

## CHEMICAL KINETICS –II PUC

The branch of physical chemistry which deals with rate of reaction, mechanism of reaction and the influence of concentration, temperature, pressure, catalyst etc., on the reaction rate is called the chemical kinetics. On the basis of rates, the chemical reactions are broadly divided into three categories.

**i) Very fast reactions,**

**ii) Very slow reactions and**

**iii) Moderately slow reactions**

**Rate of chemical reaction:**

Rate of a reaction: It is the change in molar concentration of one of the reactants or products per unit time. The rate of the reaction decreases with the time. It is expressed as  $v = \pm \frac{dc}{dt}$ . If the rate is expressed with respect to

reactants, then it is given as  $\frac{-dc}{dt}$  as the concentration of the reactants decreases with time. If the rate of the reaction is expressed with respect to the products, it is given by  $v = + \frac{dc}{dt}$  as the concentration of the products increases with time.

**Rate of reactions having same stoichiometric coefficient of all the reactants and products:**

For a hypothetical reaction:  $A + B \rightarrow C + D$

$$\text{Average rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = +\frac{\Delta[C]}{\Delta t} = +\frac{\Delta[D]}{\Delta t}$$

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

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

The negative sign along with the change in concentration of the reactants indicates that the concentration of the reactant decreases with time, while positive sign along with concentration of product indicates that concentration of product increases with time.

**Rate of reactions having different stoichiometric coefficients of the reactant and products:**

For a reaction  $A + 2B \rightarrow 3C + 4D$ , the rate of the reaction with respect to A, B, C and D is given by

$$\frac{-d[A]}{dt} = \frac{-1}{2} \frac{d[B]}{dt} = +\frac{1}{3} \frac{d[C]}{dt} = +\frac{1}{4} \frac{d[D]}{dt}$$

**For a reaction  $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO}_2 + 6\text{H}_2\text{O}$**

$$\text{Rate of reaction} = -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} = -\frac{1}{5} \frac{d[\text{O}_2]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt}$$

Rate of reaction with respect of ammonia

$$\frac{d[\text{NH}_3]}{dt} = \frac{4}{5} \frac{d[\text{O}_2]}{dt} = \frac{d[\text{NO}_2]}{dt} = \frac{4}{6} \frac{d[\text{H}_2\text{O}]}{dt}$$

**For decomposition of nitrogen pentoxide:  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$**

$$\text{Rate of reaction} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = +\frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = +\frac{\Delta[\text{O}_2]}{\Delta t}$$

### Factors affecting the rate of reaction

- Nature of reactants
- Temperature
- Concentration (pressure) of the reactants
- catalyst
- Surface area of the reactants
- Intensity of light
- Allotropic forms.

### Units of rate of reaction:

As concentration of substance is expressed in mol L<sup>-1</sup> and time is measured in seconds or minutes or hours. The units for rate of reaction are moles litre<sup>-1</sup> sec<sup>-1</sup> or moles litre<sup>-1</sup> min<sup>-1</sup>.

For gaseous reactants, concentrations are expressed in terms of partial pressure; therefore, the units of rate of reaction will be atm min<sup>-1</sup> or atm sec<sup>-1</sup> or atm hr<sup>-1</sup>.

### Average rate and instantaneous rate:

**Average rate:** It is the rate of change of concentration of a reactant or a product over measurable long time interval.

For a hypothetical reaction A → B

Average rate of reaction =  $\frac{\text{change in concentration of one of the reactant or product}}{\text{time taken}}$  =

$$\frac{-\Delta[\text{A}]}{\Delta t} = +\frac{\Delta[\text{B}]}{\Delta t}$$

### Instantaneous rate:

The rate of change of concentration of any one of the reactants or products over a very small interval of time.

