Chapter 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

Fast/instantaneous reactions

Chemical reaction which completes in less than Ips (10^{-12} s) time, IS known as fast reaction. It IS practically impossible to measure the speed of such reactions, e.g., ionic reactions. organic substitution reactions.

Slow reactions

Chemical re actions 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.

Moderately

slow reactionsChemical 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 mol L^{-1} s^{-1} or Ms^{-1} or atm $time^{-1}$ units.

Rate of reaction

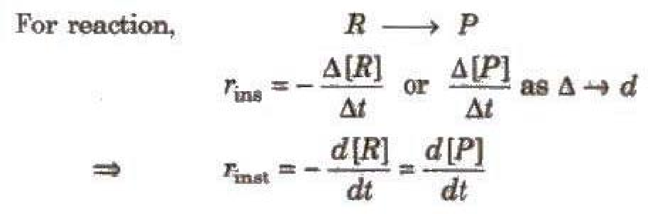
= (decrease/increase in the concentration of reactant/product/time taken)

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,

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

For reaction,



For reaction, $R \longrightarrow P$

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

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

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

1. Nature and concentration of reactant
2. Temperature
3. Surface area of reactant
4. Radiations and catalyst
5. Pressure of gas

Rate Law Expressions

According to the law of mass action,

For a chemical reaction,

$aA + bB \rightarrow$ Products

Rate α $[A]^a [B]^b = k[A]^a [B]^b$

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,

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

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

Rate Constant

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.,

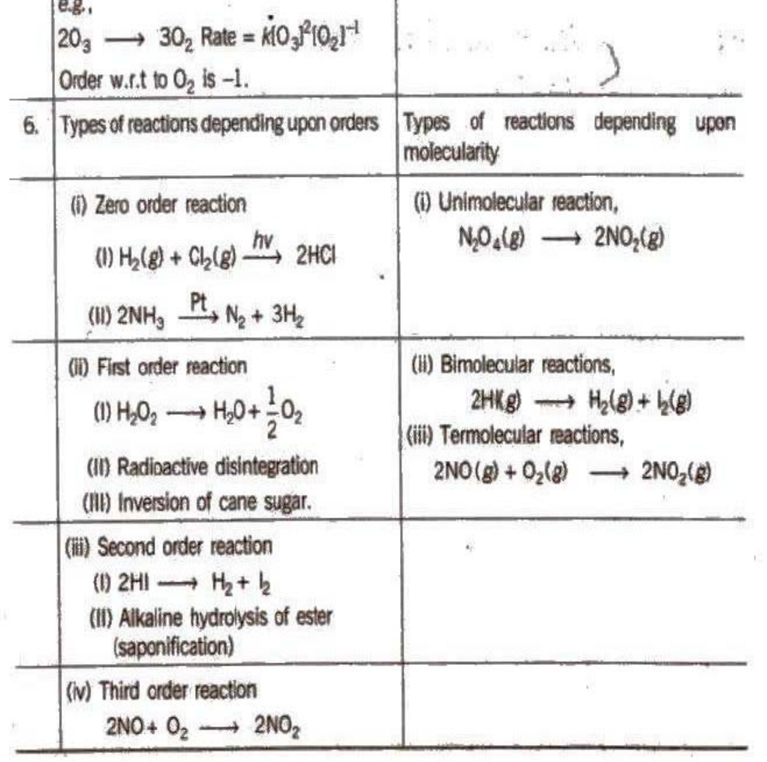
Rate = k, if [A] = [B] = 1

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

$K = (1/\text{Time}) \times (1/[\text{Conc.}]^{n-1})$

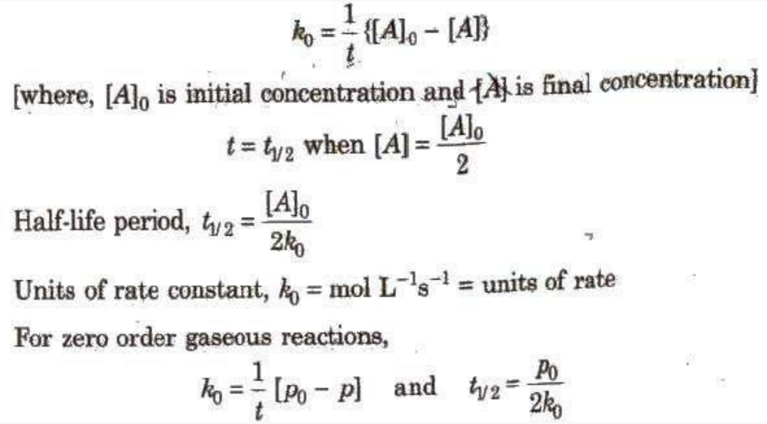
Characteristics of rate constant

1. Greater the value of rate constant, faster is the reaction.



	e.g., $2O_3 \longrightarrow 3O_2$ Rate = $k[O_3]^2[O_2]^{-1}$ Order w.r.t to O_2 is –1.	
6.	Types of reactions depending upon orders	Types of reactions depending upon molecularity
	(i) Zero order reaction (I) $H_2(g) + Cl_2(g) \xrightarrow{hv} 2HCl$ (II) $2NH_3 \xrightarrow{Pt} N_2 + 3H_2$	(i) Unimolecular reaction, $N_2O_4(g) \longrightarrow 2NO_2(g)$
	(ii) First order reaction (I) $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$ (II) Radioactive disintegration (III) Inversion of cane sugar.	(ii) Bimolecular reactions, $2HI(g) \longrightarrow H_2(g) + I_2(g)$ (iii) Termolecular reactions, $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$
