11. Chemical Kinetics

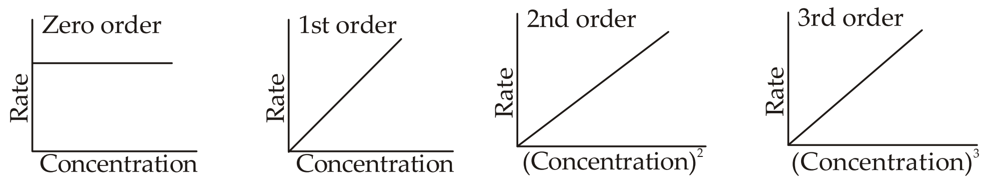
➢ **Rate of reaction =** Rate of disappearance of A

$$= \frac{\text{Decrease in concentration of A}}{\text{Time interval}} \quad \textbf{= Rate of appearance of B} \quad = \frac{\text{Increase in concentration of B}}{\text{Time interval}}$$

Order	Integrated rate equation	Unitss of k obtained by plotting t vs	Straight line to	$t_{1/2}$ proportional
0	$k = \frac{1}{t}\{[A_0]-[A]\}$	**mol L^{-1} s^{-1}**	**a – x**	**a**
1	$k = \frac{2.303}{t}\log\frac{a}{a-x}$	**s^{-1}**	**log (a – x)**	**independent of a**
2	$k = \frac{x}{ta(a-x)}$ **or**	**L mol^{-1} s^{-1}**	$\frac{1}{(a-x)}$	$\frac{1}{a}$
	$k = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}$	**L mol^{-1} s^{-1}**		$\frac{1}{a}$
n	$k = \frac{1}{t(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$	**L^{n-1} mol^{1-n} s^{-1}**	$\frac{1}{(a-x)^{n-1}}$	$\frac{1}{a^{n-1}}$

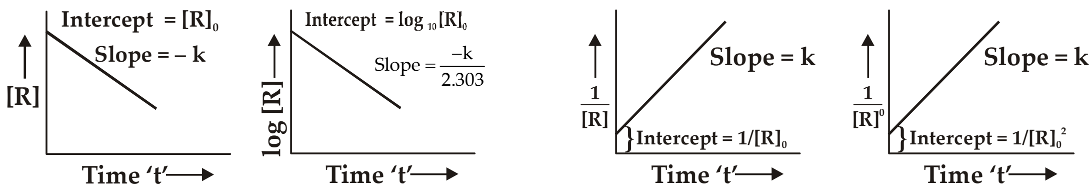
➢ **Some important graphs of diffrent order of reactions are given below :**

(a) Plots of rate vs concentrations

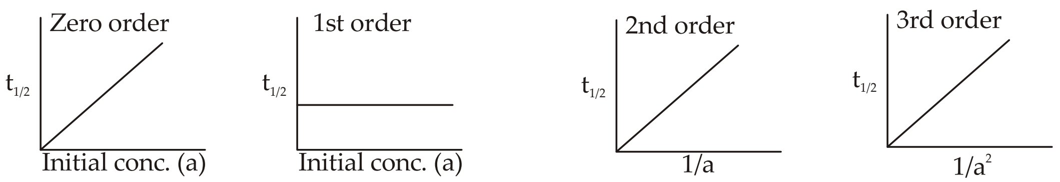


(b) Plots of integrated rate equations

Zero order **First Order** **Second Order** **Third Order**



(c) Plots of half-lives vs initial concentration



If reaction completion is given in percent, then take initial concentration (a) 100 and if reaction completion is given in fraction, then take initial concentration as 1.

Questions based on $t_{1/2}$ can be solved by another method also based on following diagram.

- **Order of reaction** It can be fraction, zero or any whole number.
- **Molecularity of reaction** is always a whole number. It is never more than three. It cannot be zero.
- **First Order Reaction :**

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)} \;\&\; t_{1/12} = \frac{0.693}{k} [A]_t = [A]_0 e^{-kt}$$

- **Zero Order Reaction :** $x = kt$ and $t_{1/2} = \frac{a}{2k}$

  The rate of reaction is independent of the concentration of the reacting substance.

- Time of n^th fraction of first order process,

$$t_{1/n} = \frac{2.303}{k}\log\left(\frac{1}{1-\frac{1}{n}}\right)$$

- Amount of substance left after 'n' half lives = $\frac{[A]_0}{2^n}$
- Arrhenius gave a mathematical expression to deduce the relationship between rate constant and temperature.

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

where, A is frequency factor and it is constant

E_a is activation energy

R is gas constant, T is temperature

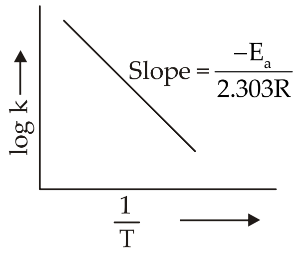
On taking log on both sides

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

Arrhenius equation : $\log k = -\frac{E_a}{2.303RT} + \log A$

This is an equation of straight line of the form y = mx + c.

If we draw a graph between log k and (1/T), we get a straight line with slope equal to $\frac{-E_a}{2.303R}$.



E_a can be calculated by measuring the slope of the lines. $E_a = -\text{slope} \times 2.303\ R$

If k_1 and k_2 are rate constants at temperatures T_1 and T_2 respectively then,

$$\boxed{\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]}$$

Factor $e^{-\frac{E_a}{RT}}$ in the Arrhenius equation is known as 'Boltzmann factor'.

Activation Energy

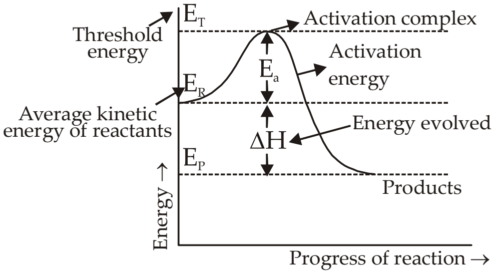
The minimum amount of energy absorbed by the reactant mole ules so that their energy becomes equal to threshold energy is called activation energy.

Or, we can say that it is the difference between threshold energy and the average kinetic energy possessed by reactant molecules.

Activation energy = Threshold energy – Average kinetic energy of reactant.

Arrhenius equation : $\log k = -\frac{E_a}{2.303RT} + \log A$

This is an equation of straight



➢ Temperature coefficient (n) = $\frac{\text{Rate constant at (T+10°)}}{\text{Rate constantat T}}$

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