Mathematically, instantaneous rate may be expressed by the expression  $\frac{dx}{dt}$

instead of  $\frac{\Delta x}{\Delta t}$ . Here dx is the change in concentration of any of the species in time interval dt. In other words when Δt becomes very small and approaches zero, the ratio  $\frac{\Delta[x]}{\Delta t}$  may be replaced by the derivative  $\frac{dx}{dt}$ . That is

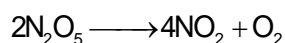
$$\text{instantaneous rate} = \left( \frac{\Delta x}{\Delta t} \right)_{\Delta t \rightarrow 0} = \frac{dx}{dt}$$

For a hypothetical reaction, n<sub>1</sub>A + n<sub>2</sub>B → m<sub>1</sub>C + m<sub>2</sub>D

The instantaneous rate may be expressed as

$$\text{Rate} = -\frac{1}{n_1} \frac{d[\text{A}]}{dt} = -\frac{1}{n_2} \frac{d[\text{B}]}{dt} = +\frac{1}{m_1} \frac{d[\text{C}]}{dt} = +\frac{1}{m_2} \frac{d[\text{D}]}{dt}$$

For example, the instantaneous rate for the gaseous reaction,



$$\text{Instantaneous rate} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}$$

The concept of average rate cannot be used to measure the true rate of a chemical reaction. This is because the calculated average rate would be constant for the whole span of time for which it is calculated. But the rate of reaction depends on molar concentration of reactants. Since concentration of reactants decreases with time, therefore the rate of a reaction also decreases with time. Since rate of reaction varies with time, it is more appropriate to express the rate of a reaction at a particular moment of time. This rate of reaction at a particular moment of time is called instantaneous rate. Thus instantaneous rate gives a true rate of reaction.

### Effect of temperature:

The rate of a reaction generally increases with increase in the temperature of the reaction. The specific rate ( $k$ ) of a reaction is approximately doubled for every  $10^\circ\text{C}$  rise of temperature for many reactions.

$$\frac{k_{t^\circ\text{C}+10^\circ\text{C}}}{K_{t^\circ\text{C}}} = 2 \text{ or } 3$$

The ratio of the two specific rates measured at temperatures that differ by  $10^\circ\text{C}$  is called the temperature coefficient of the reaction.

Normally  $t^\circ\text{C} = 25^\circ\text{C}$ ;  $(t+10)^\circ\text{C} = 35^\circ\text{C}$ .

### Collision theory of reaction rates:

This theory was first proposed by Arrhenius. This theory is based on the kinetic theory of gases. According to this theory, chemical reactions occur only when the reactant molecules collide with each other.

### Postulates of collision theory:

1. Reacting molecules shall have to collide for any reaction to occur.
2. All collisions do not lead to the formation of the products.
3. The colliding molecules shall have to possess a minimum energy to give products. This minimum energy is called Threshold energy. This is higher than that of the molecules in the normal state.
4. The energy of the molecules at STP is very much less than this threshold energy.
5. The difference between the Threshold energy and the energy of molecules in the normal state is activation energy.  
Activation energy = [Threshold energy – Energy of the normal molecules]
6. The molecules possessing the threshold energy are called activated molecules. These are formed in small numbers during collisions occurring between normal molecules.
7. Collisions occurring between activated molecules are called activated collisions. Activated collisions alone lead to the formation of the products of the reaction.
8. The collisions that do not form a product are called ineffective elastic collisions. For a collision to be effective, the following two barriers are to be cleared.
  - a) Energy barrier
  - b) Orientation barrier

### a) Energy barrier:

Out of the total number of collisions only those collisions result in the formation of products which possess energy equal to or greater than certain minimum energy called threshold energy. The kinetic energy of the reactants in many reactions is less than their threshold energy and hence these reactants are not capable to form products. It means there is an energy barrier between reactants and products which must be crossed for the reaction to occur. Thus some extra energy has to be supplied to the reactants to make their kinetic energy equal to their threshold energy. This extra energy is called activation energy of the reactants.

Activation energy = Threshold energy – average kinetic energy of reacting molecules.

