

UNIT - 4

Chemical Kinetics

The branch of chemistry, which deals with the rate of chemical reactions, the factors affecting the rate of reactions and the mechanism of the reaction, is called chemical kinetics.

Chemical Reactions on the Basis of Rate of Reaction

- (i) **Fast/Instantaneous reactions** Chemical reactions which complete in less than 1ps (10^{-12} s) time, are known as fast reaction. It is practically impossible to measure the speed of such reactions, e.g. ionic reactions, organic substitution reactions.
- (ii) **Slow reactions** Chemical reactions which completes in a long time from some minutes to some years are called slow reactions. e.g. rusting of iron, transformation of diamond etc.
- (iii) **Moderately slow reactions** Chemical reactions which are intermediate between slow and fast reactions are called moderately slow reactions.

Rate of Reaction

Rate of a chemical reaction is the change in the concentration of any one of the reactants or products per unit time. It is expressed in $\text{mol L}^{-1} \text{s}^{-1}$ or Ms^{-1} or atm time^{-1} units.

Rate of reaction

$$= \frac{\text{decrease/increase in the concentration of reactant/product}}{\text{time taken}}$$

This rate of reaction is known as **average rate of reaction** (r_{av}). (r_{av} can be calculated by dividing the concentration difference by the time interval).

For a chemical reaction,



$$\begin{aligned} \text{Average rate of reaction } (r_{av}) &= -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} \\ &= \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t} \end{aligned}$$

$$\text{Rate of disappearance of } A = -\frac{\Delta[A]}{\Delta t}$$

$$\text{Rate of disappearance of } B = -\frac{\Delta[B]}{\Delta t}$$

$$\text{Rate of appearance of } C = \frac{\Delta[C]}{\Delta t}$$

$$\text{Rate of appearance of } D = \frac{\Delta[D]}{\Delta t}$$

Instantaneous Rate of Reaction

Rate of a chemical reaction at a particular moment of time, is known as instantaneous rate of reaction.

For reaction,



$$r_{inst} = -\frac{\Delta[R]}{\Delta t} \text{ or } \frac{\Delta[P]}{\Delta t} \text{ as } \Delta \rightarrow d$$

$$\Rightarrow r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Methods for measuring reaction rate (i) pH measurement, (ii) change in optical activity, (iii) change in pressure, (iv) change in conductance.

Slowest step of a reaction was called rate determining step by van't Hoff.

Factors Affecting Rate of Reaction

- (i) Nature and concentration of reactant
- (ii) Temperature
- (iii) Surface area of reactant
- (iv) Radiations and catalyst
- (v) Pressure of gas

Rate Law Expressions

It is defined as a mathematical expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power.

For a chemical reaction,



According to the law of mass action,

$$\text{Rate} \propto [A]^a [B]^b = k[A]^a [B]^b$$

But experimentally, it is observed that the rate of reaction is found to depend upon ' α ' concentration terms of A and ' β ' concentration terms of B . Then,

$$\text{Rate} \propto [A]^\alpha [B]^\beta = k [A]^\alpha [B]^\beta$$

where, $[A]$ and $[B]$ molar concentrations of A and B respectively and k is the velocity constant or rate constant. The above expression is known as **rate law**.

Rate Constant or Specific Reaction Rate

In the above expression, k is called rate constant or velocity constant.

Rate constant may be defined as the specific rate of reaction when the molar concentrations of the reactants is taken to be unity, i.e.

$$\text{Rate} = k, \text{ if } [A] = [B] = 1$$

Units of rate constant or specific reaction rate for a n th order reaction is given as

$$k = \frac{1}{\text{Time}} \times \frac{1}{[\text{Conc.}]^{n-1}}$$

Characteristics of rate constant

- (i) Greater the value of rate constant, faster is the reaction.
- (2) Each reaction has a particular value of rate constant at a particular temperature.
- (iii) The value of rate constant for the same reaction changes with temperature.
- (iv) The value of rate constant for a reaction doesn't depend upon the concentration of the reactants.

