

# CHEMICAL KINETICS

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## 1. CLASSIFICATION OF REACTIONS : [IN TERMS OF RATES]

- (i) There are certain reactions which are too slow e.g. rusting of iron, weathering of rocks.
- (ii) Instantaneous reactions i.e. too fast e.g. Detonation of explosives, acid-base neutralization, precipitation of AgCl by NaCl and AgNO<sub>3</sub>.
- (iii) Neither too fast nor too slow e.g. combination of H<sub>2</sub> and Cl<sub>2</sub> in presence of light, hydrolysis of ethyl acetate catalysed by acid, decomposition of azomethane

## 2. RATE OF REACTION :

The change in concentration of either reactant or product per unit time.

$$\text{Formula : } v = \pm \frac{dc}{dt}$$

dc = change in concentration in a small interval dt.

[-] sign is used when we refer to reactant concentration.

[+] sign is used when we refer to product concentration.



(i) Rate of formation of ammonia =  $+\frac{d[\text{NH}_3]}{dt}$

(ii) Rate of disappearance of nitrogen =  $-\frac{d[\text{N}_2]}{dt}$

(iii) Rate of disappearance of hydrogen =  $-\frac{d[\text{H}_2]}{dt}$

$$\text{Rate of reaction} = +\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

$$\text{Thus, Rate of reaction} = -\frac{d[\text{N}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

or rate of formation of ammonia = Twice the rate of disappearance of nitrogen

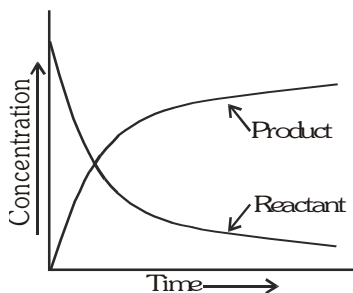
$$\text{i.e. } \frac{d[\text{NH}_3]}{dt} = \frac{2}{3} \left[ -\frac{d[\text{H}_2]}{dt} \right]$$

## 3. AVERAGE VELOCITY OF REACTION :

Change in the concentration of reactants or products per unit time is called average reaction velocity. If  $\Delta c$  is the change in the concentration of reactants and product in  $\Delta t$  time, then

$$\text{Average velocity} = \pm \frac{\Delta c}{\Delta t}$$

$$\text{or Average velocity} = \frac{(-)\text{Change in the concentration of reactants}}{\text{Time}}$$
$$\frac{(+)\text{Change in the concentration of products}}{\text{Time}}$$



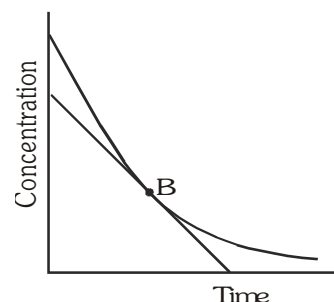
$$\text{Unit of average velocity} = \frac{\text{Unit of concentration}}{\text{Unit of time}} = \frac{\text{gram mole}}{\text{litre Second}} = \text{gram mole litre}^{-1} \text{ second}^{-1}$$

#### 4. INSTANTANEOUS RATE OF THE REACTION :

The rate of reaction determined at specified concentration or specified time is called **instantaneous rate**.

The instantaneous rate of the reaction can be determined by measuring concentration of reactant or product at a instant of time and plotting concentration versus time.

The instantaneous rate at any time is determined by the slope of the tangent at a point on the time-concentration curve corresponding to the specified time. The slope of the tangent at a point is the limiting value of  $\frac{\Delta c}{\Delta t}$ .



$$\lim_{\Delta t \rightarrow 0} \frac{\Delta c}{\Delta t} = \frac{dc}{dt}$$

In terms of the concentration of reactant, the rate of the reaction =  $-\frac{dc}{dt}$ . The -sign indicates that the concentration of reactant decreases with time.

In terms of the concentration of product, the rate of the reaction =  $+\frac{dc}{dt}$ . The +sign indicates that the concentration of product increases with time. In the reaction if at a time t the concentration of product is x and at time t + dt, the concentration becomes x + dx then the reaction rate =  $\frac{dx}{dt}$ .

◆ **For example the rate of reaction :**  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$

in terms of the concentrations of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  can be expressed as :

$$-\frac{d[\text{N}_2]}{dt}, -\frac{1}{3} \frac{d[\text{H}_2]}{dt}, +\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

**Ex.1** What should be (a) the rate of disappearance of B and (b) the rate of formation of C, if the rate of disappearance of A for the reaction  $\text{A} + \text{B} \rightarrow 2\text{C}$  is  $10^{-2}$  mole/litre/second at a particular temperature ?

