10

CHAPTER

kinetics

- **Chemical kinetics** is the branch of chemistry which deals with rate and mechanism of chemical reaction.
- The speed with which the reactants are converted into products is called **rate of the reaction**.
- The rate of reaction is defined as change in the concentration of any one of the reactants or products per unit time.
- The rate of the reaction may be expressed in either of the two ways:
  (i) The rate of the disappearance or decrease in concentration of reactant with time.
  (ii) The rate of appearance or increase in concentration of product with time.
- The significance of the negative sign in case of expressing rate of reaction in term of reactants is important. We know that rate is always positive, as also obtained from the rate of formation of products. Therefore, minus sign is put before dA/dt so that rate is positive
  e.g., $A \rightarrow B$.
  Rate of reaction = $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$
- The reaction rate cannot be determined by dividing total change in concentration by the time taken as in case of mechanical speed.
- As the reaction progresses, the rate of reaction decreases, becasue the concentration of the reactants decreases.
- The rate of a reaction that does not involve gases, does not depend upon pressure.
- The rate constant of a reaction increases with increase of temperature but not affected by concentration or catalyst.
- The rate does not depend upon the reactant present in large excess.
- The rate of reaction must be expressed with reference to particular moment of time.
- The average rate can be calculated by dividing the concentration difference by the time interval.
- The rate of reaction is not constant but it decreases with time reaching a value zero when the reaction is complete.
- The rate of change of concentration of any one of the reactants or products at a given time is called instantaneous rate.

- The time taken by a reaction to proceed to a certain definite stage (98%) is called **life time of the reaction**.
- The times, the reaction takes to proceed midway (50%) is called **half life period** ($t_{1/2}$).
- Law of the mass action was given by the two Norwegian Scientist **Guldberg** and **Waage**.
- **Rate law** or rate equation are the mathematical expression which expresses the observed rate of a reaction in terms of the concentration of the reacting species.
  e.g. $aA + bB \rightarrow$ product
  $$\text{Rate} = k[A]^a[B]^b.$$
- Rate constant of a reaction is the rate of the reaction when the molar concentration of each of the reactant is unity.
- **Order of the reaction** is the sum of exponents of the concentration terms in the rate law.
- Order of reaction can be zero, integer or fractional.
- The units of rate constant depend upon the order of reaction.
- The specific rate constant of a first order reaction depends only on temperature.
- A reaction is of first order when the rate is linearly related to the concentration of the reactant.
- For the first order reaction $A \rightarrow$ products, plot of log $[A]$ *vs* time is linear with negative slope.

Examples:

1. *Zero order reaction* : $A \xrightarrow{k_0}$ Product ; $\dfrac{-d[A]}{dt} = k_0$
2. *A first order reaction :* $A \xrightarrow{k_1}$ Product, $\dfrac{-d[A]}{dt} = k_1\,[A]$ or $k_1 = -\dfrac{1}{A} \times \dfrac{d[A]}{dt}$
3. A second order reaction

   (i) $2A \xrightarrow{k_2}$ product, $\dfrac{-d[A]}{dt} = k_2[A]^2$ or, $k_2 = \dfrac{-1}{[A]^2} \times \dfrac{d[A]}{dt}$

   (ii) $A + B \xrightarrow{k_2}$ product, $\dfrac{-d[A]}{dt} = k_2[A][B]$ or, $k_2 = \dfrac{-1}{[A][B]} \times \dfrac{d[A]}{dt}$

- Certain bimolecular reactions which follow the kinetics of first order are called pseudounimolecular reactions.
- Hydrolysis of ester in presence of alkaline medium is a second order reaction.
- The units of the rate constant can be remembered by this formula ; liter^{n-1} mole^{1-n} sec^{-1} where n is the order of the reaction.

  Molecularity of a reaction is defined as the number of reacting molecules which collide simultaneously to bring about a chemical reaction.

  e.g. $N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$ (Unimolecular)

  $H_2 + I_2 \longrightarrow 2HI$ (Bimolecular)

Difference between Order and Molecularity

	Order	Molecularity
1.	It is an experimental quantity.	It is a theoretical concept.
2.	It is the sum of the powers of the concentration terms in rate law.	It is the number of species which simultaneously collide.
3.	It may have fractional values.	It has only whole number values.
4.	It can be zero.	It cannot be zero.