Order and Molecularity of a Reaction

Find of plain order and molecularity separately given comparison differences

Order of reaction	Molecularity of reaction
<p>1. Order of reaction is the sum of the concentration terms on which rate of reaction actually depends. Or It is also defined as sum of the exponents of the molar concentrations in the rate law equation.</p>	<p>Molecularity of a reaction is the number of atoms, ions or molecules that must collide with one another to form products in a chemical reaction.</p>
<p>2. It can be fractional as well as zero.</p>	<p>It cannot be zero or fractional.</p>
<p>3. It is an experimentally determined term.</p>	<p>It is theoretically determined term.</p>
<p>4. Order of reaction is applicable to elementary as well as complex reactions.</p>	<p>Molecularity is applicable only to elementary reactions.</p>
<p>5. Negative order reaction is also possible, e.g. $2\text{O}_3 \longrightarrow 3\text{O}_2$ Rate = $k[\text{O}_3]^2[\text{O}_2]^{-1}$ Order w.r.t O_2 is -1.</p>	<p>Molecularity can never be negative.</p>
<p>6. Types of reactions depending upon orders</p> <p>(i) Zero order reaction</p> <p>(I) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \xrightarrow{h\nu} 2\text{HCl}$</p> <p>(II) $2\text{NH}_3 \xrightarrow{\text{Pt}} \text{N}_2 + 3\text{H}_2$</p> <p>(ii) First order reaction</p> <p>(I) $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$</p> <p>(II) Radioactive disintegration</p> <p>(III) Inversion of cane sugar.</p> <p>(iii) Second order reaction</p> <p>(I) $2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$</p> <p>(II) Alkaline hydrolysis of ester (saponification)</p> <p>(iv) Third order reaction</p> <p>$2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$</p>	<p>Types of reactions depending upon molecularity</p> <p>(i) Unimolecular reaction, $\text{N}_2\text{O}_4(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$</p> <p>(ii) Bimolecular reactions, $2\text{HI}(\text{g}) \longrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$</p> <p>(iii) Trimolecular reactions, $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$</p>

Integrated Rate Equation for Zero Order Reactions

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants.

$$k_0 = \frac{1}{t} \{[A]_0 - [A]\}$$

[where, $[A]_0$ is initial concentration and $[A]$ is final concentration]

$$t = t_{1/2} \text{ when } [A] = \frac{[A]_0}{2}$$

Half-life period, $t_{1/2} = \frac{[A]_0}{2k_0}$

Units of rate constant, $k_0 = \text{mol L}^{-1}\text{s}^{-1} = \text{unit of rate}$

For zero order gaseous reactions,

$$k_0 = \frac{1}{t} [p_0 - p] \quad \text{and} \quad t_{1/2} = \frac{p_0}{2k_0}$$

Integrated Rate Equation for First Order Reactions

First order reaction means that the rate of the reaction is proportional to the first power of the concentration of the reactant.

$$k_1 = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \Rightarrow [A] = [A]_0 e^{-k_1 t}$$

Half-life period ($t_{1/2}$) It is concentration independent term.

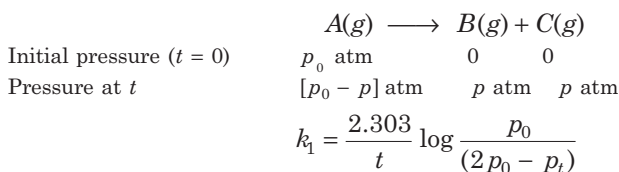
$$t = t_{1/2}, [A] = \frac{[A]_0}{2}$$

Amount of a substance after n half-lives = $\frac{[A]_0}{2^n} \Rightarrow t_{1/2} = \frac{0.693}{k_1}$

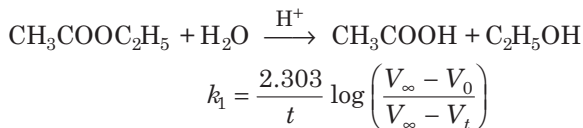
For such reactions, $t_{75\%} = 2 \times t_{50\%} \Rightarrow t_{99.9\%} = 10 \times t_{1/2}$

All radioactive changes follow the first order kinetics.