**Sol.** (a) Rate of disappearance of A = Rate of disappearance of B  
 $= 10^{-2}$  mole/litre/second

(b) Rate of disappearance of A =  $\frac{1}{2}$  Rate of formation of C

$$\begin{aligned} \text{Rate of formation of C} &= 2 \quad \text{Rate of disappearance of A} \\ &= 2 \quad 10^{-2} \text{ mole/litre/second} \end{aligned}$$

**Ex.2** A gaseous reaction :  $2A(g) + B(g) \rightarrow 2C(g)$ ,  
 Show a decrease in pressure from 120 mm to 100 mm in 10 minutes. The rate of appearance of C is -  
 [A] 2 mm/min [B] 4 mm/min [C] 10 mm/min [D] 12 mm/min. **Ans. [B]**

**Sol.** Suppose  $2p$  is the pressure of C after 10 min.  
 Fall in pressure of A =  $2p$  ; Fall in pressure of B =  $p$   
 Total fall in pressure =  $(2p + p) - 2p = p = 20$  mm  
 Pressure of C =  $2p = 40$  mm  
 Rate of appearance of C =  $40/10 = 4$  mm/min

**Ex.3** The term  $\frac{dx}{dt}$  in the rate expression refers to the -  
 [A] concentration of the reactants [B] increase in concentration of the reactants  
 [C] instantaneous rate of the reaction [D] average rate of the reaction **Ans. [C]**

**Sol.** It is expression for instantaneous rate

**Ex.4** Which of the following expression can be used to describe the instantaneous rate of the reaction ?  
 $2A + B \rightarrow A_2B$

[A]  $-\frac{1}{2} \frac{d[A]}{dt}$  [B]  $-\frac{d[A]}{dt}$  [C]  $\frac{1}{2} \frac{d[A_2B]}{dt}$  [D]  $-\frac{1}{2} \frac{d[A]}{dt} \cdot \frac{d[B]}{dt}$  **Ans. [A]**

**Sol.** The instantaneous rate of the reaction can be expressed by any of the following expressions

$$-\frac{1}{2} \frac{d[A]}{dt} \quad \text{or} \quad -\frac{d[B]}{dt} \quad \text{or} \quad \frac{d[A_2B]}{dt}$$

**Ex.5** Which of the following will react at the highest rate ?

[A] 1 mol of A and 1 mol of B in a 1 L vessel [B] 2 mol of A and 2 mol of B in a 2 L vessel  
 [C] 3 mol of A and 3 mol of B in a 3 L vessel [D] All would react at the same rate **Ans. [D]**

**Sol.** Since all have same conc. of reactants, all would react at same rate.

## 5. FACTORS AFFECTING THE RATE OF REACTION :

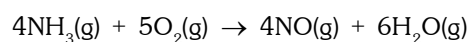
- (i) **Concentration** : Law of mass action enunciates that greater is the conc. of the reactants, the more rapidly the reaction proceeds.
- (ii) **Pressure (Gaseous reaction)** : On increasing the pressure, volume decreases and conc. increases and hence the rate increases.
- (iii) **Temperature** : It is generally observed that rise in temperature increases the reaction rate.
- (iv) **Nature of the reactants** : The rate depends upon specific bonds involved and hence on the nature of reactants.

$$g > \ell > s$$

- (v) **Surface area of the reactants** : In heterogeneous reactions, more powdered is the form of reactants, more is the velocity. [as more active centres are provided]

- (vi) **Catalyst** : Affects the rate immensely.

**Ex.6** For the reaction :



Given :  $\frac{d[NO]}{dt} = 3.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$

Calculate : (i) rate of disappearance of ammonia  
 (ii) rate of formation of water

**Sol.** From the eqn. it is clear that

$$\text{Rate} = -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} = \frac{1}{4} \frac{d[\text{NO}]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt} \quad \text{Thus :} \quad -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} = \frac{1}{4} \frac{d[\text{NO}]}{dt}$$

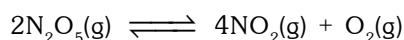
$$\text{or} \quad -\frac{d[\text{NH}_3]}{dt} = \frac{d[\text{NO}]}{dt} = 3.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} \quad \text{Also} \quad \frac{1}{4} \frac{d[\text{NO}]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt}$$

$$\frac{3}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{H}_2\text{O}]}{dt}$$

$$\frac{3}{2} \times 3.6 \times 10^{-3} = \frac{d[\text{H}_2\text{O}]}{dt}$$

$$\frac{d[\text{H}_2\text{O}]}{dt} = 5.4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

**Ex.7** The following reaction was studied in a closed vessel.



It was found that concentration of  $\text{NO}_2$  increases by  $4.0 \times 10^{-2} \text{ mol L}^{-1}$  in five seconds, calculate

- the rate of reaction
- the rate of change of concentration  $\text{N}_2\text{O}_5$ .