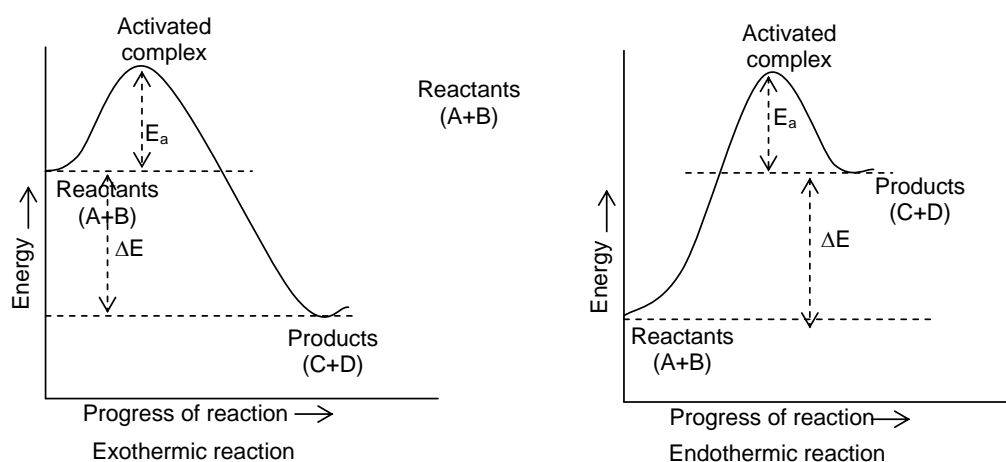
$$E_a = E_T - E_R$$

Thus, the minimum amount of energy which must be supplied to the reactants to enable them to cross over the energy barrier is called activation energy.'

Activation energy depends upon the nature of chemical bonds undergoing rupture and is independent of the initial and final energy contents of reactants. (i.e. independent of the fact that the reaction is exothermic or endothermic).

The energy changes during exothermic and endothermic reactions may be plotted against the progress of reaction as in figure.

- Rate of a reaction depends on activation energy. A reaction which has a lower value of its activation energy will proceed at a faster rate at a given temperature, while a reaction which has higher value of its activation energy proceed at low rate.



### Activated complex:

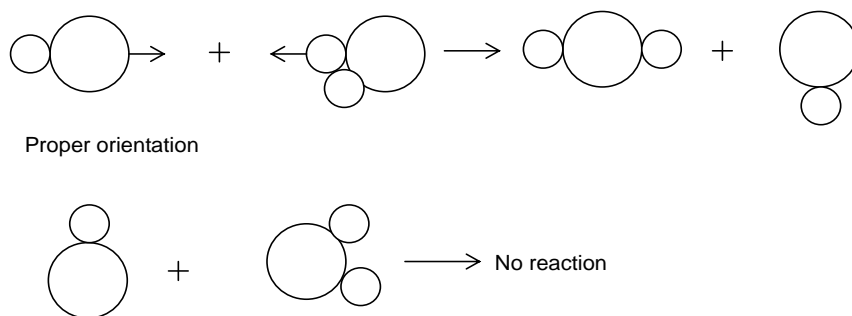
The reactants do not change directly into the desired products. In the beginning of a reaction breaking of bonds predominates, therefore energy of system starts increasing till it reaches a energy maxima. In this state reactants form activated complex. The energy of activated complex is equal to threshold energy of the reactants. After this, process of bond formation predominates, due to which energy starts decreasing and it results in the formation of products.

Thus, an activated complex is an unstable arrangement of atoms which is a very short lived high energy species. In an effective collision, the activated complex separates into products.

### b) Orientation barrier:

All the collisions among reactant molecules will not lead to the formation of products even if the energy of reactants is greater than the threshold energy. It is because; the reacting molecules should have proper orientation for the collision, only then the collision will be effective. All colliding molecules having sufficient energy but no proper orientation will bounce back without any reaction.

For example, the reaction between  $\text{NO}_2$  and  $\text{CO}$  results in the formation of products  $\text{CO}_2$  and  $\text{NO}$  the collision between  $\text{CO}$  and  $\text{NO}_2$  will be effective only if the orientation of collision is proper.



Here  $\text{CO}$  and  $\text{NO}_2$  are not properly oriented and hence do not make the required product.

