Class : 11

2023 – 24

CHEMICAL KINETICS

Rate of a Chemical Reaction :

- Speed of a reaction or the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time.
- **Average rate of a reaction, r_{av} :** Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur.
- units of rate are concentration time^{-1}.
- **Instantaneous rate :** It is obtained when we consider the average rate at the smallest time interval say dt (i.e. when Δt approaches zero).
- Hence, mathematically for an infinitesimally small dt instantaneous rate is given by

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

  As $\Delta t \rightarrow 0$ or $r_{\text{inst}}=\frac{-d[\mathrm{R}]}{dt}=\frac{d[\mathrm{P}]}{dt}$
- Reaction where stoichiometric coefficients of the reactants and products are same.

  $$\mathrm{Hg(l)}+\mathrm{Cl_2(g)} \rightarrow \mathrm{HgCl_2(s)}$$

  $$\text{Rate of reaction}=\frac{\Delta[\mathrm{Hg}]}{dt}=-\frac{\Delta[\mathrm{Cl_2}]}{dt}=-\frac{\Delta[\mathrm{HgCl_2}]}{dt}$$
- Reaction where stoichiometric coefficients of reactants or products are not equal to one

  $$2\mathrm{HI(g)} \rightarrow \mathrm{H_2(g)}+\mathrm{I_2(g)}$$

  $$\text{Rate of reaction}=\frac{1}{2}\frac{\Delta[\mathrm{HI}]}{\Delta t}=\frac{\Delta[\mathrm{H_2}]}{\Delta t}=\frac{\Delta[\mathrm{I}]}{\Delta t}$$

Factors Influencing Rate of a Reaction :

- **Concentration of the reactants :** Rate of a reaction is proportional to the concentration i.e., greater the concentration, faster is the reaction.
- **Temperature :** The rate of reaction increases (as the temperature increase) because large number of molecules cross the energy barrier.
- **Presence of catalyst :** Catalyst alters the activation energy of reaction and hence changes the rate of reaction.
- **Surface area of the reactants :** Greater the surface area, faster is the reaction.
- **Presence of light :** For many reactions, light provides the necessary activation energy to initiating the reaction. (ex : photochemical reactions).
- **Rate Expression and Rate Constant :**
  - ❖ Consider a general reaction

    $\mathrm{aA}+\mathrm{bB} \rightarrow \mathrm{CC}+\mathrm{dD}$

    where a, b, c and d are the stoichiometric coefficients of reactants and products.

    The rate expression for this reaction is

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

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

or $\quad -\dfrac{d[\text{R}]}{dt} = k[\text{A}]^x[\text{B}]^y$

(x and y may or may not be equal to the stoichiometric coefficient)

k is a proportionality constant called rate constant.

- Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.
- Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e., theoretically but must be determined experimentally.

- **Order of a Reaction :** The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

  Order of a reaction can be 0, 1, 2, 3 and even a fraction.
  - The reactions taking place in one step are called **elementary reactions**.
  - When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called **complex reactions**.

Units of Rate Constant :

Units of Rate Constant

Reaction	Order	Units of Rate Constant
Zero order reaction	0	$\dfrac{\text{molL}^{-1}}{\text{s}} \times \dfrac{1}{(\text{molL}^{-1})^0} = \text{molL}^{-1}\text{s}^{-1}$
First order reaction	1	$\dfrac{\text{molL}^{-1}}{\text{s}} \times \dfrac{1}{(\text{molL}^{-1})^1} = \text{s}^{-1}$
Second order reaction	2	$\dfrac{\text{molL}^{-1}}{\text{s}} \times \dfrac{1}{(\text{molL}^{-1})^2} = \text{mol}^{-1}\text{Ls}^{-1}$

- **Molecularity of a Reaction :** The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.
- The overall rate of the reaction is controlled by the slowest step in a reaction called the rate **determining step**.

Difference between order of reactions and Molecularity

Order	Molecularity
Order of a reaction is an experimental quantity. It can be zero and even a fraction.	Molecularity cannot be zero or a non-integer.
Order is applicable to elementary as well as complex reactions.	Molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning.
For complex reaction, order is given by the slowest step.	Molecularity of the slowest step is same as the order of the overall reaction.

Integrated Rate Equations :

- **Zero Order Reactions :** Rate of the reaction is proportional to zero power of the concentration of reactants.

