

## CHEMICAL KINETICS

### Topic-2

### Order and molecularity of reactions with examples, zero and first order reaction with examples

#### VERY SHORT ANSWER QUESTIONS

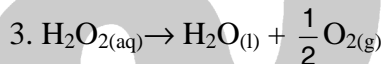
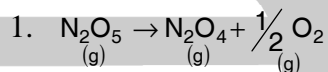
#### 1. What is order of a reaction?

**Ans:** The sum of the powers of the concentration terms of reactants in the rate equation is called order of the reaction.

Order of reaction may be zero or fraction or negative or a whole number (n). Order of the reaction can be determined experimentally

#### 2. Name two first order reactions?

**Ans: Examples :**



#### 3. What is first order reaction?

**Ans:**

First Order reaction is that reaction whose order is one.

$A \rightarrow \text{products}$

$$r = k_1 [A]^1$$

equation for rate constant :

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

Units for rate constant:  $\text{sec}^{-1}$

#### 4. What is zero order reaction give two examples?

**Ans: Order of reaction zero,**

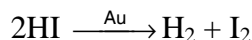
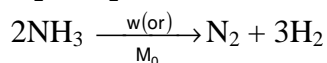
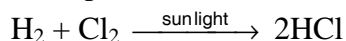
$A \rightarrow \text{products}$

The concentration of reactant decreases linearly with time. The rate of reaction is uniform. The time required for the completion of reaction is zero.

- Equation for rate constant:  $K_0 = \frac{x}{t}$ .
- Units for rate constant:  $\text{moles} \cdot \text{lit}^{-1} \cdot \text{sec}^{-1}$ .
- Half life :  $t_{1/2} \propto a$ .

a = initial conc. of the reactants

Examples:



## 5. What is half life period?

**Ans: Half life:** It is the time taken for 50% completion of reaction or the time taken for concentration of reactant to become half of its initial value.

- For 1<sup>st</sup> order reactions,  $t_{1/2}$  is independent of initial concentration of reactant.
- The concentration of the reactant left after 'n' half lives,

$$(\mathbf{a-x}) = \frac{\mathbf{a}}{2^n}.$$

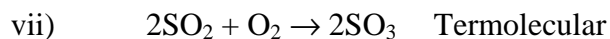
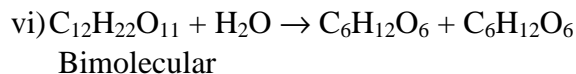
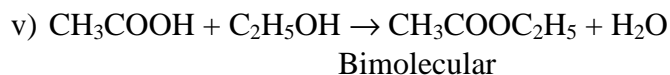
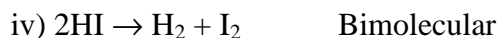
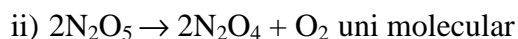
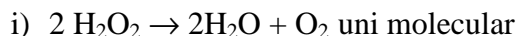
## 6. What is molecularity of a reaction?

**Ans:**

### **Molecularity of the reaction:**

Molecularity of a reaction is the number of reactant molecules taking part in rate determining step. A chemical reaction may take place in one or more steps. Different steps may proceed with different speeds. The slowest step is rate determining step. Molecularity of simple reactions is equal to the stoichiometric coefficients in balanced equation. Molecularity is a theoretical concept. Molecularity is related to mechanism of reaction. Molecularity is always a whole number. Molecularity cannot be zero, -ve, fractional, infinite and imaginary. Generally, molecularity of a reaction can not be greater than three because more than 3 molecules may not mutually collide with each other.

*Examples :*



## SHORT ANSWER QUESTIONS

### 1. Define order and molecularity of a reaction?

**Ans:**

#### Order of a reaction:

The sum of the powers of the concentration terms of reactants in the rate equation is called order of the reaction.