### Molecularity of reaction:

Molecularity of an elementary reaction is the total number of molecules or atoms which collide simultaneously to form the product molecules or the number of atoms or ions or molecules participating in an elementary step which must collide simultaneously to bring about a chemical reaction is called the molecularity of the elementary step or the number of atoms or ions or molecules participating in the elementary step is known as the molecularity of that reaction step. Molecularity of the reaction can be 1, 2, or 3. for example

- (i) Hydrolysis of methyl acetate is a bimolecular reaction **molecularity = 1**  
 $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$
- (ii) Dissociation of  $\text{PCl}_5$  is a unimolecular reaction **molecularity = 1**  
 $\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$
- (iii) Dissociation of  $\text{HI}$  is a bimolecular reaction **molecularity = 2**  
 $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$
- (iv) Oxidation of nitric oxide is a bimolecular reaction **molecularity = 2**  
 $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$
- (v) Reaction between  $\text{NO}$  and  $\text{O}_2$  is a trimolecular reaction. **molecularity = 3**  
 $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ .
- (vi) Reaction between  $\text{SO}_2$  and  $\text{O}_2$  is a trimolecular reaction. **molecularity = 3**  
 $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$   
 Other examples for trimolecular reactions  
 $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$   
 $2\text{FeCl}_3 + \text{SnCl}_2 \rightarrow \text{SnCl}_4 + 2\text{FeCl}_2$

The molecularity does not exceed three. The slowest step of the reaction is called the rate determining step, hence the molecularity of this reaction also

depends on slowest step. Molecularity cannot be zero, negative, fractional, infinite.

### **Mechanism of elementary and complex reactions:**

- In chemical kinetics, reactions which occur in single step are called elementary reaction, and the reactions which occur in two or more steps are termed as complex reactions.
- In case of complex reaction, molecularity is the minimum number of reacting particles that collide in a rate determining step to form products.
- Complex reactions proceed through a sequence of steps. Each step is an elementary step and involves the simultaneous collision of two or three species only.

### **Law of mass action (Guldberg and Waage):**

The rate of a chemical reaction is directly proportional to the product of active masses of the reactants at constant temperature.

For a reaction  $aA + bB \rightarrow cC + dD$ ,

$V = k [A]^a [B]^b$  where  $k$  is called rate constant of all the reactants are unity.

### **Rate law or Rate equation:**

The equation that describes mathematically the dependence of the rate of a reaction on the concentration terms of the reactants is known as the rate equation or rate law. For example

- a)  $A \rightarrow P$ , rate =  $k[A]^1$
- b)  $2A \rightarrow 2P$ , rate =  $k[A]^2$
- c)  $A + B \rightarrow P$ , rate =  $k [A] [B]$
- d)  $A + B + C \rightarrow P$ , rate =  $k[A][B][C]$

**Rate constant (k):** It is the rate of a reaction when the concentrations of all the reactants are unity.

The characteristics of rate constant are

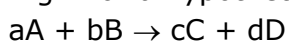
- a) Higher value of  $k$ , faster is the reaction
- b) The value of rate constant does not depend upon initial concentration
- c) It does not change during the course of the reaction
- d) It changes with the temperature

### **Order of reaction:**

Order of a simple reaction is the number of molecules or atoms whose concentrations change as a result of chemical reaction.

Mathematically "The sum of powers to which the concentration terms are raised in the rate law expression is called order of reaction.

E.g. For a hypothetical reaction;

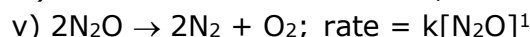
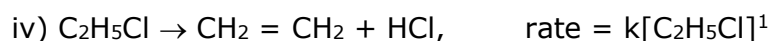
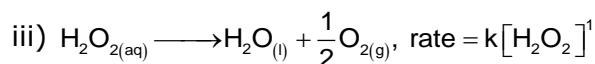
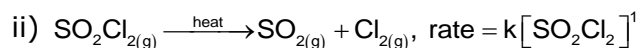
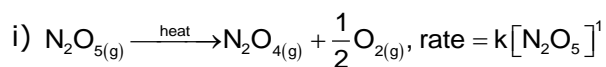


$$\text{Rate of reaction} = k[A]^m [B]^n$$

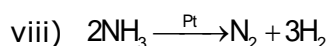
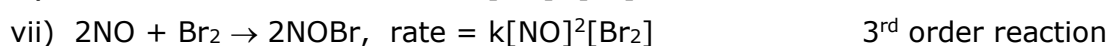
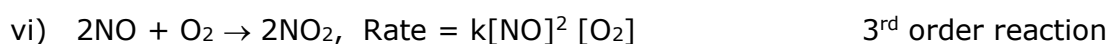
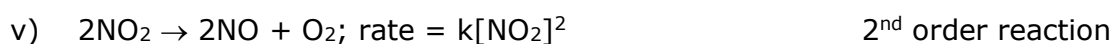
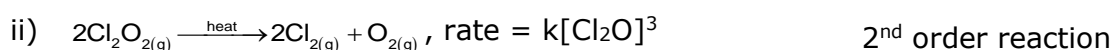
The exponents  $m$  and  $n$  are known as the order of the reaction with respect to  $A$  and  $B$  respectively.  $m + n$  gives the overall order of the reaction.

m and n may and may not be equal to stoichiometric coefficients a and b respectively in the net reaction.