  $\text{Rate} = -\frac{d[\text{R}]}{dt} = k[\text{R}]^0$

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

  Integrating both sides

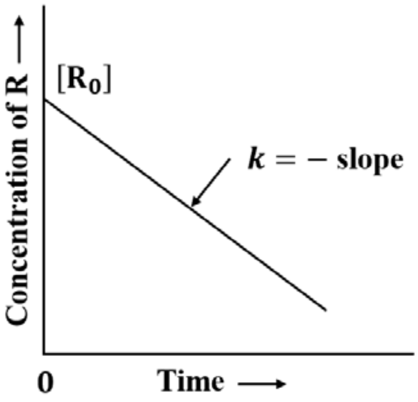
  $[\text{R}] = -k\ t + \text{I}$; At $t = 0$, $\text{R} = [\text{R}]_0$,

  Substituting in equation

  $[\text{R}]_0 = -k \times 0 + \text{I}$; $[\text{R}]_0 = \text{I}$.

  Substituting the value of I in the equation

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

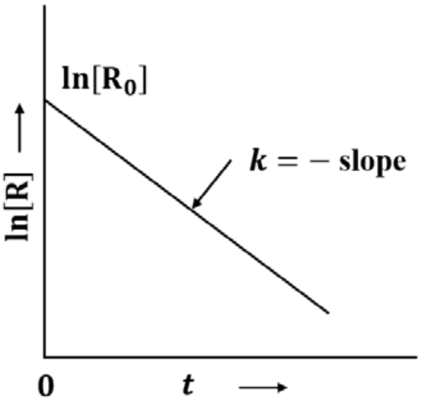


Variation in the concentration vs time plot for a zero order reaction

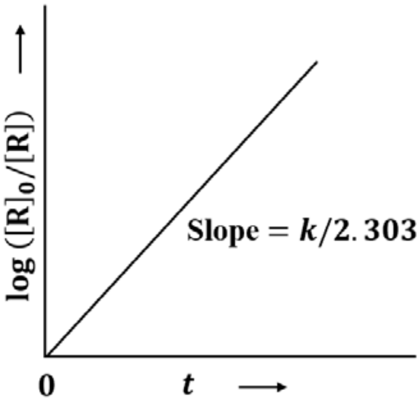
- **First Order Reactions :**
  - The rate of the reaction is proportional to the first power of the concentration of the reactant R.

    $\text{Rate} = \frac{d[\text{R}]}{dt} = k[\text{R}]$
  - The first order rate equation can written in the form

    $k = \frac{2.303}{t} \log \frac{[\text{R}]_0}{[\text{R}]}$



A plot between $\ln[\text{R}]$ and t for a first order reaction



Plot of $\log[\text{R}]_0/[\text{R}]$ vs time for a first order reaction

- All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

$$^{226}_{88}\mathrm{Ra} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{222}_{86}\mathrm{Rn}$$

  Rate $= k[\mathrm{Ra}]$

- Decomposition of N_2O_5 and N_2O are some more examples of first order reactions.
- Consider a typical first order gas phase reaction.

$$\mathrm{A(g)} \rightarrow \mathrm{B(g)} + \mathrm{C(g)}$$

  Integrated rate equation for such a reaction can be

$$k = \left(\frac{2.303}{t}\right)\left(\log\frac{p_i}{p_\mathrm{A}}\right)$$

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

  Where, p_i = Initial pressure

  p_A = Portial pressure of A

  p_t = total pressure $(p_A + p_B + p_C)$

- **Half-Life of a Reaction :**
  - For a zero-order reaction,

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

  - For the first order reaction,

$$k = \frac{2.303}{t}\log\frac{[\mathrm{R}]_0}{[\mathrm{R}]}$$

$$\text{at } t_{1/2}[\mathrm{R}] = \frac{[\mathrm{R}]_0}{2} \qquad \therefore t_{1/2} = \frac{0.693}{k}$$

  - For zero order reaction $t_{1/2} \propto [\mathrm{R}]_0$ and for first order reaction $t_{1/2}$ is independent of $[\mathrm{R}]_0$.