Order of reaction may be zero or fraction or negative or a whole number (n). Order of the reaction can be determined experimentally

#### Molecularity of the reaction:

Molecularity of a reaction is the number of reactant molecules taking part in rate determining step. A chemical reaction may take place in one or more steps. Different steps may proceed with different speeds. The slowest step is rate determining step. Molecularity of simple reactions is equal to the stoichiometric coefficients in balanced equation. Molecularity is a theoretical concept. Molecularity is related to mechanism of reaction. Molecularity is always a whole number. Molecularity cannot be zero, -ve, fractional, infinite and imaginary. Generally, molecularity of a reaction can not be greater than three because more than 3 molecules may not mutually collide with each other.

*Examples :*

- i)  $2 \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$  uni molecular
- ii)  $2\text{N}_2\text{O}_5 \rightarrow 2\text{N}_2\text{O}_4 + \text{O}_2$  uni molecular
- iii)  $\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$  uni molecular
- iv)  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$  Bimolecular
- v)  $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$   
Bimolecular
- vi)  $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$   
Bimolecular
- vii)  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$  Termolecular
- viii)  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$  Termolecular

### 2. How is half life method useful in the determination of order of reaction?

#### Half life method

A general expression for the half life,  $(t_{1/2})$ , is given by

$$t_{(1/2)} \propto 1/a^{n-1}$$

where 'n' is the order of the reaction.

Starting with different initial concentration  $a_1$  and  $a_2$  for the same reaction, the half lives are  $(t_{1/2})_1$  and  $(t_{1/2})_2$  respectively are determined. As we know,

$$t_{(1/2)1} \propto 1/a^{n-1}$$

$$\text{and } t_{(1/2)2} \propto 1/a_2^{n-1}$$

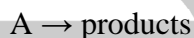
Dividing (i) by (ii),

$$t_{(1/2)1}/t_{(1/2)2} = (a_2/a_1)^{n-1}$$

### 3. Derive relation between the rate constant (K) and half life period ( $t_{1/2}$ ) for the first order reaction?

**Ans:** A reaction is said to be first order if its rate is determined by the change of one concentration term only.

Consider the reaction



Let  $a$  be the concentration of A at the start and after time  $t$ , the concentration becomes  $(a-x)$ , i.e,  $x$  has been changed into products. The rate of reaction after time ' $t$ ' is given by the expression

$$dx/dt = k(a-x)$$

$$\text{or } dx/(a-x) = k dt$$

Upon integration of above equation,

$$\int dx/(a-x) = k \int dt$$

$$\text{or } -\log_e (a - x) = kt + c$$

where  $c$  is integration constant.

$$\text{When } t = 0, \quad x = 0,$$

$$\therefore c = -\log_e a$$

Putting the value of ' $c$ ',

$$-\log_e (a - x) = kt - \log_e a$$

$$\text{or } \log_e a - \log_e (a - x) = kt$$

$$\text{or } \log_e \frac{a}{a-x} = kt$$

$$\text{or } k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

The time taken for the completion of same fraction of change is independent of initial concentration. For example, for half change,

$$x = 0.5a \quad \text{and} \quad t = t_{1/2}$$

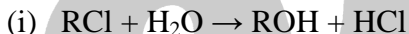
$$\begin{aligned} \text{So } k &= \left( \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{0.5a} \right) = \frac{2.303}{t_{1/2}} \log_{10} 2 \\ &= \frac{0.693}{t_{1/2}} \end{aligned}$$

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

#### 4. What is Pseudo first order reaction? Explain?

**Ans: PSEUDO-ORDER REACTION**

Reactions whose actual order is different from that expected using rate law expression are called pseudo-order reactions; e.g.,



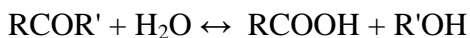
**Expected rate law:**

$$\text{Rate} = k[\text{RCl}] [\text{H}_2\text{O}] \quad \text{Expected order} = 1+1 = 2$$

**Actual rate law:**

$$\text{Rate} = k'[\text{RCl}]; \quad \text{Actual order} = 1$$

Water is taken in excess; therefore, its concentration may be taken constant. The reaction is, therefore, pseudo first order. Similarly, the acid catalysed hydrolysis of ester, viz.,



Follow first order kinetics:

$$\text{Rate} = k[\text{RCOOR}']$$

It is also a pseudo-first order reaction.