- a) If the sum of the power is equal to one, the reaction is called first order reaction. e.g.,



- b) If the sum of the powers is two or three, the reaction is 2<sup>nd</sup> order or 3<sup>rd</sup> order respectively. e.g.,



### Specific rate or Rate constant:

The rate of a reaction corresponding to the unit concentrations of all the reactants of the reaction is called specific rate or rate constant (k).

### Units of rate constant for reactions of different orders:

(i) For zero order reactions: Rate =  $\frac{dx}{dt} = k[A]^0$ ;  $k = \text{mol L}^{-1} \text{sec}^{-1}$ .

(ii) For first order reactions: Rate =  $k[A] = \frac{dx}{dt}$ ; hence  $k \cdot [\text{mol L}^{-1}] = \left(\frac{\text{mol}}{\text{L} \cdot \text{sec}}\right)$

$$\therefore k = (\text{sec}^{-1}).$$

(iii) For second order reactions: Rate =  $k[A]^2 = \frac{dx}{dt}$ ;  $k \left(\frac{\text{mol}}{\text{L}}\right)^2 = \left(\frac{\text{mol}}{\text{L} \cdot \text{sec}}\right)$

$$\text{Hence } k = \text{L mol}^{-1}\text{sec}^{-1}.$$

(iv) For third order reactions: Rate =  $k[A]^3 = \frac{dx}{dt}$

$$k \left(\frac{\text{mol}}{\text{L}}\right)^3 = \left(\frac{\text{mol}}{\text{L} \cdot \text{sec}}\right) \therefore k = \text{L}^2 \text{mol}^{-2} \text{sec}^{-1}.$$

Rate constant has different units for reactions of different order. General rule for rate of reaction may be given as  $\text{Rate} = \frac{dx}{dt} = k[\text{conc.}]^n$

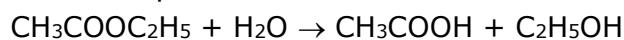
$$\therefore k = \frac{1}{[\text{conc.}]^n} \frac{dx}{dt} = \frac{1}{[\text{conc.}]^n} \times \frac{[\text{conc.}]}{\text{time}} = [\text{conc.}]^{1-n} \times \text{time}^{-1}$$

Or In general  **$k = (\text{mol L}^{-1})^{1-n} \text{sec}^{-1}$** .

For gaseous reactants, concentration is expressed in atmosphere, hence units of k for gaseous reactants =  **$(\text{atm})^{1-n} \times \text{sec}^{-1}$**  where n is the order of reaction.

### Pseudo first order reactions:

Reactions whose order is different from that expected using rate law expression are called pseudo order reactions. For example, acidic hydrolysis of ethyl acetate is pseudo first order reaction.



When water is taken in excess, then its concentration does not change appreciably during the reaction. It means rate of reaction will depend on the single concentration term and it will follow the kinetics of the first order.

Expected rate law:

$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}] \quad \text{order} = 2$$

Actual rate law

$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5] \quad \text{order} = 1$$

### Method of determination of order of reaction:

#### 1. Integrated rate law method:

Instantaneous rate of the reaction is given by the differential equations, but differential rate law equations involve infinitesimally small quantities like  $d[x]$ ,  $d[A]$ ,  $dt$  etc. which cannot be practically measured. Hence differential rate law equations are transformed to integrated form of a rate law by the method of calculus. Integrated rate law equations involve measurable quantities, thus these equations can be used for determining the rate constant, k, of the reaction.

##### (i) Zero order reaction:

A reaction is said to be of zero order if its rate is independent of the concentration of the reactants, for the reaction

$$kt = [A]_0 - [A] \quad \text{or} \quad k = \frac{1}{t}([A]_0 - [A])$$

Photochemical reaction between hydrogen and chlorine is also a zero order reaction.