	(iii) Second order reaction (I) $2HI \longrightarrow H_2 + I_2$ (II) Alkaline hydrolysis of ester (saponification)	
	(iv) Third order reaction $2NO + O_2 \longrightarrow 2NO_2$	

Integrated Rate Equation for Zero Order Reactions



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

[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 = mol $L^{-1}s^{-1}$ = units 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

Initial pressure	p_0 atm	0	0
Pressure at t	$[p_0 - p]$ atm	p atm	p atm

$$k_1 = \frac{2.303}{t} \log \frac{p_0}{(2p_0 - p_t)}$$

For first order chemical reactions,

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

$$k_1 = \frac{2.303}{t} \log\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$

(V_o, V_t, and $_\infty$ 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 order reactions. In case of pseudo first order reaction, chemical reaction between two sr” stances takes place and one of the reactant is present in execess. e.g., hydrolysis of ester.

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

So, in this reaction,

$$\text{Rate} = k\,[CH_3COOC_2H_5]$$

For chemical reaction,

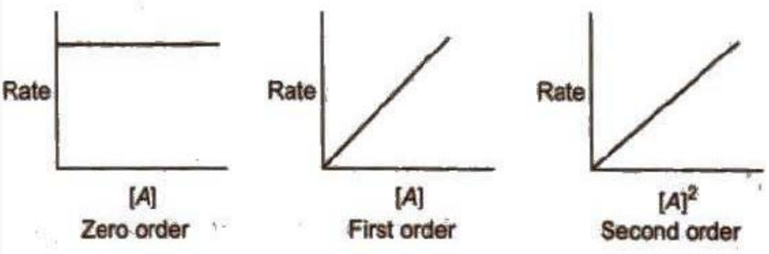
$$\underset{}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$k = \frac{2.303}{t} \log\left(\frac{r_0 - r_\infty}{r_t - r_\infty}\right)$$

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

Methods to Determine Order of Reaction

(i) Graphical method



(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

Temperature coefficient = $_{t} + 10/_{t} \approx 2$ to 3

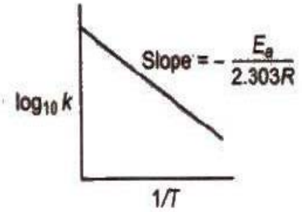
Arrhenius Equation

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



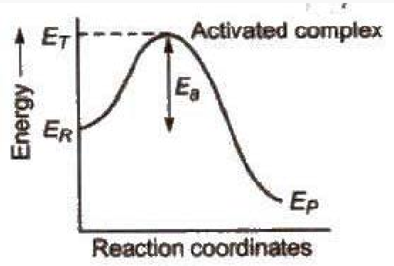
where, A = frequency or Arrhenius factor. It is also called pre-exponential factor

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 (ET) 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.

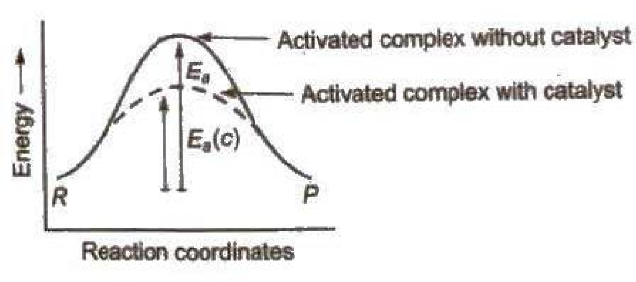
$E_a = E_T - E_R$ Lower the activation energy, faster is the reaction.

becomes independent 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.**

Here, rate = – (dv/dt) = collision frequency x fraction of effective collision

$= Z_{AB} \times f = Z_{AB} \times e^{-E_a/RT}$

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 Ea.

