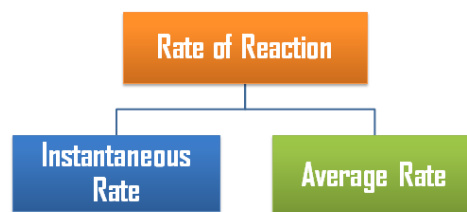
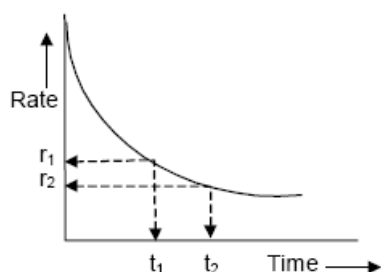


# Revision Notes on Chemical Kinetics:

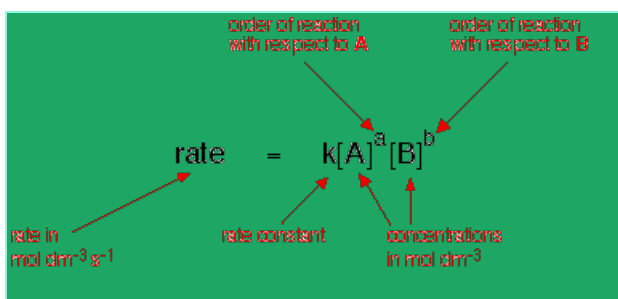
## Rate of Reaction:

- Rate of change of extent of reaction is the rate of reaction.
- Rate of reaction is positive for product and negative for reactant.
- For reaction  $aA \rightarrow bB$   
 $\text{Rate} = 1/b(\Delta[B]/\Delta t) = -1/a(\Delta[A]/\Delta t)$
- It goes on decreasing as the reaction progress due to decrease in the concentration(s) of the reactant(s).



- Unit of rate of reaction :  $\text{mol L}^{-1} \text{s}^{-1}$
- The rate measured over a long time interval is called average rate and the rate measured for an infinitesimally small time interval is called instantaneous rate.
- In a chemical change, reactants and products are involved. As the chemical reaction proceeds, the concentration of the reactants decreases, i.e., products are produced.
- The rate of reaction (average rate) is defined as the change of concentration of any one of its reactants (or products) per unit time.

## Order of Reaction



**For reaction**  $aA + bB + \dots \rightarrow cC + \dots$

$$R \propto [A]^m [B]^n \text{ or } R = k[A]^m [B]^n \dots$$

Where m and n may or may not be equal to a & b.

m is order of reaction with respect to A and n is the order of reaction with respect to B.

$m + n + \dots$  is the overall order of the reaction.

## Elementary Reaction:

- It is the reaction which completes in a single step.
- A reaction may involve more than one elementary reactions or steps also.
- Overall rate of reaction depends on the slowest elementary step and thus it is known as rate determining step.

## Molecularity of Reaction:

- Number of molecules taking part in an elementary step is known as its molecularity.
- Order of an elementary reaction is always equal to its molecularity.
- Elementary reactions with molecularity greater than three are not known because collisions in which more than three particles come together simultaneously are rare.

| Chemical Reaction   | Molecularity |
|---|--------------|
| $\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$                       | Unimolecular |
| $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$                            | Bimolecular  |
| $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$                        | Trimolecular |
| $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$               | Bimolecular  |
| $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$                          | Trimolecular |
| $2\text{FeCl}_3 + \text{SnCl}_2 \rightarrow \text{SnCl}_2 + 2\text{FeCl}_2$ | Trimolecular |

## Differential and Integrated Rate Laws:

### Zero Order Reactions:

### For Reaction: $A \rightarrow \text{Product}$

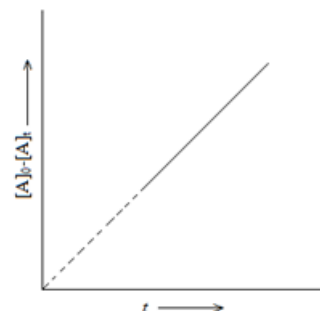
$$[A]_0 - [A]_t = k_0 t$$

Where,

$[A]_0$  = Initial concentration of A

$[A]_t$  = Concentration of A at time t.

$k_0$  = Rate constant for zero order reaction.



### Half Life:

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

Unit of rate constant =  $\text{mol dm}^{-3} \text{s}^{-1}$

### Examples:

- Enzyme catalyzed reactions are zero order with respect to substrate concentration.
- Decomposition of gases on the surface of metallic catalysts like decomposition of HI on gold surface.