Integrated rate equation for first order gaseous reactions,



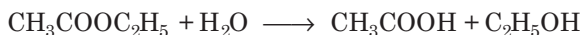
For first order chemical reactions,



(V_0 , V_t and V_∞ are the volumes of NaOH solution used for the titration of same volume of the reaction mixture after times 0, t and ∞ respectively.)

Pseudo First Order Reaction

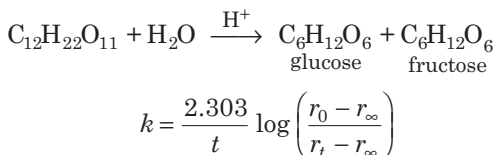
Chemical reactions which appear to be of higher order but actually are of the lower order are called pseudo first order reactions. In case of pseudo first order reaction, chemical reaction between two substances takes place and one of the reactant is present in excess, e.g. hydrolysis of ester.



So, in this reaction,

$$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5]$$

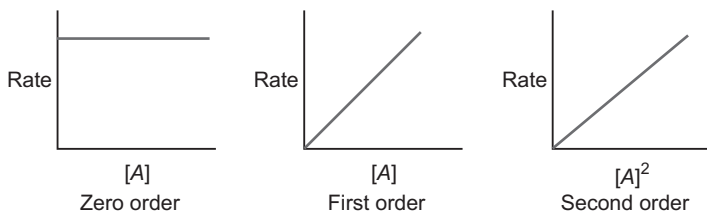
For chemical reaction,



[r_0 , r_t and r_∞ are the polarimetric readings at $t=0$, t and ∞ respectively.]

Methods to Determine Order of Reaction

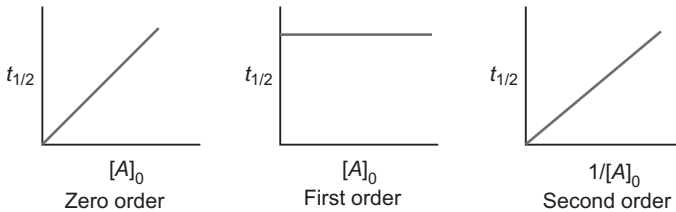
- (i) **Graphical method** In this method, rate of reaction is plotted against the concentration.



PAGE NO. 7

- (ii) **Initial rate method** In this method, the order of a reaction is determined by varying the concentration of one of the reactants while others are kept constant.
- (iii) **Integrated rate law method** In this method out of different integrated rate equation which gives the most constant value for the rate constant corresponds to a specific order of reaction.
- (iv) **Half-life period ($t_{1/2}$) method** In general half-life period ($t_{1/2}$) of a reaction of n th order is related to initial concentration of the reactant as

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$



This method is employed only when the rate law involved only one concentration term.

- (v) **Ostwald's isolation method** This method is employed in determining the order of complicated reactions by isolating one of the reactants so far as its influence on the reaction rate is concerned.

Temperature Dependence of Rate of a Reaction

For every 10°C rise in temperature, the rate of reaction becomes double, but only 16% collisions increases. It can be explained by Arrhenius equation.

Temperature coefficient is the ratio of rate constant of a reaction at two temperature differing by 10. Temperature selected are usually 298 K and 308 K.

$$\text{Temperature coefficient} = \frac{k_{t+10}}{k_t} \approx 2 \text{ to } 3$$

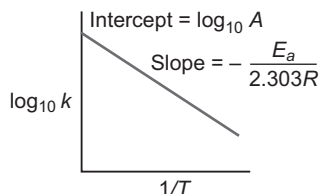
Arrhenius Equation

Arrhenius equation is a mathematical expression to give a quantitative relationship between rate constant and temperature, and the expression is

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

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

or $\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$



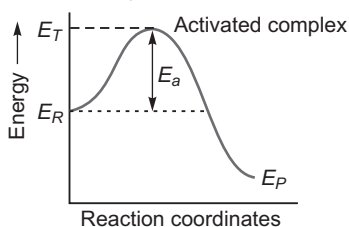
where, A = frequency or Arrhenius factor. It is also called pre-exponential factor

R = gas constant

E_a = activation energy

Activated Complex (or Transition State)

Activated complex is the highest energy unstable intermediate between the reactants and products and gets decomposed immediately (having very short life), to give the products. In this state, bonds of reactant are not completely broken while the bonds of products are not completely formed.