**Sol.** (a)  $\text{Rate} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt}$

$$\text{But } \frac{d[\text{NO}_2]}{dt} = \frac{4.0 \times 10^{-2} \text{ mol L}^{-1}}{5 \text{ sec}} = 8 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\therefore \text{Rate of reaction} = \frac{1}{4} \times 8 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} = 2 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

- (b) Rate of change of conc. of  $\text{N}_2\text{O}_5$

$$= \frac{-d[\text{N}_2\text{O}_5]}{dt} = -\frac{1}{2} \text{ Rate of formation of } \text{NO}_2$$

$$= -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = -\frac{1}{2} \times 8 \times 10^{-3} = 4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

**Ex.8** The rate of change in concentration of R in the reaction,  $2\text{P} + \text{Q} \longrightarrow 2\text{R} + 3\text{S}$ , was reported as  $1.0 \text{ mol L}^{-1} \text{ sec}^{-1}$ . Calculate the reaction rate as well as rate of change of concentration of P, Q and S.

**Sol.**  $\frac{-1}{2} \frac{d[\text{P}]}{dt} = -\frac{d[\text{Q}]}{dt} = \frac{1}{2} \frac{d[\text{R}]}{dt} = \frac{1}{3} \frac{d[\text{S}]}{dt} = \text{Rate of reaction}$

$$\therefore \frac{d[\text{R}]}{dt} = 1.0 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\therefore -\frac{d[\text{P}]}{dt} = \frac{d[\text{R}]}{dt} = 1.0 \text{ mol L}^{-1} \text{ s}^{-1}$$

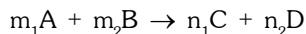
$$\frac{-d[\text{Q}]}{dt} = \frac{1}{2} \frac{d[\text{R}]}{dt} = \frac{1}{2} \times 1.0 = 0.5 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\frac{-d[\text{S}]}{dt} = \frac{3}{2} \frac{d[\text{R}]}{dt} = \frac{3}{2} \times 1.0 = 1.5 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{Rate of reaction} = \frac{1}{2} \frac{d[\text{R}]}{dt} = \frac{1}{2} \times 1.0 = 0.5 \text{ mol L}^{-1} \text{ s}^{-1}$$

## 6. SPECIFIC REACTION RATE :

Applying law of mass action to the reaction :



$$\text{Rate} \propto [A]^{m_1} [B]^{m_2}$$

$$\text{or } v = k[A]^{m_1} [B]^{m_2}$$

This equation is known as rate law. Where k is the proportionality constant and is called

(i) Velocity constant      or      (ii) Velocity coefficient      or      (iii) Specific reaction rate.

On putting  $[A] = [B] = 1$ , where have :  $v = k$

Hence specific reaction rate is the rate of the reaction when the concentration of each reactant is taken as unit.

### ◆ Unit of Specific Reaction Rate

$$v = k [A]^{m_1} \cdot [B]^{m_2}$$

$$\frac{\text{conc.}}{\text{time}} = k [\text{conc.}]^{m_1+m_2}$$

$$[\text{conc.}]^{[1-(m_1+m_2)]} [\text{time}]^{-1} = k \quad \text{or} \quad k = \left[ \frac{\text{mole}}{\text{litre}} \right]^{1-(m_1+m_2)} \cdot [\text{second}^{-1}]$$

## 7. DISTINCTION BETWEEN UNIT OF RATE AND RATE CONSTANT :

◆ **Rate of a reaction** : Its units are always  $\text{mole litre}^{-1} \text{ time}^{-1}$ .

◆ **Rate constant** : Its unit depends upon the order of reaction.

## 8. RATE LAW :

(a) It may also not depend upon the concentration of each reactant or product of the reaction.

Suppose,  $mA + nB \rightarrow \text{Product}$

$$R \propto [A]^m [B]^n$$

(b) Rate of a chemical reaction is directly proportional to the product of the concentration of reactants raised to the power of their stoichiometric coefficient.

(c) The rate law represents the experimentally observed rate of reaction which depends upon the slowest step of the reaction.

(d) Rate law cannot be deduced from the equation for a given reaction. It can be found by experiments only.

(e) The rate law may not bear a simple relationship of the stoichiometric equation.