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

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

The Activated Complex Theory or Transition State Theory

- Chemical kinetics:
  It is the branch of chemistry that deals with the study of reaction rates and their mechanisms.
- Rate of reaction:
  It is the change in concentration of reactant (or product) in unit time.
- The unit of rate of reaction is mol $L^{-1}s^{-1}$.
- $A + B \rightarrow C + D$

  Rate of disappearance of $A = \frac{-d[A]}{dt}$

  where d[A] is small change in conc. of 'A' and dt is small interval of time

  Rate of disappearance of $B = \frac{-d[B]}{dt}$

  Where d[B] is small change in conc. of 'B' and dt is small interval of time

  Rate of appearance of $C = \frac{+d[C]}{dt}$

  Where d[C] is small change in conc. of 'C' and dt is small interval of time

  Rate of appearance of $D = \frac{+d[D]}{dt}$

  Where d[D] is small change in conc. of 'D' and dt is small interval of time

  Rate $= \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{+d[C]}{dt} = \frac{+d[D]}{dt}$

- Rate law or rate equation:
  It is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality 'k' is known as rate constant.
- Average rate:
  It is the rate of reaction measured over a long time interval.

  Average rate $= \frac{\Delta x}{\Delta t}$

  where is Δx change in concentration and Δt is large interval of time.
- Instantaneous rate:
  It is the rate of reaction when the average rate is taken over a particular moment of time.

  Instantaneous rate $= \frac{dx}{dt}$.

  where dx is small change in conc. and dt is the smallest interval of time.

It is the expression which relates the rate of reaction with concentration of the reactants.

- Rate constant:

  When the concentration of reactants is unity, then the rate of reaction is known as rate constant. It is also called specific reaction rate.
- The constant of proportionality 'k' is known as rate constant.
- Molecularity of a reaction:

  The total number of atoms, ions or molecules of the reactants involved in the reaction is termed as its molecularity. It is always in whole number and is never more than three. It cannot be zero.
- Order of a reaction:

  The sum of the exponents (power) of the concentration of reactants in the rate law is termed as order of the reaction. It can be in fraction. It can be zero also.
- If rate law expression for a reaction is

  Rate = k [A]x [B]y

  Then its order of reaction = x + y
- Order cannot be determined with a given balanced chemical equation. It can be experimentally determined.
- Integrated rate law for zero order reaction:

$$R \rightarrow P$$

$$\frac{dx}{dt} = k[R]^0$$

$$k = \frac{[R_0]-[R]}{t}$$

- If we plot a graph between concentration of R vs time t, the graph is a straight line with slope equal to -k and intercept is equal to [Ro].
- Half- life of a reaction:

  The time taken for a reaction, when half of the starting material has reacted is called half- life of a reaction.
- For zero order reaction, the half-life time is

$$t_{1/2} = \frac{[R_0]}{2k}$$

- For first order reaction, the half-life time is

$$t_{1/2} = \frac{0.693}{k}$$

  where 'k' is rate constant

  It is independent of initial concentration for first order reaction.
- Rate law for first order reaction:

  $R \rightarrow P$

$$k = \frac{2.303}{t}\log\frac{[R_0]}{[R]}$$

where ‘k’ is rate constant or specific reaction rate, [Ro] is initial molar conc., [R] is final molar conc. after time ‘t’.

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

where ‘a’ is initial conc. reacted in time ‘t’ final conc., after time ‘t’ is (a – x).

- If we plot a graph between ln[R] with time, we get a straight line whose slope = - k and intercept ln[Ro].
- To calculate rate constant for first order gas phase reaction of the type

  A (g) →B(g) + C(g)

$$k = \frac{2.303}{t}\log\frac{p_1}{(2p_i - p_t)}$$

Where pi is initial pressure of A, pt is total pressure of gaseous mixture containing A , B, C

p t = p A + p B + p C

- Pseudo first order reaction:

  The reaction which is bimolecular but order is one is called pseudo first order reaction. This happens when one of the reactants is in large excess.

  Example - Acidic hydrolysis of ester (ethyl acetate).

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

- Activation energy (E_a):

  It is extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to the formation of product molecules.
- Arrhenius equation of reaction rate:

  It gives the relation between rate of reaction and temperature.

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

$$\ln k = \ln A - E_a / RT$$

$$\log k = \log A - \frac{E_a}{2.303RT}$$

where k = rate constant, A = frequency factor, Ea = energy of activation R = gas constant, T = temperature in Kelvin,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

- Probability factor or Steric factor

$$Rate = PZ_{AB}.e^{\frac{-E_a}{RT}}$$

Where ZAB represents the collision frequency of reactants, A and B, $e^{\frac{-E_a}{RT}}$ represents the fraction of molecules with energies equal to or greater than Ea and P is called the probability or steric factor.

- Mechanism of reaction:

It is the sequence of elementary processes leading to the overall stoichiometry of a chemical reaction.

- Activated complex:

  It is an unstable intermediate formed between reacting molecules. Since, it is highly unstable and it readily changes into product.
- Rate determining step:

  It is the slowest step in the reaction mechanism.
- The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).