### First Order Reactions:

$A \rightarrow \text{Product}$

$$(\Delta [A] / A) = -k_1 \Delta t$$

$$\text{or } k_1 = (2.303 / t) \log ([A]_0 / [A]_t)$$

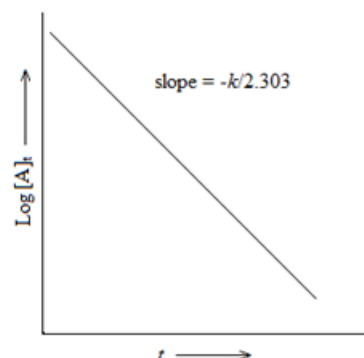
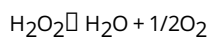
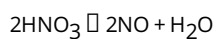
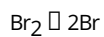
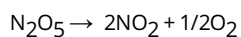
### Half Life:

$$t_{1/2} = 0.693 / k_1$$

Half life is independent of the initial concentration of the reactant for a first order reaction.

Units of  $k_1 = \text{s}^{-1}$

### Examples:



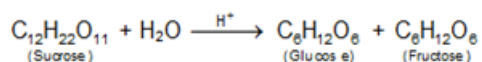
### Pseudo First Order Reactions:

These are the reactions in which more than one species is involved in the rate determining step but still the order of reaction is one.

Examples:

- **Acid hydrolysis of ester:**  $\text{CH}_3\text{COOEt} + \text{H}_3\text{O}^+ \rightleftharpoons \text{CH}_3\text{COOH} + \text{EtOH}$

- **Inversion of cane sugar:**



- Decomposition of benzenediazonium halides  $\text{C}_6\text{H}_5\text{N}=\text{NCl} + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{HCl}$

## Half – Life of a nth Order Reaction:

$$kt_{1/2} = (2^{n-1}-1)/(n-1)[A_0]^{n-1}$$

Where, n = order of reaction  $\neq 1$

## Parallel Reactions:

The reactions in which a substance reacts or decomposes in more than one way are called parallel or side reactions.

If we assume that both of them are first order, we get.

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A] = k_{av}[A]$$

$k_1$  = fractional yield of B  $\times k_{av}$

$k_2$  = fractional yield of C  $\times k_{av}$

If  $k_1 > k_2$  then

A  $\rightarrow$  B main and

A  $\rightarrow$  C is side reaction

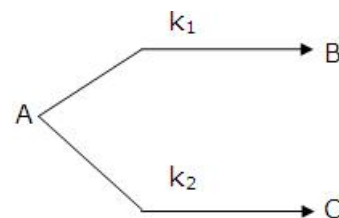
Let after a definite interval x mol/litre of B and y mol/litre of C are formed.

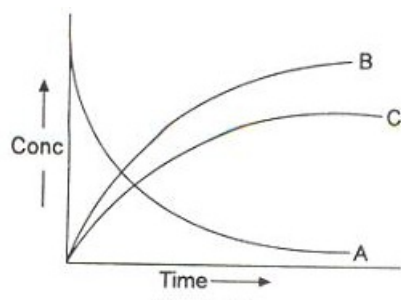
$$\frac{x}{y} = \frac{k_1}{k_2}$$

i.e

$$\frac{\frac{d[B]}{dt}}{\frac{d[C]}{dt}} = \frac{k_1}{k_2}$$

This means that irrespective of how much time is elapsed, the ratio of concentration of B to that of C from the start (assuming no B and C in the beginning) is a constant equal to  $k_1/k_2$ .





Parallel Reactions

▪ Substance reacts or decomposes in more than one way.

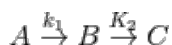
Sequential reactions

▪ Proceeds from reactants to final products through one or more intermediate stages.

## Sequential Reactions:

This reaction is defined as that reaction which proceeds from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successive or consecutive steps.

$A \rightarrow B \rightarrow C$  and so on



$$-\frac{d[A]}{dt} = k_1[A] \quad \dots\dots(i)$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \quad \dots\dots(ii)$$

$$\frac{d[C]}{dt} = k_2[B] \quad \dots\dots(iii)$$

Integrating equation (i), we get

$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] = \frac{k_1 [A]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

$$[C] = \frac{[A]_0}{k_2 - k_1} \left[ k_2 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_2 t}) \right]$$