**Ex.9** In the reaction,  $A + 2B \rightarrow 6C + 2D$ , if the initial rate  $-\frac{d[A]}{dt}$  at  $t = 0$  is  $2.6 \times 10^{-2} \text{ M sec}^{-1}$ , what will be the

value of  $-\frac{d[B]}{dt}$  at  $t = 0$  ?

$$[A] \ 8.5 \times 10^{-2} \text{ M sec}^{-1}$$

$$[B] \ 2.5 \times 10^{-2} \text{ M sec}^{-1}$$

$$[C] \ 5.2 \times 10^{-2} \text{ M sec}^{-1}$$

$$[D] \ 7.5 \times 10^{-2} \text{ M sec}^{-1}$$

**Ans. [C]**

**Sol.** From the reaction it is evident that when a mole of A is reacting, 2 moles of B must react. Hence the decrease in the concentration of B must be twice that of A

$$\therefore -\frac{d[B]}{dt} = 2 \left[ -\frac{d[A]}{dt} \right]$$

$$= 2 \times 2.6 \times 10^{-2} = 5.2 \times 10^{-2} \text{ M sec}^{-1}$$

**Ex.10** The dimensions of rate constant of a second order reaction involves :

[A] time and concentration

[B] neither time nor concentration

[C] time only

[D] concentration only

**Ans. [A]**

**Sol.**  $k = \frac{\text{Rate}}{[A]^2} = \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})^2} = \frac{\text{s}^{-1}}{\text{mol L}^{-1}} = (\text{mol L}^{-1})^{-1} \text{s}^{-1}$

**Ex.11** The rate constant of a reaction has same units as the rate of reaction. The reaction is of

[A] zero order

[B] first order

[C] second order

[D] none of these

**Ans. [A]**

**Sol.** For a zero order reaction,  $r = k[A]$ . Thus the units of  $k$  are the same as that of rate of reaction.

**Ex.12** The rate constant of  $n^{\text{th}}$  order reaction has units :

[A]  $\text{litre}^{1-n} \text{mol}^{1-n} \text{sec}^{-1}$

[B]  $\text{mol}^{1-n} \text{litre}^{1-n} \text{sec}$

[C]  $\text{mol}^{1-n^2} \text{litre}^{n^2} \text{sec}^{-1}$

[D]  $\text{mol}^{1-n} \text{litre}^{n-1} \text{sec}^{-1}$

**Ans. [D]**

**Sol.** For an  $n^{\text{th}}$  order reaction :  $\text{rate} = k [\text{conc.}]^n$

$$k = \frac{\text{rate}}{[\text{conc.}]^n}$$

$$\text{Units of } k = \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})^n} = \text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$$

**Ex.13** On which of the following factors, the rate constant does not depend ?

[A] Temperature

[B] Concentration

[C] Presence of catalyst

[D] Nature of reactants

**Ans. [B]**

**Sol.** Rate constant is independent of the conc. of the reactants.

## 9. ORDER OF REACTION :

The sum of the power of the concentration terms on which the rate of reaction actually depends as observed experimentally is called the order of the reaction. For example,

$$\text{Order of reaction} = x + y$$

Thus, the order of reaction may also be defined as the sum of the exponents (powers) to which the concentration terms in the rate law equation are raised in order to express the observed rate of the reaction.

Thus, reaction is said to be of the first order if its rate is given by the expression of the type,

$$r = k_1 C_A$$

Second order if the rate is given by the expression of the type,

$$r = k_2 C_A^2$$

$$\text{or } r = k_2 C_A C_B$$

third order if the rate is given by the expression of the type

$$r = k_3 C_A^3 \text{ or } r = k_3 C_A^2 C_B \text{ or } r = k_3 C_A C_B^2 \text{ or } k_3 C_A C_B C_C \text{ and so on}$$

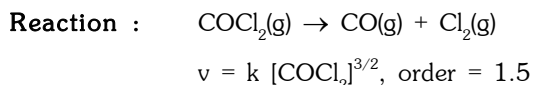
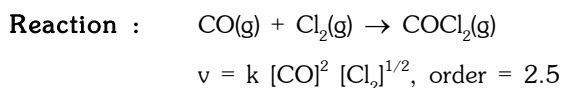
For zero order reaction, the rate equation is written as  $R = k_0$ . It is to be noted that the order of reaction is essentially an experimental quantity.

**Note:** Order may be zero, fractional, integer or negative.

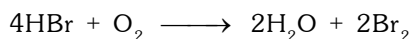
**Example :**

Reaction	Experimental rate equation	order
$\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$	$v = k$	zero
$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$	$v = k [\text{H}_2] [\text{Br}_2]^{1/2}$	one and half
$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	$v = k [\text{H}_2] [\text{I}_2]$	two

◆ **Examples of fractional order reaction**

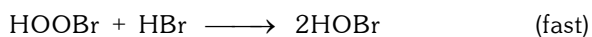


**Ex.14** For the chemical reaction,

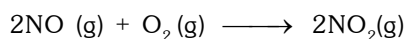


$$\text{Rate} = k [\text{HBr}] [\text{O}_2]$$

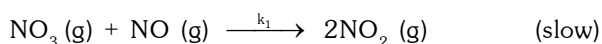
What is the probable mechanism of the reaction ?