Integrated Rate Laws for the Reactions of Zero and First Order

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of k
0	R → P	$\frac{d[\mathrm{R}]}{dt} = -k$	$kt = [\mathrm{R}]_0 - [\mathrm{R}]$	$[\mathrm{R}]$ vs t	$\frac{[\mathrm{R}]_0}{2k}$	conc. time^{-1} or $\mathrm{molL^{-1}s^{-1}}$
1	R → P	$\frac{d[\mathrm{R}]}{dt} = -k[\mathrm{R}]$	$[\mathrm{R}] = [\mathrm{R}]_0 e^{-kt}$ or $kt = \ln\left\{\frac{[\mathrm{R}]_0}{[\mathrm{R}]}\right\}$	$\ln[\mathrm{R}]$ vs t	$\frac{\ln 2}{k}$	time^{-1} or s^{-1}

Pseudo First Order Reaction :

- The reactions which appears to be second order reactions but follows first order kinetics.
  e.g.: hydrolysis of ester, inversion of cane sugar.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

- The concentration of water does not get altered much during the course of the reaction. So, the reaction behaves as first order reaction.
  Rate $= k'[CH_3COOC_2H_5][H_2O]$

The term $[H_2O]$ can be taken as constant

Rate $= k[CH_3COOC_2H_5]$

Where $k = k'[H_2O]$

Temperature Dependence of the Rate of a Reaction :

- Most of the chemical reactions are accelerated by increase in temperature.
- For a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.
- The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation $k = \mathrm{A}\, e^{-\mathrm{E}a/\mathrm{RT}}$ where A is the Arrhenius factor or the frequency factor. It is also called pre-exponential factor.
- R is gas constant and E_a is activation energy measured in joules/mole (J mol^{-1}).
- Consider following reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$.
- According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate. It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.

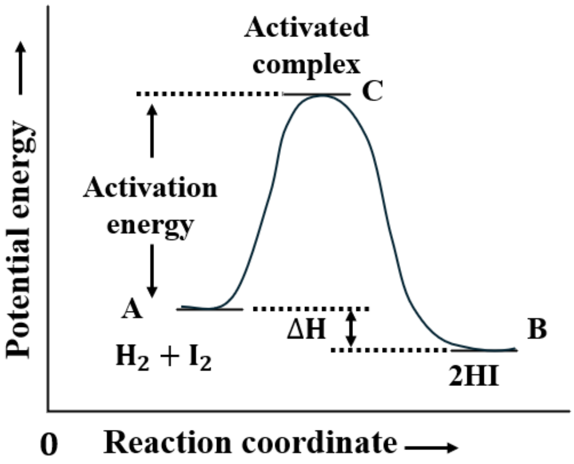
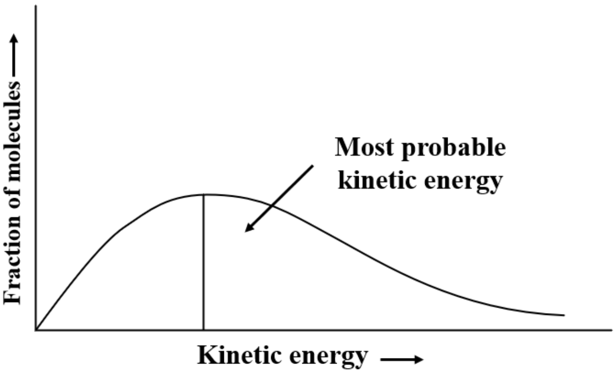


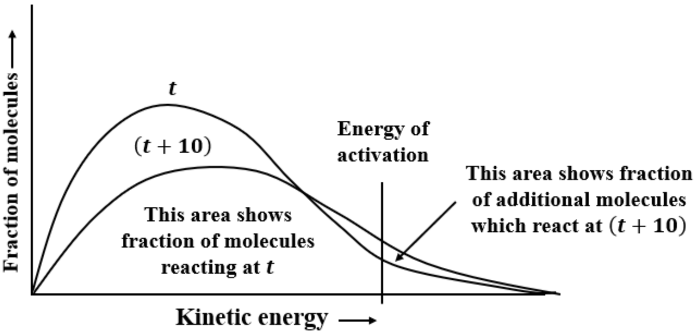
Diagram showing plot of potential energy vs reaction coordinate

- The energy required to form unstable intermediate or activated complex is called activation energy.
- **Plot of fraction of molecules vs Kinetics energy :**
  - ❖ The peak of the curve corresponds to most probable kinetic energy. i.e., the kinetic energy possessed by maximum fraction of molecules.