$$t_{\max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

$$B_{\max} = [A]_0 \left[ \frac{k_2}{k_1} \right]^{k_2/k_1 - k_2}$$

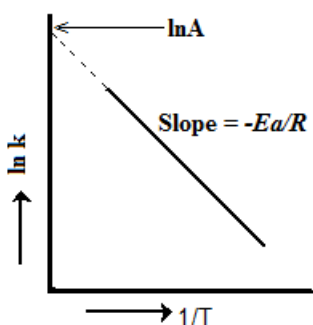
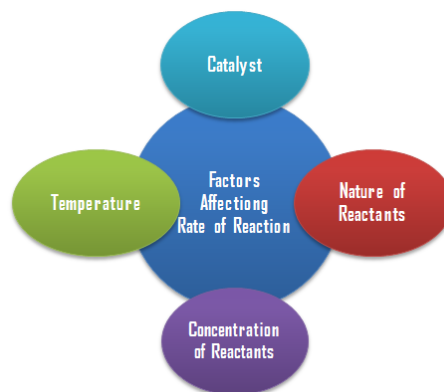
## Arrhenius Equation:

$$k = A \exp(-E_a/RT)$$

Where,  $k$  = Rate constant

$A$  = pre-exponential factor

$E_a$  = Activation energy



## Temperature Coefficient:

The temperature coefficient of a chemical reaction is defined as the ratio of the specific reaction rates of a reaction at two temperature differing by  $10^\circ\text{C}$ .

$$\mu = \text{Temperature coefficient} = k_{(t+10)}/k_t$$

Let temperature coefficient of a reaction be ' $\mu$ ' when temperature is raised from  $T_1$  to  $T_2$ ; then the ratio of rate constants or rate may be calculated as

$$\frac{k_{T2}}{k_{T1}} = \mu^{\frac{T_2 - T_1}{10}} = \mu^{\frac{\Delta T}{10}}$$

$$\log \frac{k_{T2}}{k_{T1}} = \mu^{\frac{T_2 - T_1}{10}} = \Delta T \log \mu$$

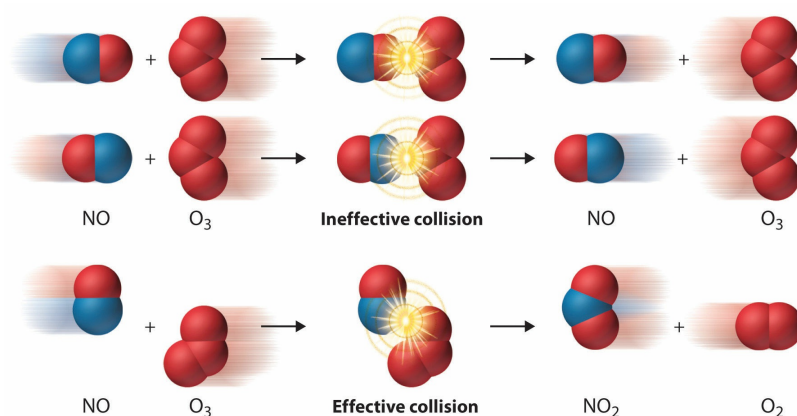
$$\frac{k_{T2}}{k_{T1}} = \text{antilog} \left[ \frac{\Delta T}{10} \log \mu \right]$$

Its value lies generally between 2 and 3.

## Collision Theory of Reaction Rate

- A chemical reaction takes place due to collision among reactant molecules.
- The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency ( $Z$ ).

- The value of collision frequency is very high, of the order of  $10^{25}$  to  $10^{28}$  in case of binary collisions.
- Every collision does not bring a chemical change.
- The collisions that actually produce the products are effective collisions.
- The effective collisions which bring chemical change are few in comparison to the form a product are ineffective elastic collisions, i.e., molecules just collide and disperse in different directions with different velocities.
- For a collision to be effective, the following two barriers are to be cleared.
  1. Energy Barrier
  2. Orientation Barrier



## Radioactivity:

All radioactive decay follow 1<sup>st</sup> order kinetics

For radioactive decay  $A \rightarrow B$

$$-(dN_A/dt) = \lambda N_A$$

Where,  $\lambda$  = decay constant of reaction

$N_A$  = number of nuclei of the radioactive substance at the time when rate is calculated.

Arrhenius equation is not valid for radioactive decay.

$$\text{Integrated Rate Law: } N_t = N_0 e^{-\lambda t}$$

$$\text{Half Life: } t_{1/2} = 0.693/\lambda$$

$$\text{Average life time: Life time of a single isolated nucleus, } t_{av} = 1/\lambda$$

Activity: Rate of decay

$$A = dN_A/dt, \text{ Also, } A_t = A_0 e^{-\lambda t}$$

Specific Activity: activity per unit mass of the sample.

$$\text{Specific activity} = \frac{\left( \lambda \times \frac{w}{M} \times Av \right)}{w} = \frac{\lambda \times Av}{M}$$

**Units:** dps or Becquerel