##### (ii) First order reaction:

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

This equation is called integrated rate equation for the first order reaction.

This equation can also be represented as

$$\frac{kt}{2.303} = \log \frac{[A]_0}{[A]} \quad \text{or} \quad \frac{kt}{2.303} = \log [A]_0 - \log [A] \quad \text{or} \quad \log [A] = \frac{-kt}{2.303} + \log [A]_0$$



The graph between  $\log[A]$  and time 't' is a straight line, and the slope of this line is given by

$$\text{Slope} = -\frac{k}{2.303}$$

The intercept on y-axis would be equal to  $\log [A]_0$ .

For first order reactions, any quantity which is proportional to concentration can be used in place of concentration for evaluation of k.

All natural and artificial radioactive decay of nuclei follow the first order kinetics.

A) half life of a first order reaction is given by  $t_{1/2} = \frac{0.693}{k}$

B) Half life of a first order reaction is independent of initial concentration

C) Unit of rate constant is given by  $\text{time}^{-1}$  ( $\text{s}^{-1}$  or  $\text{min}^{-1}$  or  $\text{hr}^{-1}$ )

D) For a first order reaction,  $t_{19\%} = 2t_{10\%}$ ,

$$t_{99\%} = 2t_{90\%},$$

$$t_{75\%} = 2t_{50\%},$$

$$t_{99.9\%} = 10 t_{1/2}$$

E) For a first order reaction

No. of half lives	1	2	3	4	5	10
Percentage reacted	50	75	87.5	93.75	96.87	99.9

### Units of Rate constant

For  $n^{\text{th}}$  order reaction,  $k = [\text{conc.}]^{1-n} \times \text{time}^{-1}$

a) when concentration is taken in  $\text{mol litre}^{-1}$  and time in seconds.

$$\text{Units of } k = \left[ \frac{\text{mol}}{\text{litre}} \right]^{1-n} \times \text{sec}^{-1}$$

b) In case of a gaseous reaction,

$$\text{units of } k = [\text{atm}]^{1-n} \times \text{sec}^{-1}$$

Order of reaction	Rate law expression	Units of rate constant
Zero	Rate = $k[\text{conc.}]^0$	$\text{Mol litre}^{-1} \text{sec}^{-1}$ or $\text{atm sec}^{-1}$
First	Rate = $k[\text{conc.}]^1$	$\text{Sec}^{-1}$ or $\text{min}^{-1}$
Second	Rate = $k[\text{conc.}]^2$	$\text{Litre mol}^{-1} \text{sec}^{-1}$ or $\text{atm}^{-1} \text{sec}^{-1}$
Third	Rate = $k[\text{conc.}]^3$	$\text{Litre}^2 \text{mol}^{-2} \text{sec}^{-1}$ or $\text{atm}^2 \text{sec}^{-1}$

- For a first order reaction the time required to complete 99.9% of the reaction is 10 times that required for completion of half of the reaction. Similarly for a first order reaction, the time required for a 50% reaction is half that for 75% reaction.

### Half life of a reaction:

The time in which the initial concentration of reactants becomes half is termed as half life period.

Half life of a zero order reaction is directly proportional to initial concentration.

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

- Half life of first order reaction does not depend upon initial concentration of the reactants.

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

- For the first order reaction, the time required to reduce the concentration of the reactant to any fraction of the initial concentration is also independent of the initial concentration.

In general for nth order

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}} \text{ where } n \text{ is the order of reaction.}$$

For zero order reaction  $t_{1/2} \propto [A]_0$

For first order reaction  $T_{1/2} \propto \frac{1}{[A]_0^0}$  i.e., does not depend.