**Ex.15** Nitric oxide (NO) reacts with oxygen to produce nitrogen dioxide :



What is the predicted rate law, if the mechanism is :-



**Sol.** From the slow step,

$$\text{Rate} = k_1 [\text{NO}_3] [\text{NO}] \quad \dots\dots\dots(\text{i})$$

From fast step :

$$\text{Equilibrium constant (K)} = \frac{[\text{NO}_3]}{[\text{NO}][\text{O}_2]} \quad \dots\dots\dots(\text{ii})$$

Substituting the value of  $[\text{NO}_3]$  from equation (ii) into equation (i), we get

$$\text{Rate} = k' [\text{NO}]^2 [\text{O}_2]$$

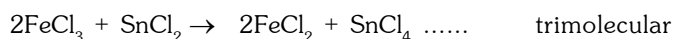
**10. MOLECULARITY OF A REACTION :**

“Molecularity is defined as the number of molecules, atoms, or radicals that must collide simultaneously in order for the reaction to take place.” It is always a whole number and cannot be negative.

In the elementary processes :

Participating species	Molecularity
One species participates .....	unimolecular, 1
Two species participates .....	bimolecular, 2
Three species participates .....	trimolecular, 3

◆ **Example :**

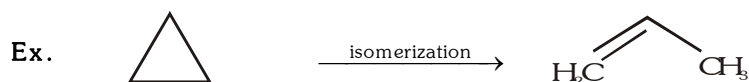


**Note :** If the reaction takes place in two or more steps then the overall molecularity of the reaction is monitored by the slow or rate determining step.

Molecularity		Order of Reaction	
1.	Molecularity can neither be zero nor fractional	1.	Order of a reaction can be zero, fractional or integer
2.	It is the number of molecules of reactants concentration terms taking part in elementary step of a reaction.	2.	It is sum of power raised or the rate expression
3.	It can not have negative value.	3.	Order of a reaction may have negative value.
4.	Molecularity is a theoretical property.	4.	Order is an experimental property.
5.	Molecularity concerns with mechanism.	5.	Order concerns with kinetic (rate law).

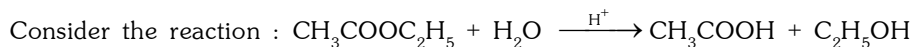
Ex.	Reaction	Rate law	Order
	$\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO}$	$\text{Rate} \propto [\text{CH}_3\text{CHO}]^{3/2}$	1.5
	$\text{NH}_3 \longrightarrow \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2$	$\text{Rate} \propto [\text{NH}_3]^0$	0
	$2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$	$\text{Rate} \propto [\text{HI}]^0$ , i.e. $\text{Rate} = k$	0

Order may change with change in experimental conditions while molecularity can't.



This reaction follows first order kinetics at high pressure and 2<sup>nd</sup> order kinetics at low pressure of cyclopropane.

## 12. PSEUDO UNIMOLECULAR REACTION :



Since water is present in large excess, its concentration hardly changes during the course of the reaction. And as such rate depends only on the concentration of ester. The order is one but the molecularity is two. Such reactions are called **pseudo unimolecular reaction**.

**Ex.16** For a chemical reaction,  $A \rightarrow \text{products}$ , the rate of reaction doubles when the concentration of A is increased by 4 times. The order of reaction is

[A] 4                  [B] 0                  [C]  $\frac{1}{2}$                   [D] 1                  Ans. [C]

**Ans.**  $r = k[A]^n$  ..... (i) ;  $2r = k [4A]^n$  ..... (ii)

$$\text{Dividing (ii) by (i)} \quad \frac{2r}{r} = \frac{k}{k} \left[ \frac{4A}{A} \right]^n$$

$$\text{or } 2 = 2^{2n} \text{ or } 2n = 1 \text{ or } n = 1/2$$

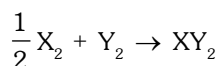
**Ex.17** For a hypothetical reaction

A + B → products, the rate law is,  $r = k [B] [A]$ , the order of reaction is :

[A] 0                  [B] 1                  [C] 2                  [D] 3                  Ans. [B]

