

# CHEMICAL KINETICS & REDIOACTIVITY

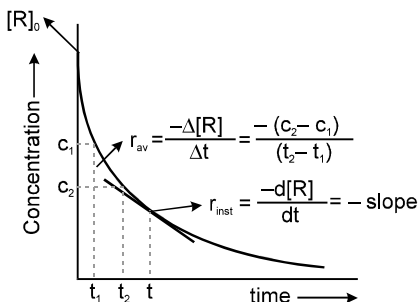
## RATE/VELOCITY OF CHEMICAL REACTION :

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

### Types of Rates of chemical reaction :

For a reaction  $R \longrightarrow P$

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



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

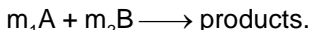
## RATE LAW (DEPENDENCE OF RATE ON CONCENTRATION OF REACTANTS) :

**Rate =  $K(\text{conc.})^{\text{order}}$  – 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 :



$R \propto [A]^p [B]^q$  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 1<sup>st</sup> order reaction is,  $A \longrightarrow \text{Products}$

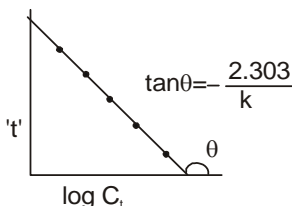
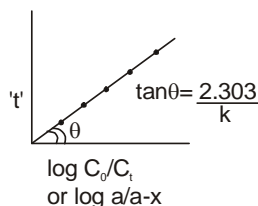
$$t = \frac{2.303}{k} \log \frac{a}{a-x} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

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

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

### Graphical Representation :

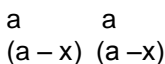
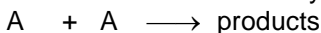
$$t = -\frac{2.303}{k} \log C_t + \frac{2.303}{k} \log C_0$$



### (c) Second order reaction :

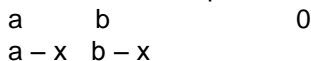
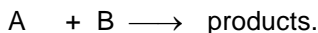
2<sup>nd</sup> order Reactions

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 :

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

then for two different initial concentrations of A we have

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

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

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

### (c) Method of half lives :

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

### (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.*

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

{Formula is not applicable when  $n = 1$ , the value of  $n$  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.

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

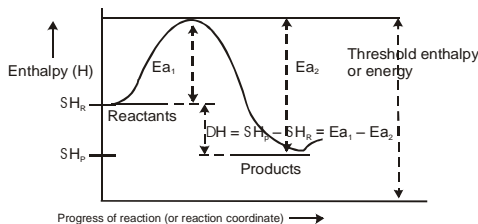
### (c) *By measuring optical rotation produced by the reaction mixture :*

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

## EFFECT OF TEMPERATURE ON RATE OF REACTION.

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

### Arrhenius theory of reaction rate.



$SH_R$  = Summation of enthalpies of reactants  
 $SH_P$  = Summation of enthalpies of products  
 $DH$  = Enthalpy change during the reaction  
 $E_{a1}$  = Energy of activation of the forward reaction  
 $E_{a2}$  = Energy of activation of the backward reaction

$$E_P > E_R \rightarrow \text{endothermic}$$

$$E_P < E_R \rightarrow \text{exothermic}$$

$$\Delta H = (E_P - E_R) = \text{enthalpy change}$$

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

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

### Arrhenius equation

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

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

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

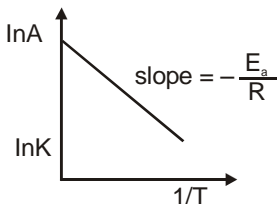
$$\log k = \left( -\frac{E_a}{2.303 R} \right) \frac{1}{T} + \log A$$

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

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



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



$$E_a \geq 0$$



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