CHEMICAL KINETICS

- Measurement of rates of reactions proceeding under given conditions of temperature, pressure and concentration
- Useful in determining the factors which influence rates of reactions as well as in understanding mechanisms of reactions

RATE OF A REACTION

Definition:

It is defined as the change in concentration of any of the reactants in unit time.

$$A \longrightarrow B$$

$$\text{Rate} = \frac{-\,[\text{Change in the concentration of the reactants}]}{(\text{Change in time})}$$

r = - d[A] / dt

r = k[A]

where r = rate constant

k = proportionality constant

RATE CONSTANT

Definition:

It is defined as the change in conconcentrationof reactants or products per unit time in a reaction in which all the reactants are at unit concentration.

UNIT OF RATE OF A REACTION

$$\text{unit of rate} = \frac{\text{unit of concentration}}{\text{unit of time}}$$

$$\text{mol L}^{-1}\text{s}^{-1}$$

DIFFERENCE BETWEEN RATE AND RATE CONSTANT OF A REACTION

S.no	Rate of a reaction	Rate constant of a reaction
1	It represents the speed at which the reactants are converted into products at any instant.	It is a proportionality constant
2	It is measured as decrease in the concentration of the reactants or increase in the concentration of products.	It is equal to the rate of reaction, when the concentration of each of the reactants in unity
3	It depends on the initial concentration of reactants.	It does not depend on the initial concentration of reactants.

ORDER OF A REACTION

It is the sum of the powers of concentration terms involved in the experimentally determined rate law.

It is the minimum number of molecules or atoms of reactants whose concentrations determine the velocity or rate of a reaction.

MOLECULARITY OF A REACTION

It is the total number of reactant species that are involved in an elementary step.

It is the minimum number of molecules or atoms of the reactants necessary for the reaction to take place.

DIFFERENCE BETWEEN ORDER AND MOLECULARITY OF A REACTION

S.no	Order of a reaction	Molecularity of a reaction
1	It is the sum of the powers of concentration terms involved in the experimentally determined rate law.	It is the total number of reactant species that are involved in an elementary step.
2	It can be zero (or) fractional (or) integer	It is always a whole number, cannot be zero or a fractional number.
3	It is assigned for a overall reaction.	It is assigned for each elementary step of mechanism.

RATE LAWS

Let us consider a reaction,

$$A \rightarrow B$$

If –dC = decrease in concentration of A in a time dt

C = molecular concentration of A

Then, $-dC/dt \propto C$

$$-dC/dt = KC$$

Where K = rate constant

For a reaction, 2A → products

$$-dC/dt = KC^2$$

For a reaction, A + B → products

$$-dC/dt = KC_AC_B$$

ZERO ORDER REACTIONS

The reaction in which the rate is entirely independent of the concentration of the reactant is known as zero order reaction.

EXAMPLES FOR ZERO ORDER REACTIONS

1. Photochemical reaction between hydrogen and chlorine to form hydrogen chloride
2. Thermal decomposition of HI on a gold surface
3. Some enzyme catalysed reaction

CHARACTERISTICS OF ZERO ORDER REACTIONS

1. The rate of the reaction does not depend on any concentration term
2. The sum of the powers of the concentration terms that occur in the rate equation is zero.
3. The half life period of a zero order reaction is directly prportional to the initial concentration of the reactant.

FIRST ORDER REACTIONS

The reaction in which the rate depends on one concentration term only is known as zero order reaction.

In first order reaction, the rate is proportional to the concentration of the reactant.

EXAMPLES FOR FIRST ORDER REACTIONS

1. Decomposition of hydrogen peroxide in aqueous solution in presence of Pt
2. Hydrolysis of methyl acetate in presence of acids
3. Inversion of cane sugar in presence of acid
4. Decomposition of nitrogen pentoxide in carbon tetrachloride
5. Radioactive decay of an unstable nucleus.

CHARACTERISTICS OF FIRST ORDER REACTIONS

1. The rate of the reaction depends on one concentration term only
2. The rate of the reaction is proportional to the concentration of the reactant.
3. The sum of the powers of the concentration terms that occur in the rate equation is one.
4. The rate constant k will be independent of the units in which the concentration of the reactant is expressed.
5. The half life period of a first order reaction is independent of the initial concentration of the reactant.

SECOND ORDER REACTIONS

The rate of the reaction depends on two concentration terms.

The rate of the reaction is proportional to the square of the concentration of one substance or to the product of the concentration of two reactants.

EXAMPLES FOR SECOND ORDER REACTIONS

1. Conversion of ozone into oxygen at 100° C
2. Decomposition of chlorine monoxide at 200° C
3. Decomposition of nitrous oxide by heat
4. Thermal decomposition of acetaldehyde
5. Saponification of esters

CHARACTERISTICS OF SECOND ORDER REACTIONS

1. The rate of the reaction depends on two concentration terms
2. The sum of the powers of the concentration terms that occur in the rate equation is two
3. The half-life period of a second order reaction is inversely proportional to the initial concentration of the reactants.