**Sol.**  $1 + 0 = 1$

**Ex.18** The slowest step of a particular reaction is found to be



The order of the reaction is

[A] 2                      [B] 3                      [C] 3.5                      [D] 1.5                      Ans. [D]

**Sol.**  $r = k[X_o]^{1/2} [Y_o]^1 \quad \therefore \text{Order} = 0.5 + 1 = 1.5$



**Ex.19** The rate of certain hypothetical reaction  $A + B + C \rightarrow \text{products}$ , is given by

$$r = \frac{dA}{dt} = k [A]^{1/2} [B]^{1/3} [C]^{1/4}$$

The order of a reaction is given by

[A] 1

[B] 1/2

[C] 2

[D] 13/12

**Ans. [D]**

**Sol.** Order of reaction =  $\frac{1}{2} + \frac{1}{3} + \frac{1}{4} = \frac{6+4+3}{12} = \frac{13}{12}$

### 13. ZERO ORDER REACTION :

Reaction whose rate is not affected by concentration said to be of zero order reaction.

**Example :**

(i) Reaction between Acetone and Bromine

(ii) Dissociation of HI on gold surface

**(A) Unit of Rate Constant :**

$$k = \text{mol L}^{-1} \text{sec}^{-1} \quad \text{Unit of rate of reaction} = \text{Unit of rate constant.}$$

**(B) Rate Constant of Zero Order Reaction :**

$$x = kt$$

The rate of reaction is independent of the concentration of the reaction substance.

**(C) Determination of Half life Period of Zero Order Reaction :**

$$\text{At } t = t_{1/2} ; \quad x = \frac{a}{2}$$

$$t_{1/2} = \frac{a}{2k} \quad \text{or} \quad t_{1/2} \propto a$$

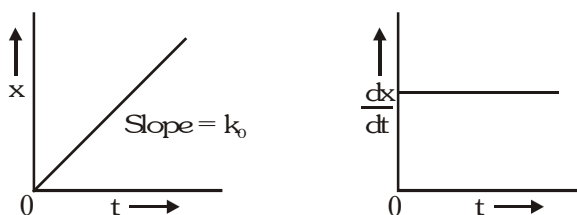
The half life period is directly proportional to the initial concentration of the reactants.

**Ex.20** The rate equation of a reaction is  $k[A]^{1/2}[B]^{1/2}[C]^{-1}$ . What should be the order of the reaction ?

**Sol.**  $n = \frac{1}{2} + \frac{1}{2} - 1 = 0$

$\therefore$  Order of the reaction is zero.

### ◆ Graphical representation



**Example :**

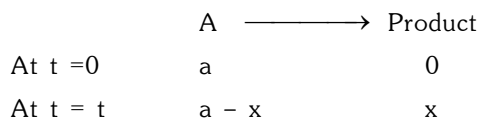
- ◆ Photochemical reactions, like  $H_2 + Cl_2 \longrightarrow 2HCl$ , are zero order reaction.
- ◆ Decomposition of  $NH_3$  on platinum surface is also zero order reaction.

#### 14. FIRST ORDER REACTION :

When the rate of reaction depends only on one concentration term of reactant.

A first order reaction is one whose rate varies as first power of the concentration of the reactant, i.e. the rate increases as number of times as the concentration of reactant is increased.

Let us, consider a unimolecular first order reaction represented by the general equation,



The initial concentration of A is a mole L<sup>-1</sup> and its concentration after time t is (a - x) mole L<sup>-1</sup>. This means during the time interval t, x mole L<sup>-1</sup> of A has reacted.

The rate of reaction at any time t is given by the following first order kinetics.

$$\frac{d(a-x)}{dt} \propto (a-x)$$

$$\text{or } \frac{d(x)}{dt} \propto (a-x) \quad \text{or} \quad \frac{dx}{dt} = k(a-x)$$

where k is the rate constant of the reaction.

$$\frac{dx}{a-x} = k dt$$

This is differential rate equation and can be solved by integration.

$$\int \frac{dx}{a-x} = k \int dt$$

$$\text{or } -\ln(a-x) = k.t + C \quad \dots\dots\dots(1)$$

where C is integration constant.

The constant C can be evaluated by applying the initial condition of the reaction i.e. when t = 0, x = 0. Putting these in equation (1), we get

$$C = -\ln a$$

Putting the value of C in equation (1), we get

$$-\ln(a-x) = k.t - \ln a$$

$$\text{or } k = \frac{1}{t} \ln \frac{a}{a-x} = \frac{2.303}{t} \log \frac{a}{a-x} \quad \dots\dots\dots(2)$$

$$\text{Also, } k = \frac{2.303}{(t_2 - t_1)} \log \frac{(a-x_1)}{(a-x_2)}$$

$$\text{and } k = \frac{2.303}{(t_2 - t_1)} \log \frac{R_1}{R_2}$$

where (a - x<sub>1</sub>) is concentration at time t<sub>1</sub> and (a - x<sub>2</sub>) is concentration after time t<sub>2</sub> and R<sub>1</sub> is rate at time t<sub>1</sub> and R<sub>2</sub> is rate at time t<sub>2</sub>.