## LONG ANSWER QUESTIONS

1. What is meant by rate law/ Write the rate laws of elementary reactions of first and second order reactions. Deduce the units for the rate constant (K) of Zero and first order reactions?

**Ans: Rate law and rate constant:**

- The equation which relates the rate of the reaction and the concentration of the reactants is known as rate equation or rate law.
- Rate equation is written after the experiment only. It is not related to coefficients of reactants in balanced equation.
- Rate of reaction does not depend on the reactant if its concentration is large excess.
- "Isolation" methods are usually followed to study rate of the reaction.
- $nA + mB \rightarrow \text{products}$
- rate  $r \propto [A]^n [B]^m$ ; rate =  $K[A]^n [B]^m$
- K is called rate constant or specific rate or rate per unit concentration of the reactants.

**Order of reaction : zero, A  $\rightarrow$  products**

The concentration of reactant decreases linearly with time. The rate of reaction is uniform. The time required for the completion of reaction is zero.

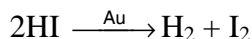
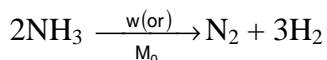
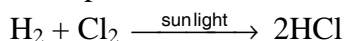
Equation for rate constant:  $K_0 = \frac{x}{t}$ .

Units for rate constant: moles- lit<sup>-1</sup>- sec<sup>-1</sup>.

Half life:  $t_{1/2} \propto a$ .

a = initial conc. of the reactants

Examples:



**Order of reaction: First**

A  $\rightarrow$  products

$$r = k_1 [A]^1$$

**Equation for rate constant:**

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

Units for rate constant: sec<sup>-1</sup>

The exponential form of the above equation is,

$$(a-x) = a.e^{-kt}$$

$$x = a(1-e^{-kt})$$

**Half life:** It is the time taken for 50% completion of reaction or the time taken for concentration of reactant to become half of its initial value.

For 1<sup>st</sup> order reactions,  $t_{1/2}$  is independent of initial concentration of reactant.

The concentration of the reactant left after 'n'

half lives,  $(a-x) = \frac{a}{2^n}$ .

Rate constant, k depends on the

Nature of reactant

Temperature of reaction

Catalyst

Rate constant, k is independent of

Initial concentration of reactant

Time

Half life time:  $t_{1/2} \propto a^0$ .

$$t_{1/2} = \frac{0.693}{k_1}$$

## 2. Define and explain Molecularity and order of a reaction with suitable examples?

Ans: **MOLECULARITY OF REACTION**

In general, molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation.

OR

The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction.

e.g.,  $\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$  (Unimolecular)

$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$  (Bimolecular)

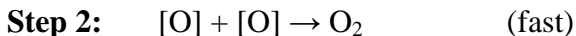
$2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$  (Trimolecular)

The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products is called the molecularity of a reaction.

For example, decomposition of  $\text{H}_2\text{O}_2$  takes place in the following two steps:

$\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + 1/2\text{O}_2$  (overall reaction)

**Step 1:**  $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + [\text{O}]$  (Slow)

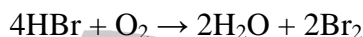


The slowest step is rate-determining. Thus from step 1, reaction appears to be unimolecular.

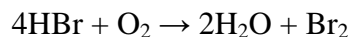
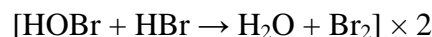
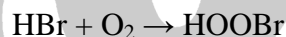
**Note:**

- (i) Molecularity is a theoretical concept.
- (ii) Molecularity cannot be zero, -ve, fractional, infinite and imaginary.
- (iii) Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.

There are some chemical reactions whose molecularity appears to be more than three from stoichiometric equations, e.g. in



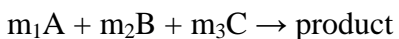
In the first reaction molecularity seems to be '5' and in the second reaction molecularity seems to be '23'. Such reactions involve two or more steps; each step has its own molecularity not greater than three, e.g., in first reaction.



