Chapter_04

Chemical Kinetics

- 1. Chemical kinetics is the branch of Chemistry which deals with the study of reaction rates and their mechanisms.
- 2. The **speed** or the **rate of a chemical reaction** can be defined as the change in concentration of reactants or products in unit time.
- **3.** The **average rate of reaction** is the appearance of product or disappearance of reactants over a period of time interval.

$$I_{\rm av} = -\frac{\Delta[R]}{\Delta t} = + \frac{\Delta[P]}{\Delta t}$$

4. Reaction rate, at a particular moment of time is called **instantaneous rate** of the reaction.

$$\therefore \qquad r_{\text{inst}} = \frac{-d[R]}{dt} = +\frac{d[P]}{dt}$$

As, $\Delta t \rightarrow 0$

Average rate approaches to instantaneous rate.

Unit of the rate of reaction

Rate of reaction
$$= \frac{dx}{dt} = \frac{\text{mol } L^{-1}}{s}$$

- **5.** Rate of a chemical reaction depends upon the experimental conditions, like concentration of one or more reactants (pressure in case of gases), temperature, catalyst and surface area of the reactants.
- 6. Rate law is the expression in which the 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. It cannot be decided from the balanced chemical equation, i.e. theoretically. It has to be determined experimentally.

7. The sum of the powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

It can be zero or have fractional value but molecularity of a reaction cannot be zero or a non-integer. It is always an integer and cannot be more than three.

- 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.
- 9. Rate constant (k) is the rate of chemical reaction when concentration of each reactant is unity. The rate constant is also called the specific reaction rate.

For *n*th order of reaction,

Units of $k = (\text{mol } L^{-1})^{1-n} (\text{time})^{-1}$, where, n = order of reaction.

10. Half-life $(t_{1/2})$ is the time in which the concentration of a reactant is reduced to one half of its initial

concentration. For first order reaction, $t_{1/2} = 0.693/k$.

11. Given table summarises the mathematical features of integrated laws of zero and first order reactions.

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of <i>k</i>
0	$R \rightarrow P$	d[R]/dt = -k	$kt = [R]_0 - [R]$	[<i>R</i>] vs <i>t</i>	$[R]_0/2k$	Conc. time ^{-1} or mol L ^{-1s^{-1}}
1	$R \rightarrow P$	d[R]/dt = -k[R]	$[R] = [R]_0 e^{-kt}$ or $kt = \ln \{[R]_0 / [R]\}$	ln [<i>R</i>] vs <i>t</i> (with negative slope) $\log \frac{[R_0]}{[R]}$ vs <i>t</i> (with positive slope)	$\ln 2/k = \frac{0.693}{k}$	time ⁻¹ or s ⁻¹

Integrated Rate Laws for the Reactions of Zero and First Order

- 12. The reactions which are not actually of first order but behave, so due to changed conditions are called pseudo first order reactions. For example, hydrolysis of ethyl acetate, as in this case concentration of water is not considered in calculation because its concentration does not get changed much with time.
- **13.** For a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.

Temperature coefficient is the ratio of rate constant at temperature (T + 10) K to the rate constant at temperature T (K).

Temperature coefficient = $\frac{\text{Rate constant } (k) \text{ at } (T + 10) \text{ K}}{\text{Rate constant } (k) \text{ at } T \text{ K}}$

14. The temperature dependence of rate for a chemical reaction is expressed by **Arrhenius equation**.

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

Where, *A* is the Arrhenius factor or the frequency factor, also called **pre-exponential factor**.

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

• The plot of ln *k* vs 1/*T* gives a straight line with slope $= -\frac{E_a}{D}$ and intercept = ln *A*

• Rate constants k_1 and k_2 at two different temperatures T_1 and T_2 repectively can written as,

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

- **15.** Activation energy (E_a) is the extra energy required by the reactant molecules that results into effective collision between them to form the products.
- Threshold energy is the minimum energy which the colliding molecules must have for effective collisions. (Collisions which lead to the formation of product molecules).
- **17.** According to **collision theory**, rate collisions which lead to the formation of product molecules

 $= Z_{AB} e^{-E_a/RT}$ where, Z_{AB} = collision frequency of the reactants *A* and *B*.

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