If [A]<sub>0</sub> and [A] be the concentrations of reactant at zero time and time t respectively, then Eq. (2) may be put as

$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]}$$

$$\text{Also, } [A] = [A]_0 e^{-kt}$$

This is the integrated rate expression for first order reaction.

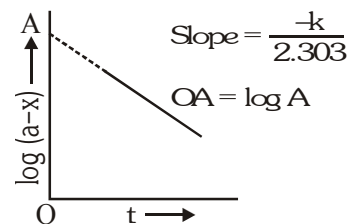
$$\text{As, } k = \frac{1}{t} \ln \frac{a}{a-x} \Rightarrow \log(a-x) = \log(a) - \frac{kt}{2.303}$$

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

$$\text{Also, } (a-x) = ae^{-kt}$$

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

$$\therefore \text{Degree of dissociation} \left( \frac{x}{a} \right) = (1 - e^{-kt})$$



#### ◆ Unit of Rate constant

The differential rate expression for  $n^{\text{th}}$  order reaction is as follows :

$$-\frac{dx}{dt} = k(a-x)^n$$

$$\text{or } k = \frac{dx}{(a-x)^n dt} = \frac{(\text{concentration})}{(\text{concentration})^n \text{ time}} = (\text{conc.})^{1-n} \text{ time}^{-1}$$

If concentration be expressed in mole  $\text{L}^{-1}$  and time in minutes, then

$$k = (\text{mole } \text{L}^{-1})^{1-n} \text{ min}^{-1}$$

For zero order reaction,  $n = 0$  and hence,  $k = \text{mole } \text{L}^{-1} \text{ min}^{-1}$

For first order reaction,  $n = 1$  and hence,

$$k = (\text{mole } \text{L}^{-1})^0 \text{ min}^{-1} = \text{min}^{-1}$$

For second order reaction,  $n = 2$  and hence,

$$k = (\text{mole } \text{L}^{-1})^{-1} \text{ min}^{-1} = \text{mole}^{-1} \text{ L min}^{-1}$$

The rate constant of a first order reaction has only time in its unit. It has no concentration term in the unit. This means the numerical value of  $k$  for a first order reaction is independent of the unit in which concentration is expressed. If concentration unit is changed, the numerical value of  $k$  for a first order reaction will not change. However, it would change with change in time. Say,  $k$  is  $6.0 \times 10^{-3} \text{ min}$  then it may also be written as  $1 \times 10^{-4} \text{ s}^{-1}$ , i.e., numerical value of  $k$  will decrease 60 times if time unit is changed from hour to minute or from minute to second.

#### ◆ Half - time or half - life period of a first order reaction :

The half - time of a reaction is defined as the time required to reduce the concentration of the reactant to half of its initial value. It is denoted by the symbol  $t_{1/2}$ . Thus,

$$\text{When } x = \frac{a}{2}, t = t_{1/2}$$

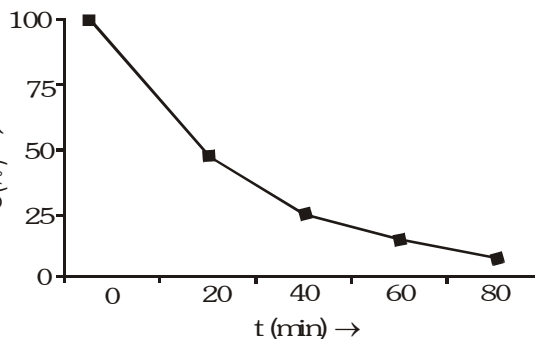
Putting these values in Eq. (2), we get

$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - \frac{a}{2}} = \frac{2.303}{t_{1/2}} \log 2 = \frac{2.303}{t_{1/2}} \times 0.30103$$

$$(\because \log 2 = 0.30103)$$

$$t_{1/2} = \frac{0.693}{k} \dots\dots\dots(3)$$

Since  $k$  is a constant for a given reaction at a given temperature and the expression lacks any concentration term so from Eq. (3) it is evident that half-time of a first order reaction is a constant independent of initial concentration of reactant. This means if we start with 4 moles  $L^{-1}$  of a reactant reacting by first order kinetics, then after 20 minutes it is reduced to 2 moles  $L^{-1}$ . That is, after 20 minutes from the start of reaction the concentration of the reactant will be 2 moles  $L^{-1}$



after 40 minutes from the start of reaction, the concentration is 1 mole  $L^{-1}$ . After 60 minutes from the start of reaction, the concentration of the reactant will be reduced to 0.5 mol  $L^{-1}$ . In other words, if during 20 minutes 50% of the reaction completes, then in 40 minutes 75%, in 60 minutes 85.5% of the reaction and so on, will complete as shown in the figure above.