Distribution curve showing energies among gaseous molecules

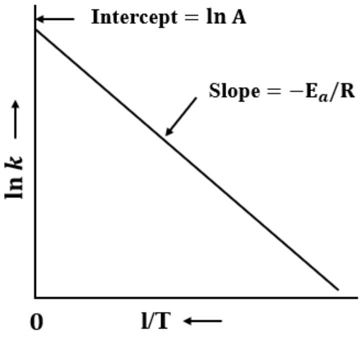
- Increasing temperature, increases the fraction of molecules.



Distribution curve showing temperature dependence of rate of a reaction

- Taking natural logarithm of both sides of Arrhenius equation

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



A plot between ln k and $1/T$

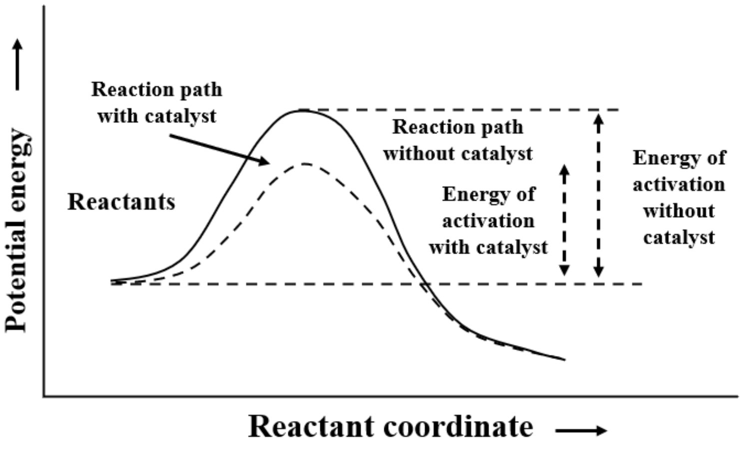
- If k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively.

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

- **Effect of Catalyst :**
  - A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change.

$$2KClO_3 \xrightarrow{\text{Catalyst } MnO_2} 2KCl + 3O_2$$

  - When the added substance reduces the rate of reaction. The substance is then called inhibitor.



Effect of catalyst on activation energy

- It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier.
- A small amount of the catalyst can catalyse a large amount of reactants.
- A catalyst does not alter Gibbs energy, ΔG of a reaction.
- It catalyses the spontaneous reactions but does not catalyse non- spontaneous reactions.
- It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster.
- It catalyses the forward as well as the backward reactions to the same extent.

Collision Theory of Chemical Reactions :

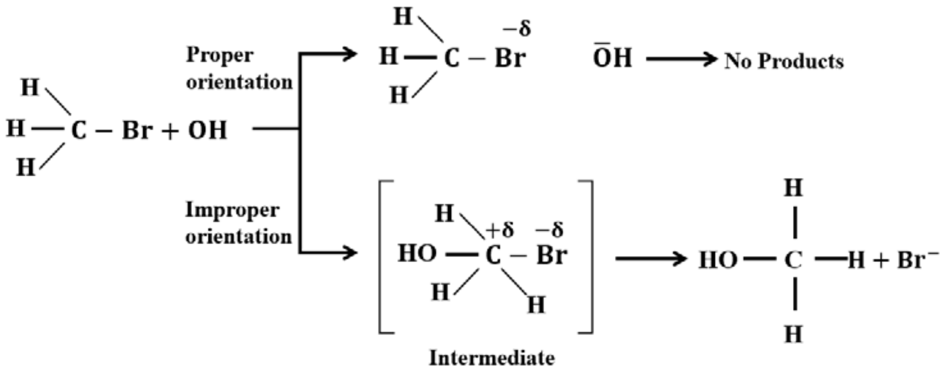
- According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other.
- The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).
- For a bimolecular elementary reaction

  $A + B \rightarrow \text{Products}$

  Rate of reaction can be expressed as

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

  where, Z_{AB} represents the collision frequency of reactants, A and B and $e^{-}E_a/RT$ represents the fraction of molecules with energies equal to or greater than E_a.
- The collisions in which molecules collide with sufficient kinetic energy (called threshold energy*) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as **effective collisions**.



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

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

  In collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

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