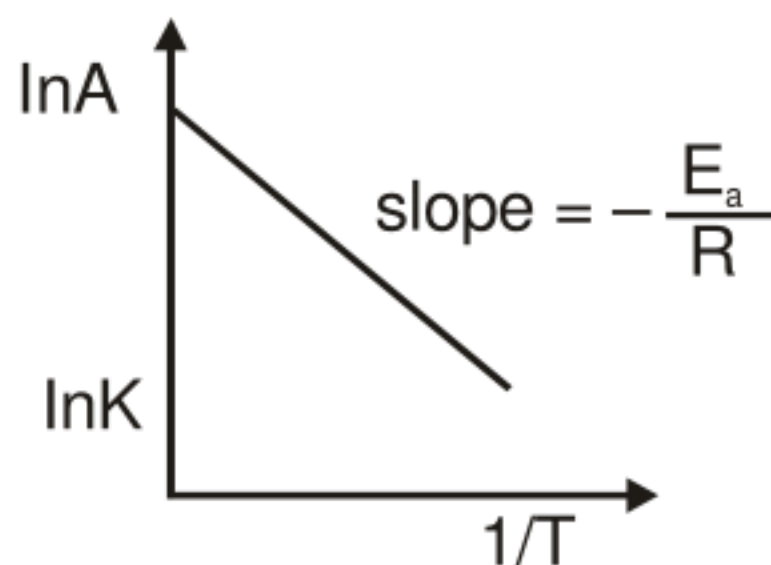
$$\log k = \left(-\frac{E_a}{2.303 R} \right) \frac{1}{T} + \log A$$

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

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



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



$$E_a \geq 0$$



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