Molecularity of each of the above steps is 2.

**ORDER OF REACTION**

Let us consider a good reaction:





Let active moles of 'A', 'B' and 'C' be ' $\alpha$ ', ' $\beta$ ' and ' $\gamma$ ' respectively. Then, rate of reaction may be given as:

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

Sum of powers of concentration terms involved in rate law expression is called order of reaction.

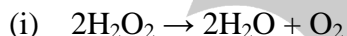
$$\alpha + \beta + \gamma \text{ order.}$$

When  $\alpha + \beta + \gamma = m_1 + m_2 + m_3$ , then

Order of reaction = molecularity of reaction

Order is an experimentally determined quantity. It may be equal to zero, positive, negative, fractional and greater than three. Infinite and imaginary values are not possible.

**Examples:**



(Observed from law of mass action)



Actual rate  $-\text{d}x/\text{d}t = k[\text{H}_2\text{O}_2]$

Thus, order of reactions in unity.

**3. Describe methods for the determination of order of reaction. ?**

**Ans: METHODS FOR DETERMINATION OF ORDER OF A REACTION**

The important methods used for the following:

**1. Method of integration (Hit and trial method)**

The most simple method is the one in which the quantities a, x and t are determined and substituted in the kinetic equations of various orders. The equation which gives the most constant value for the specific rate constant (k) for a series of time intervals is the one corresponding to the order of reaction. If all the reactants are at the same molar concentrations, the kinetic equations are:

$k = 2.303/t \log_{10} a/((a-x))$ ; for first order reactions;

$k = 1/t [1/((a-x))-1/a]$ ; for second order reactions;

$k = 1/t [1/(a-x)^2 - 1/a^2]$ ; for third order reactions;

## 2. Graphical method

A graphical method based on the respective rate laws can also be used.

If the plot of  $\log(a-x)$  versus 't' is a straight line, the reaction follows second order.

If the plot of  $1/(a-x)^2$  versus 't' is a straight line, the reaction follows third order.

In general, for a reaction of nth order, a graph of  $1/(a-x)^{n-1}$  versus 't' must be a straight line.

## 3. Half life method

A general expression for the half life,  $(t_{1/2})$ , is given by

$$t_{(1/2)} \propto 1/a^{n-1}$$

where 'n' is the order of the reaction.

Starting with different initial concentration  $a_1$  and  $a_2$  for the same reaction, the half lives are  $(t_{1/2})_1$  and  $(t_{1/2})_2$  respectively are determined. As we know,

$$t_{(1/2)1} \propto 1/a_1^{n-1}$$

and  $t_{(1/2)2} \propto 1/a_2^{n-1}$

Dividing (i) by (ii),

$$t_{(1/2)1}/t_{(1/2)2} = (a_2/a_1)^{n-1}$$

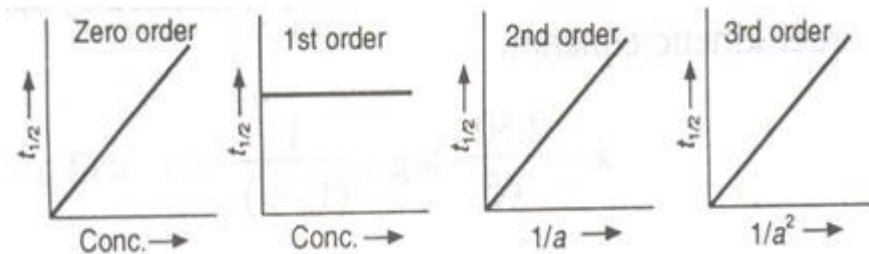
Taking logarithms on both sides,

$$\log_{10} (t_{1/2})_1 - \log_{10}(t_{1/2})_2 = (n-1)(\log_{10} a_2 - \log_{10} a_1)$$

$$n - 1 = (\log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2)/(\log_{10} a_2 - \log_{10} a_1)$$

$$\text{or } n = 1 + (\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2)/(\log_{10} a_2 - \log_{10} a_1)$$