For second order reaction  $t_{1/2} \propto \frac{1}{[A]_0}$

For third order reaction  $t_{1/2} \propto \frac{1}{[A]_0^2}$

### Graphical method:

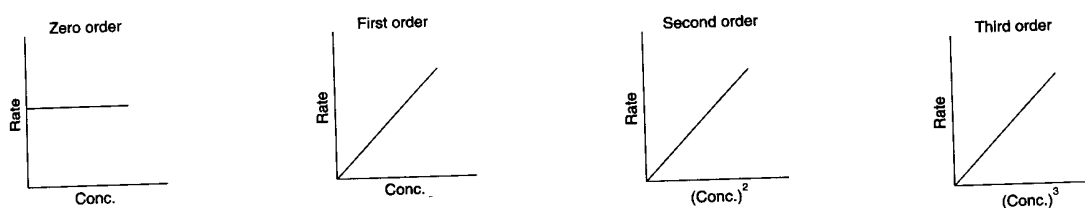
The various steps of this method are

- The concentration of reactant are determined at different time intervals.
- A graph is plotted between time 't' and the concentration of reactant or product from which a tangent is drawn.
- The rate of reaction corresponding to different concentrations is determined by calculating slope of the tangent.
- Different graphs are now plotted between reaction rate and concentration with different powers.

If a straight line is obtained between rate of reaction and concentration, then rate = k[conc.]; order = 1

For second order reaction, rate = [conc.]<sup>2</sup>

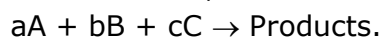
For third ordered rate = k[conc.]<sup>3</sup>.



### Ostwald isolation method:

In this method, the concentration of all the reactants are taken in large excess except that of one, the concentration change only for this reactant is significant as other are so much in excess that practically there is no change in their concentrations. The reactant which is not taken in excess, is said to be isolated from other reactants which are not taken in excess. The total order of reaction will be the sum of the order of all isolated reactions.

For a reaction,



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

If a is the order when A is isolated, b when [B] is isolated and c when [C] is isolated.

$$\therefore \text{Order of reaction} = a + b + c.$$

### Activation energy:

The difference between this barrier energy (i.e., threshold energy)  $E_T$  and the energy of normal molecules  $E_B$  called activation energy,  $E_a$ .

$$\therefore E_a = E_T - E_R$$

### Arrhenius equation (Temperature dependence of rate constant):

Arrhenius suggested an equation which describes rate constant as a function of temperature i.e.

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

where A  $\rightarrow$  frequency factor

$E_a \rightarrow$  Energy of activation; R  $\rightarrow$  the gas constant.

T  $\rightarrow$  Temperature in Kelvin.

At two temperatures  $T_1$  and  $T_2$  their rate constant are given by  $k_1$  and  $k_2$ .

$$\log_e k_2 - \log_e k_1 = \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad \text{or} \quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

Another form of Arrhenius equation which is more useful for calculation of activation energy is

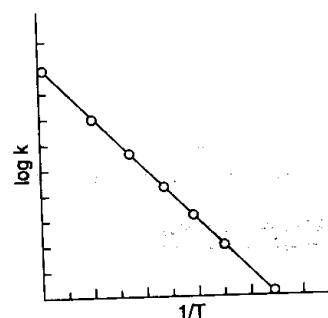
$$\log k = \log A - \frac{E_a}{2.303R} \frac{1}{T}$$

when a graph is plotted between  $\log k$  and  $1/T$  then the

slope of this curve is equal to  $-\frac{E_a}{2.303R}$

$$\therefore \text{Slope} = \frac{-E_a}{2.303R}$$

$$\therefore E_a = -2.303R \times \text{slope}$$



- As the value of  $E_a$  increases, the value of  $k$  decreases and, therefore reaction rate decreases.

### Effect of catalyst on reaction rate:

In the presence of a catalyst, the reaction follows a path of lower activation energy. Under this condition a large number of reacting molecules are able to cross over the energy barrier and thus the rate of reaction increases.

A negative catalyst increases the activation energy of reaction by forming a new intermediate of high energy i.e. by changing the reaction mechanism i.e. by changing the reaction mechanism.

**Photochemical reactions:**

Rates of some reactions are influenced by radiations particularly visible and ultraviolet radiations. Such reactions are called photochemical reactions. In these reactions photons of radiant energy are absorbed by reactant molecules. Activation energy required for reaction is supplied by radiant energy. Temperature has no marked effect on the rate of photo chemical reactions. The value of  $\Delta G$  may be +ve or -ve for photochemical reactions.

Examples of photochemical reactions:

- (i) Reaction between  $H_2$  and  $Cl_2$  to form HCl.
- (ii) Photosynthesis, photography etc.