Chemical Kinetics

For a reaction R → P

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

$$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$$

Rate of reaction $= -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$

Factors influencing the rate of a reaction:
Rate of a reaction depends upon the concentration of reactants (pressure in the case of gas), temperature and catalyst.

- Rate expression and rate constant
  aA + bB → cC + dD
  Rate expression
  $\therefore \text{Rate} \propto [A]^x [B]^y$
  Differential rate equation ®
  $$\Rightarrow -\frac{d[R]}{dt} = k[A]^x[B]^y \qquad (1)$$
  Where, k is called rate constant

- Order of a reaction:

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

x is Order of the reaction with respect to A
y is Order of the reaction with respect to B
$x + y$ is Overall order of the reaction

1. Order of a reaction can be 0, 1, 2, 3 and even a fraction
2. Units of rate constant

$$aA + bB \rightarrow cC + dD$$

Rate = $k\,[A]^x\,[B]^y$

$x + y = n$ = Order of the reaction

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

$$= \frac{\text{Concentration}}{\text{Time}} \times \frac{1}{(\text{Concentration})^n}$$

[[A] = [B] and $x + y = n$ = Order of the reaction]

1. For a zero-order reaction, $n = 0$

   Unit of $\dfrac{\text{mol L}^{-1}}{\text{s}} \times \dfrac{1}{\left(\text{mol L}^{-1}\right)^0} = \text{mol L}^{-1}\text{s}^{-1}$

1. For a first-order reaction, $n = 1$

   Unit of $\dfrac{\text{mol L}^{-1}}{\text{s}} \times \dfrac{1}{\left(\text{mol L}^{-1}\right)^1} = \text{s}^{-1}$

1. For a second-order reaction, $n = 2$

   Unit of $\dfrac{\text{mol L}^{-1}}{\text{s}} \times \dfrac{1}{\left(\text{mol L}^{-1}\right)^2} = \text{mol}^{-1}\,\text{L}\text{s}^{-1}$

- **Molecularity of a reaction:**
  The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction

- **Order versus molecularity**

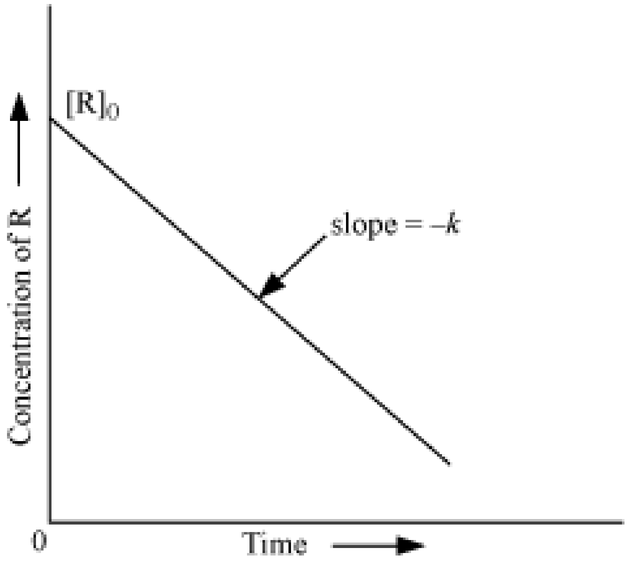
1. Order can be zero and even a fraction. But molecularity cannot be zero or a non-integer.
2. Order is applicable to both elementary and complex reactions whereas molecularity is applicable to elementary reactions only.

Integrated rate equations:

- **Zero-order reactions:**

$R \rightarrow P$

$$k = \frac{[R]_0 - [R]}{t}$$

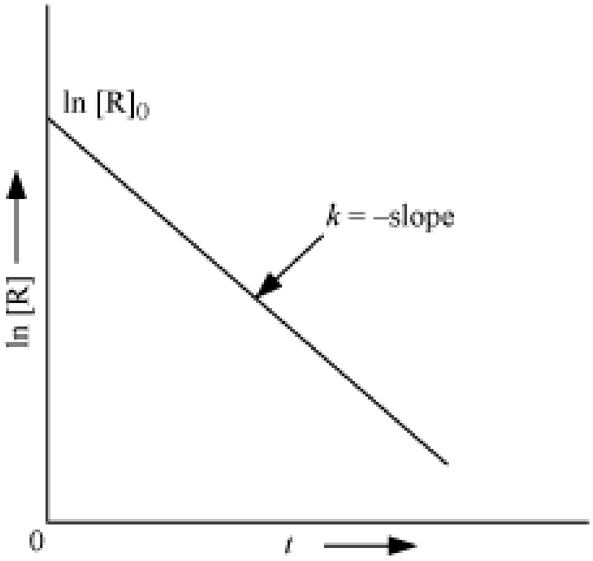


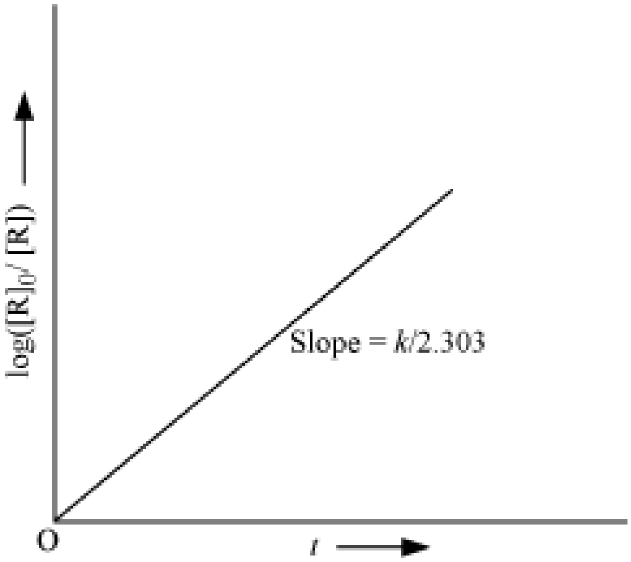
- **First-order reactions:**

$R \rightarrow P$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

$$\therefore \frac{d[R]}{[R]} = -k\,dt$$





1. For a typical first-order gas phase reaction:

$A_{(g)} \rightarrow B_{(g)} + C_{(g)}$

Here, p_i is initial pressure of A

$p_t = (p_A + p_B + p_C)$ = Total pressure at time t

$$\therefore k = \frac{2.303}{t} \log \frac{p_i}{p_A}$$

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

- **Half-life of a reaction:**

1. **For a zero-order reaction:**

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

1. For a first-order reaction:

$$t_{1/2} = \frac{0.693}{k}$$

That is, $t_{\frac{1}{2}}$ is independent of $[R]_0$

- **Pseudo first-order reaction:**

Hydrolysis of ethyl acetate –

	$CH_3COOC_2H_5$	+	H_2O	$\xrightarrow{H^+}$	CH_3COOH	+	C_2H_5OH
$t = 0$	0.01 mol		10 mol		0 mol		0 mol
t	0 mol		9.99 mol		0.01 mol		0.01 mol

Rate = $k'[CH_3COOC_2H_5][H_2O]$

Here, $[H_2O]$ is constant
So, rate = $k\,[CH_3COOC_2H_5]$
Where, $k = k'\,[H_2O]$

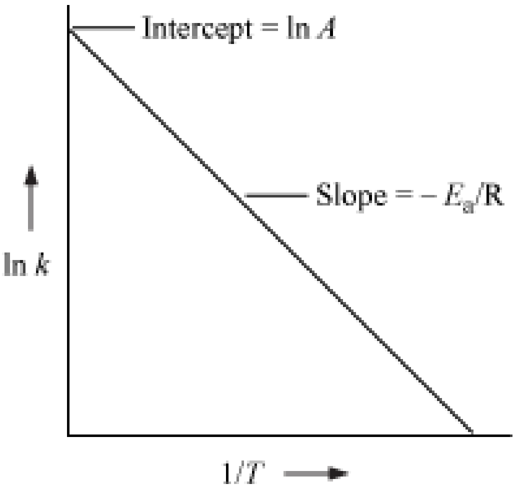
Temperature dependence of the rate of reaction:

- For a chemical reaction, with a rise in temperature by 10^{o}, the rate constant is nearly doubled.
- **Arrhenius equation:**

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

  Where,
  A is Arrhenius factor or frequency factor or pre-exponential factor
  R is Gas constant
  E_a is Activation energy
  On taking natural logarithm on both sides, we have

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

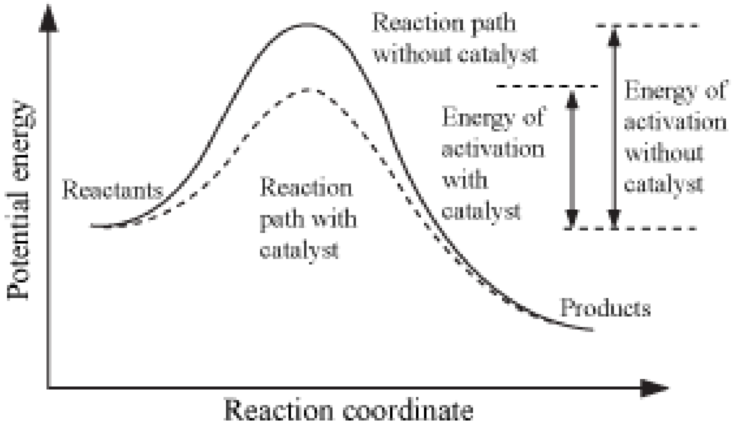


If k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively, then

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\text{or, } \log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

- **Effect of a catalyst:**
  A catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy.



- Collision frequency (Z) →The number of collisions per second per unit volume of the reaction mixture
  For the reaction A + B ®Products,

Rate =

$$Z_{AB}e^{-E_a/RT}$$

Where,

Z_{AB} → Collision frequency of reactants A and B

$e^{-E_a/RT}$ → The fraction of molecules with energies equal to or greater than E_a

To account for effective collisions, another factor P (called the probability or steric factor) is introduced.

Then, rate =

$$PZ_{AB}e^{-E_a/RT}$$