Plots of half-lives concentration ( $t_{1/2} \propto a^{1-n}$ ):



This relation can be used to determine order of reaction 'n'

#### 4. Van't hof differential method.

As we know that, the rate of a reaction varies as the nth power of the concentration of the reactant where 'n' is the order of the reaction. Thus, for two different initial concentrations  $C_1$  and  $C_2$ , equations can be written in the form

$$-(dC_1)/dt = kC_1^n \text{ and } -(dC_2)/dt = kC_2^n$$

Taking logarithms,

$$\log_{10}(-(dC_1)/dt) = \log_{10}k + n \log_{10} C_1 \quad \dots (i)$$

$$\text{and } \log_{10}(-(dC_2)/dt) = \log_{10}k + n \log_{10} C_2 \quad \dots (ii)$$

Subtracting Eq. (ii) from (i),

$$\log_{10}(-(dC_1)/dt) - \log_{10}(-(dC_2)/dt) = n(\log_{10} C_1 - \log_{10} C_2)$$

$$\text{or } n = \frac{\log_{10}(-(dC_1)/dt) - \log_{10}(-(dC_2)/dt)}{\log_{10} C_1 - \log_{10} C_2} \quad \dots (iii)$$

$-dc_1/dt$  and  $-dc_2/dt$  are determined from concentration vs. time graphs and the value of 'n' can be determined.

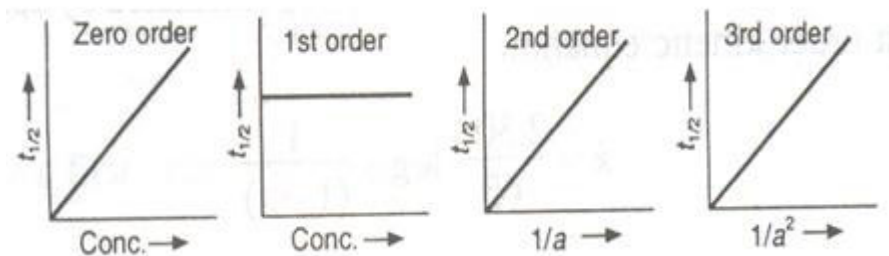
Taking logarithms on both sides,

$$\log_{10} (t_{1/2})_1 - \log_{10}(t_{1/2})_2 = (n-1)(\log_{10} a_2 - \log_{10} a_1)$$

$$n - 1 = \frac{(\log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2)}{(\log_{10} a_2 - \log_{10} a_1)}$$

$$\text{or } n = 1 + \frac{(\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2)}{(\log_{10} a_2 - \log_{10} a_1)}$$

Plots of half-lives concentration ( $t_{1/2} \propto a^{1-n}$ ):



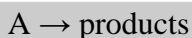
This relation can be used to determine order of reaction 'n'

**4. Derive rate equation for first order reaction and derive expression for half life period?**

**Ans: First order reactions**

A reaction is said to be first order if its rate is determined by the change of one concentration term only.

Consider the reaction



Let  $a$  be the concentration of A at the start and after time  $t$ , the concentration becomes  $(a-x)$ , i.e,  $x$  has been changed into products. The rate of reaction after time 't' is given by the expression

$$dx/dt = k(a-x)$$

$$\text{or } dx/(a-x) = k dt$$

Upon integration of above equation,

$$\int dx/(a-x) = k \int dt$$

$$\text{or } -\log_e (a - x) = kt + c$$

where  $c$  is integration constant.

$$\text{When } t = 0, \quad x = 0,$$

$$\therefore c = -\log_e a$$

Putting the value of 'c',

$$-\log_e (a - x) = kt - \log_e a$$

$$\text{or } \log_e a - \log_e (a - x) = kt$$

$$\text{or } \log_e a/(a-x) = kt$$

$$\text{or } k = 2.303/t \log_{10} a/(a-x)$$

This is known as the kinetic equation for a reaction of the first order. The following two important conclusions are drawn from this equation:

(i) A change in concentration unit will not change the numerical value of  $k$ . Let the new unit

$$\text{So } k = 2.303/t \log_{10} na/n(a-x)$$

$$\text{or } k = 2.303/t \log_{10} a/(a-x)$$

Thus for first order reaction, any quantity which is proportional to concentration can be used in place of concentration for evaluation of ' $k$ '.