- The finer the particles, the faster is the rate, hence rate of the chemical reaction is increased when the particle size of the solid substance is decreased.
- According to collision theory of reaction rates, the rate of reaction depends on energy factor and orientation factor.
- The number of collision that takes place per second per unit volume of the reaction mixture is known as **collision frequency** (z).
- The collision which actually produce the products and result in the chemical reaction are called **effective collisions**.
- The minimum amount of energy which the colliding molecules must possess is known as **threshold energy**.
- Collision frequency is proportional to the square root of the absolute temperature. *i.e.* $z \propto \sqrt{T}$.
- Increase in the rate of reaction with the rise in temperature is mainly due to the increase in the number of effective collisions.
- The excess energy (above the average energy of the reactant) required by the reactant to undergo chemical reaction is called **activation energy**.
  Activation energy = threshold energy – average kinetic energy of the reactants.
- Low activation energy ⇒ Fast reaction
  High activation energy ⇒ Slow reaction.
- **Activation energy barrier** is the energy acquired by the reactant molecules to cross the threshold energy to form products.
- Substances which increase the rate of reactions (both backwards and forwards) and either remain unaltered during the reaction or are regenerated after the reaction are called **catalysts**.
- Although a catalyst speeds up the reactions but it does not shift the position of equilibrium.
- The catalyst does not change ΔE of the reaction means that the addition of catalyst does not change energies of reactant (E_r) and product (E_p) so that ΔE and ($E_p - E_r$) remains same.
- The number of reacting species which collide simultaneously to bring about a chemical reaction is called molecularity.
- Molecularity of reaction cannot be zero. It has a whole number values only. *e.g.*, 1, 2, 3, etc.
- $A \rightleftharpoons B$.
  Net rate of reaction = rate of forward reaction – rate of backward reaction.

- An endothermic reaction which proceeds with the decrease in volume will give maximum yield of the products at high pressure and temperature.
- The state at which the concentration of reactants and products do not change with time is called a **state of equilibrium**.
- The reaction which takes place in both forward and backward direction is called **reversible reaction**.

  e.g., $H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2HI_{\,(g)}$.
- The chemical reaction in which the products formed do not combine to give back the reactant are known as **irreversible reaction**.
- The equilibrium can be approached from either direction and catalyst does not alter the equilibrium point.
- The rate of chemical reaction is directly proportional to the product of the molar concentration of the reactants at a constant temperature. This is known as **law of mass action**.

  e.g. $A + B \rightarrow$ product.

  $\text{Rate} \propto [A]\,[B]$
- Photochemical reaction takes place only in presence of light as each reactant molecule absorbs radiant energy.
- H_2 dissociates in presence of light only when Hg vapours are present. This is an example of **photosensitization**.
- Reaction which takes place in fraction of second is called fast reaction such as photosynthetic reaction has half life one pico second (10^{-12} s).
- Change in energy (ΔE) for the exothermic reaction are negative

  $\Delta E = E_a$ (forward) $- E_a$ (backward).
- The change in energy (ΔE) for the endothermic reaction are positive

  $\Delta E = E_a$ (forward) $- E_a$ (backward).
- Molecularity is a theoretical concept whereas order of the reaction is determined experimentally.
- For the feasibility of a reaction, the free energy should decrease (ΔG should be negative).
- The reaction rate can not be determined by dividing the total change in concentration by the time taken, therefore, the reaction must be expressed with reference to a particular moment of time, It is therefore also called instantaneous rate of reaction.
- Rate of radioactive disintegration follows 1st order kinetics.
- The population growth follows the 1st order kinetic, when the death and birth rates are equal.
- Order of the reaction cannot be more than 3rd order, but there is some exception.
- Reaction between iodide ion and iodate ion follow fifth order kinetic in acidic medium.

  Rate $= dx/dt = K\,[I^-]\,[IO_3^-]^2\,[H^+]^2$

  $n = 1 + 2 + 2 = 5$.

End