Threshold energy (E_T) The minimum amount of energy which the reactant must possess in order to convert into products is known as threshold energy.

Activation energy (E_a) The additional amount of energy, required by the reactant so that their energy becomes equal to the threshold value is known as activation energy.

$$\Rightarrow E_a = E_T - E_R$$

Lower the activation energy, faster is the reaction.

Different reactions have different rates because their activation energies are different. Larger the value of E_a , smaller the value of rate constant and greater is the effect of a given temperature rise on K .

Important points about Arrhenius equation

(i) If k_2 and k_1 are rate constant at temperature T_2 and T_1 then

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

PAGE NO. 9

- (ii) Fraction of molecules with energy equal to or greater than the activation energy is called Boltzmann factor and is given by

$$x = \frac{n}{N} = e^{-E_a/RT} \quad \text{and} \quad \log_e x = \frac{-E_a}{2.303 RT}$$

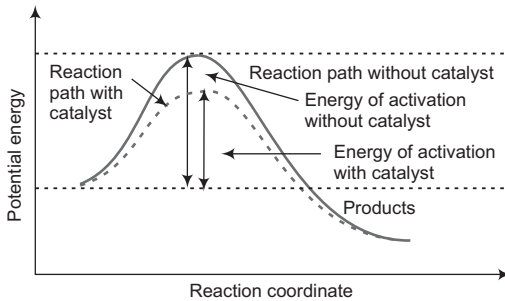
- (iii) E_a is constant for a particular reaction.
 (iv) E_a doesn't depend on temperature, volume, pressure, etc., but gets affected by catalyst.

In the Arrhenius equation, when $T \rightarrow \infty$ then $k = A e^0 = A$ when $E_a = 0$, $k = A$ and the rate of reaction becomes independent of temperature.

Role of Catalyst in a Chemical Reaction

A catalyst is a chemical substance which alters the rate of a reaction without itself undergoing any permanent chemical change.

In the chemical reactions, catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence, lowering the potential energy barrier as shown.



In the presence of catalyst, activation energy decreases and hence,

$$\frac{k_P}{k_a} = e^{(E_a - E_P)/RT} = e^{\Delta E/RT}$$

where, P denotes presence of catalyst and a denotes absence of catalyst.

Theory of Reaction Rates

Collision Theory

According to this theory, the reactant molecules are assumed to be hard spheres and the reaction is postulated to occur, when molecules collide with each other.

The number of collisions between the reacting molecules taking place per second per unit volume is known as **collision frequency** (Z_{AB}).

But only those collisions in which the colliding species are associated with certain minimum amount of energy and collide in proper orientation result in the product formation, such collisions are called **fruitful collisions** or **effective collision**.

$$\begin{aligned} \text{Here, rate} &= -\frac{dv}{dt} = \text{collision frequency} \times \text{fraction of effective collision} \\ &= Z_{AB} \times f = Z_{AB} \times e^{-E_a/RT} \end{aligned}$$

where, Z_{AB} represents the collision frequency of reactants, A and B $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a .

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

$$\text{So,} \quad \text{rate} = PZ_{AB} e^{-E_a/RT}$$

The Activated Complex Theory or Transition State Theory



This theory is based on the fact that bond cleavage and bond formation, involved in a chemical reaction, must occur simultaneously. Hence, the reactants are not converted directly into the products. There is an energy barrier or activated complex [intermediate product with partially formed bond] between the reactants and products. The reactants must cross this energy barrier before converting into products. The height of the barrier determines the threshold energy.

Photochemical Reactions

Chemical reactions, that occur on exposure to visible radiation are called photochemical reactions.

(i) The rate of a photochemical reactions is affected by the intensity of light.

(ii) Temperature has little effect on photochemical reactions.

Quantum yield or quantum efficiency of a photochemical reaction,

$$\phi = \frac{\text{number of reactant molecules reacting in a given time}}{\text{number of photons (quanta) of light absorbed in the same time}}$$