(i) The time taken for the completion of same fraction of change is independent of initial concentration. For example, for half change,

$$x = 0.5a \quad \text{and} \quad t = t_{1/2}$$

$$\begin{aligned} \text{So } k &= 2.303/t_{1/2} \log_{10} a/0.5a = 2.303/t_{1/2} \log_{10} 2 \\ &= 0.693/t_{1/2} \end{aligned}$$

$$\text{or } t_{1/2} = 0.693/k$$

Thus,  $t_{1/2}$  is independent of initial concentration ' $a$ '.

This time ' $t$ ' in which the initial concentration becomes half is termed as half life period. Half life period of a first order reaction is independent of the initial concentration of the reactant.

Since the velocity constant is independent of concentration and depends inversely on the time, the unit of  $k$  will be  $\text{time}^{-1}$ , i.e.,  $\text{sec}^{-1}$  or  $\text{min}^{-1}$  or  $\text{hour}^{-1}$ . The equation of the first order can also be written in the following form when initial concentration is not known.

## 5 Derive rate equations for zero order reaction?

### Zero order reactions

A reaction is said to be of zero order if its rate is independent of the concentration of the reactants, i.e., the rate is proportional to the zeroth power of the concentration of the reactants.

For the reaction

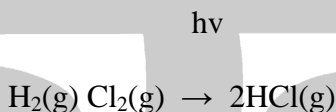
$A \rightarrow$  products to be of zero order,

$$-dx/dt = k[A]^0 = k$$

Some photochemical reaction and a few heterogeneous reactions are zero-order reactants. Such reactions are not common.

### **Example:**

#### **1. Photochemical reaction between hydrogen and chlorine:**



This photochemical reaction is zero-order reaction. The reaction is studied by placing  $\text{H}_2$  and  $\text{Cl}_2$  gases over water. the rate of reaction is studied by noting the rate at which water rises in the vessel due to dissociation of  $\text{HCl}$  formed. the rate of rise of water is the same as the rate of disappearance of  $\text{H}_2$  and  $\text{Cl}_2$ , i.e., the concentration of the gases phase will not change with time, although the quantities will change.

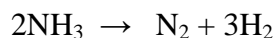
#### **2. Decomposition of $\text{N}_2\text{O}$ on hot platinum surface:**



$$\text{Rate } [\text{N}_2\text{O}]^0 = k[\text{N}_2\text{O}]^0 = k$$

$$d[\text{N}_2 \text{O}]/dt = k$$

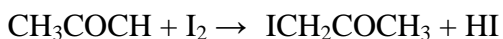
#### **3. Decomposition of $\text{NH}_3$ in presence of molybdenum or tungsten is a zero-order reaction.**



The surface of the catalyst is almost completely covered by  $\text{NH}_3$  molecules. The adsorption of gas on the surface cannot change by increasing the pressure or concentration of  $\text{NH}_3$ . Thus, the concentration of gas phase remains constant although the product is formed. Therefore, this reaction zero order kinetics.

**Other examples of zero order are:**

4. **Decomposition of NI on the gold surface.**
5. **Iodations of acetone in presence of  $\text{H}^+$  ions.**



The rate equation of this reaction does not include  $[\text{I}_2]$  factor, i.e.,

$$-dx/dt = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

**Characteristics of zero order reaction**

- (a) The concentration of reactant decreases linearly with time.

$$[\text{A}]_t = [\text{A}]_0 - kt$$

- (b) The time required for the reaction to be complete, i.e., time at which  $[\text{A}]$  is zero.

$$t_{\text{completion}} = [\text{A}]_0/k = (\text{Initial concentration})/(\text{Rate constant})$$

- (c) The units of  $k$  are  $\text{mol L}^{-1} \text{time}^{-1}$ .

