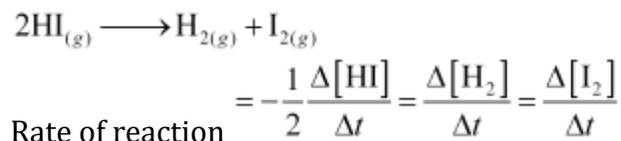


## Chemical Kinetics

---

For a reaction  $R \rightarrow P$

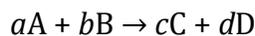
$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$



### 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



Rate expression

$$\therefore \text{Rate} \propto [A]^x [B]^y$$

Differential rate equation ®

$$\Rightarrow -\frac{d[R]}{dt} = k[A]^x [B]^y \quad (1)$$

Where,  $k$  is called rate constant

- Order of a reaction:

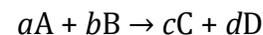
$$\text{Rate} = k[A]^x [B]^y$$

$x$  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



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

$x + y = n = \text{Order of the reaction}$

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

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

[[A] = [B] and  $x + y = n = \text{Order of the reaction}$ ]

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

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

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

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

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

$$\text{Unit of } \frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1} \text{L s}^{-1}$$

- **Molecularity of a reaction:**

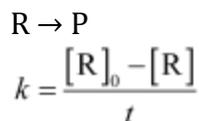
The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction

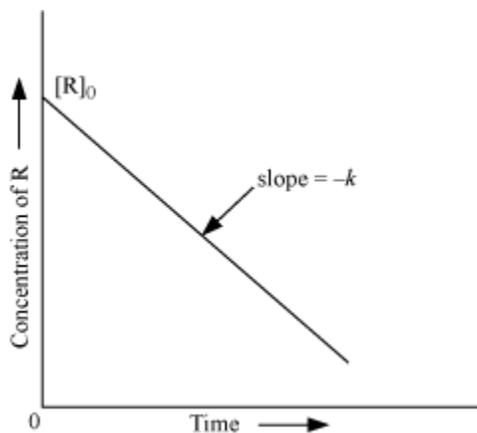
- **Order versus molecularity**

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:**



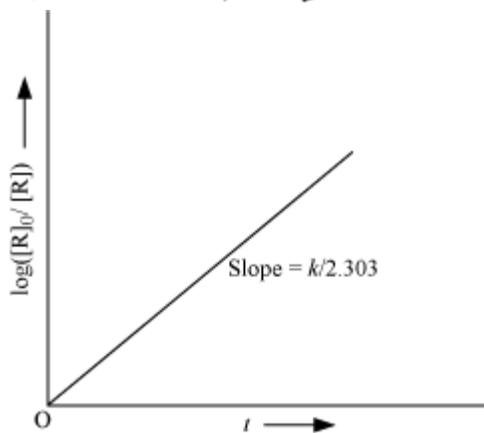
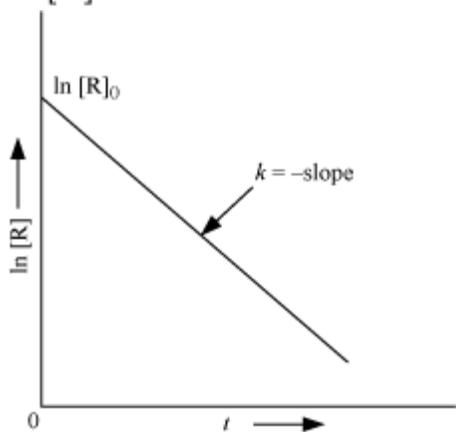


- **First-order reactions:**

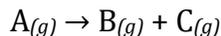


$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

$$\therefore \frac{d[R]}{[R]} = -kdt$$



- For a typical first-order gas phase reaction:



Here,  $p_i$  is initial pressure of A

$P_t = (p_A + p_B + p_C) = \text{Total pressure at time } t$

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

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

- Half-life of a reaction:**

- For a zero-order reaction:

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

- For a first-order reaction:

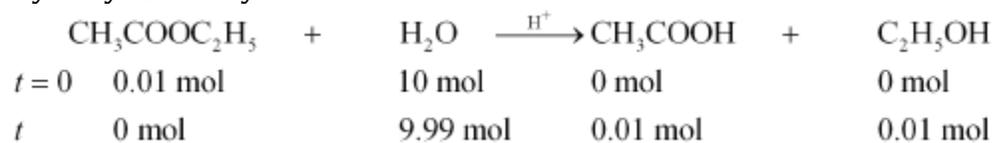
$$t_{1/2} = \frac{0.693}{k}$$

$t_{1/2}$

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

- Pseudo first-order reaction:**

Hydrolysis of ethyl acetate –



$$\text{Rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

Here,  $[\text{H}_2\text{O}]$  is constant

So, rate =  $k [\text{CH}_3\text{COOC}_2\text{H}_5]$

Where,  $k = k' [\text{H}_2\text{O}]$

### Temperature dependence of the rate of reaction:

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

$$k = A e^{-E_a/RT}$$

Where,

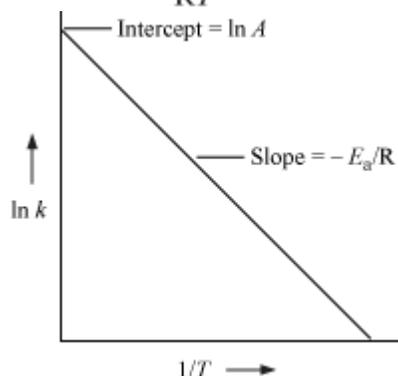
A is Arrhenius factor or frequency factor or pre-exponential factor

R is Gas constant

$E_a$  is Activation energy

On taking natural logarithm on both sides, we have

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



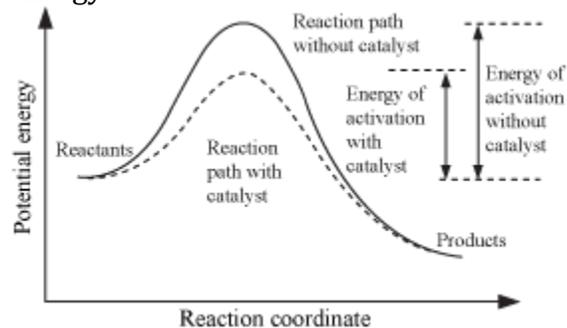
If  $k_1$  and  $k_2$  are the values of rate constants at temperatures  $T_1$  and  $T_2$  respectively, then

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

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

- **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  $A + B \rightarrow \text{Products}$ ,

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

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 =

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