

# REACTION KINETICS

## CONCEPT MAP

**Class XII**

Apart from playing an important role in industries and study of biological processes, kinetics also plays a role in environmental and atmospheric chemistry as part of an effort to understand a variety of issues ranging from the fate of prescription pharmaceutical in waste water to cascade of reactions involved in the ozone cycle.

### Rate of Reaction

Change in concentration of reactants or products as function of time (Unit:  $\text{mol L}^{-1} \text{s}^{-1}$  or  $\text{M s}^{-1}$ )

#### Differential Rate Equation



$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

#### Instantaneous Rate

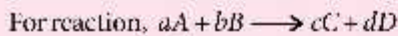
$$r_{\text{ins}} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

#### Average Rate

$$r_{\text{av}} = -\frac{\Delta R}{\Delta t} = \frac{\Delta P}{\Delta t}$$

#### Rate Law/Rate Equation

- The expression of rate in terms of molar concentration of reactants.



$$\text{Rate} = k[A]^x[B]^y$$

Where,  $k$  = rate constant or specific reaction rate.

- Depends only upon temperature.

- Unit of  $k = \left(\frac{\text{mol}}{\text{L}}\right)^{1-n} \text{s}^{-1}$   
where,  $n$  = order of reaction.

#### Order of Reaction

- Sum of powers of concentration terms in the rate law expression.

e.g.,  $\text{Rate} = k[A][B]^2$

$\therefore$  Order =  $1 + 2 = 3$

- For  $n^{\text{th}}$  order,  $t_{1/2} \propto \frac{1}{a^{n-1}}$

- Experimental concept and can be zero or fractional.

- Depends upon pressure and temperature.

#### Molecularity of Reaction

- The number of molecules of reactants taking part in elementary step of a reaction.
- Theoretical concept and can never be zero or fractional.
- Independent of pressure and temperature.

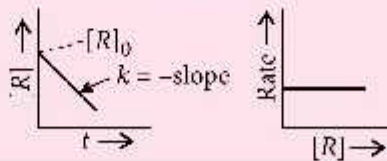
### Integrated Rate Equation

#### Zero Order Reaction

- Rate =  $k$  or  $kt = [R]_0 - [R]$

- Unit of  $k = \text{mol L}^{-1} \text{s}^{-1}$

- $t_{1/2}$  (half-life) =  $\frac{[R]_0}{2k}$



#### First Order Reaction

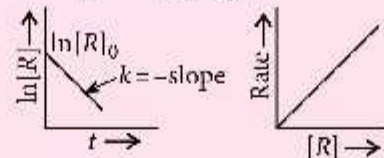
- Rate =  $k[R]$  or  $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

- Unit of  $k = \text{s}^{-1}$

- $t_{1/2} = 0.693/k$

- In terms of pressure,

$$k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$$



#### Useful Relations for First Order Reaction

$$t_{75\%} = 2t_{1/2}, t_{87.5\%} = 3t_{1/2}, t_{93.75\%} = 4t_{1/2}$$

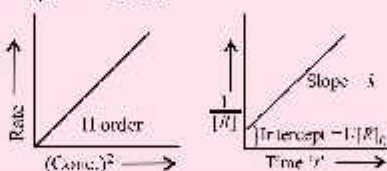
$$t_{96.87\%} = 5t_{1/2}, t_{99.9\%} = 10t_{1/2}$$

#### Second Order Reaction

- Rate =  $k[R]^2$  or  $1/[R]_t = kt + 1/[R]_0$

- Unit of  $k = \text{L mol}^{-1} \text{s}^{-1}$

- $t_{1/2} = 1/k[R]_0$



#### $n^{\text{th}}$ Order Reaction

- Rate =  $k[R]^n$

$$\text{or } (n-1)kt = \frac{1}{[R]^{n-1}} - \frac{1}{[R]_0^{n-1}}$$

- Unit of  $k = (\text{mol L}^{-1})^{1-n} \text{s}^{-1}$

- $t_{1/2} = 2^{n-1} - 1 / k(n-1) [R]_0^{n-1}$

### Dependency of Rate on Temperature

#### Arrhenius Equation

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

Here,  $A$  = pre-exponential factor

$R$  = Gas constant

$E_a$  = Activation energy

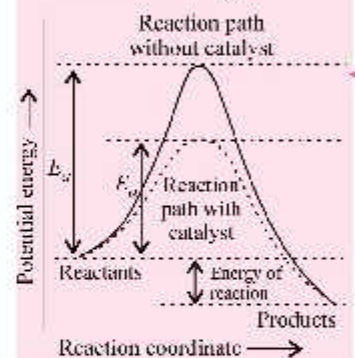
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left( \frac{T_2}{T_1 T_2} \right)$$

#### Activation Energy ( $E_a$ )

- Energy required by the reactant molecules for effective collisions to form products.
- The slope of  $\ln k$  vs  $1/T$  has the value  $-E_a/R$  and is used to calculate value of  $E_a$ .

#### Effect of Catalyst on Activation Energy

- A catalyst increases the rate of reaction by providing a path of lower activation energy.



#### Temperature Coefficient

- It is the ratio of  $k_{293}$  to  $k_{308}$ .
- For every  $10^\circ$  rise in temperature the rate becomes double.

#### Collision Theory

$$\text{Rate} = P \cdot Z_{AB} e^{-E_a/RT}$$