**6. Explain the collision theory of rate of reaction?**

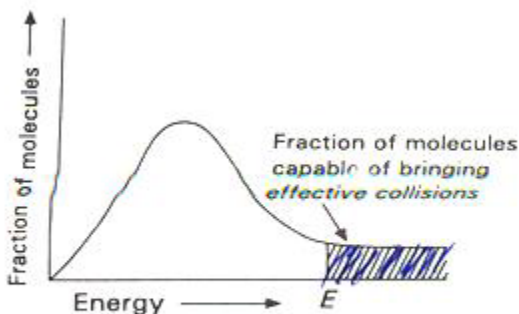
### **COLLISION THEORY OF REACTION RATE (ARRHENIUS THEORY OF REACTION RATE)**

(1) A chemical reaction takes place due to collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency ( $Z$ ). The value of collision frequency is very high, of the order of  $10^{25}$  to  $10^{28}$  in case of binary collisions.

(2) Every collision does not bring a chemical change. The collisions that actually produce the products are effective collisions. The effective collisions which bring chemical change are few in comparison to the form a product are ineffective elastic collisions, i.e., molecules just collide and disperse in different directions with different velocities. For a collision to be effective, the following two barriers are to be cleared.

## Energy barrier

The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as threshold energy.



In the graph 'E' corresponds to minimum or threshold energy for effective collision in a hypothetical reaction.

There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy as to cross the energy barrier.

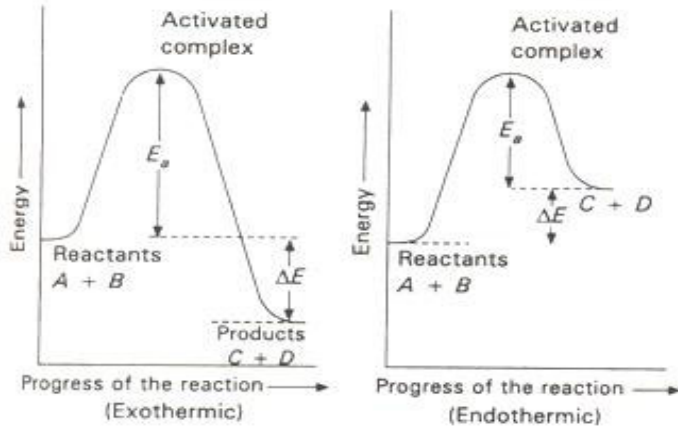
The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy.

Activation energy = threshold energy - average kinetic energy of reacting molecules

Threshold energy = initial potential energy of reactant molecules + activation energy.

A collision between high energy molecules overcomes the forces of repulsion and brings the formation of an unstable molecule cluster, called the activated complex. The life span of an activated complex is very small. Thus, the activated complex breaks either into reactants again or new substances, i.e., products. The activation energy ( $E_a$ ) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products. The energy changes during exothermic and endothermic reactions versus the progress of the reaction are shown in the figure given below.





### NUMERICALS

1. The rate constant of a first order reaction is  $0.693 \text{ sec}^{-1}$ . What is its  $t_{1/2}$ ?

**Sol:** Rate constant (K) =  $\frac{0.693}{\text{Half - life } (t_{1/2})}$

Given  $K = 0.693 \text{ sec}^{-1}$

$$\Rightarrow t_{1/2} = \frac{0.693}{K} = \frac{0.693}{0.693 \text{ sec}^{-1}} = 1 \text{ sec}$$

$$\therefore t_{1/2} = 1 \text{ sec}$$

2. The initial concentration of 'A' is 0.3 moles /lit. The concentration after 2.3 minutes is 0.15 moles /lit. What is the value of rate constant?

**Sol:** Rate constant (K) =  $\frac{\text{Change in concentration}}{\text{time}}$

Given change in concentration =  $0.3 - 0.15 = 0.15 \text{ moles /lit}$

Time = 2.3 min

$$(K) = \frac{\text{Change in concentration}}{\text{Time}} = \frac{0.15}{2.3} = 0.0652 \text{ moles.lit}^{-1}.\text{min}^{-1}$$

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