Thus, fraction left after  $n$  half-lives  $= \left(\frac{1}{2}\right)^n$

Concentration left after  $n$  half-lives,  $[A] = \left(\frac{1}{2}\right)^n [A]_0$

It is also to be noted that Eq. (3) helps to calculate  $t_{1/2}$  or  $k$ .

A general expression for  $t_{1/2}$  is as follows.

#### ◆ Half - life of a $n^{\text{th}}$ order reaction

Let us find out  $t_{1/2}$  for  $n^{\text{th}}$  order reaction where  $n \neq 1$ .

$$\therefore \frac{-d[A]}{dt} = k_n [A]^n \Rightarrow \frac{-d[A]}{[A]^n} = k dt \Rightarrow - \int_{[A]_0}^{[A]_0/2} \frac{d[A]}{[A]^n} = k \int_0^{t_{1/2}} dt$$

$$\int_{[A]_0/2}^{[A]_0} [A]^{-n} d[A] = k_n t_{1/2} \quad \left[ \frac{[A]^{1-n}}{1-n} \right]_{[A]_0/2}^{[A]_0} = k_n t_{1/2}$$

$$\Rightarrow \frac{1}{1-n} \left( [A]_0^{1-n} - \left[ \frac{[A]_0}{2} \right]^{1-n} \right) = k_n t_{1/2} \Rightarrow \frac{[A]_0^{1-n}}{1-n} \left[ 1 - \left( \frac{1}{2} \right)^{1-n} \right] = k_n t_{1/2}$$

$$\Rightarrow \frac{1}{(1-n)[A]_0^{n-1}} [1 - 2^{n-1}] = k_n t_{1/2} \Rightarrow \frac{(2^{n-1} - 1)}{k_n (n-1)[A]_0} = t_{1/2} \text{ (order } n \neq 1)$$

Therefore, for  $n^{\text{th}}$  order reaction, the half-life is inversely related to the initial concentration raised to the power of  $(n - 1)$ .

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

where  $n$  = order of reaction.

- Example :**
- (i) All radioactive reactions
  - (ii)  $A \rightarrow \text{Product}$
  - (iii)  $2NO \rightleftharpoons 2N_2 + O_2$
  - (iv)  $2Cl_2O_7 \rightarrow 2Cl_2 + 7O_2$

#### (A) Unit of rate constant of first order reaction

$$K = (\text{sec})^{-1} \quad \Delta n = 1$$

#### (B) Velocity constant for first order reaction

$$\boxed{k_1 = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}} \quad \Rightarrow \quad \boxed{t = \frac{2.303}{k_1} \log_{10} \frac{a}{(a-x)}}$$

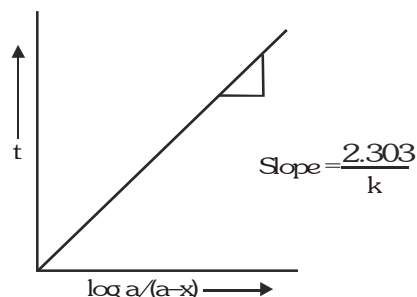
where  $t$  = time,  $a$  = initial concentration at  $t = 0$

$(a - x)$  = concentration after time  $t$

$K$  = Rate constant

(C) Graphical Representation

Graph between  $t$  v/s  $\log \frac{a}{(a-x)}$  is a straight line



**Ex.21** A first order reaction gets 90% completed in 40 minute. Find out the half-life period of the reaction.

**Sol.** Suppose that the initial concentration of reactant (a) = 100       $t = 40$  minutes

90% of the reaction get completed in 40 minutes.

Therefore,

$$x = 90$$

$$\begin{aligned} k_1 &= \frac{2.303}{t} \log \frac{a}{a-x} \\ &= \frac{2.303}{40} \log \frac{100}{100-90} \Rightarrow k_1 = \frac{2.303}{40} \log 10 \\ &= \frac{2.303}{40} \times 1 = 5.757 \times 10^{-2} \text{ minutes}^{-1} \end{aligned}$$

$$t_{1/2} = \frac{0.693}{5.757 \times 10^{-2}} = 10.3 \text{ minutes}$$

**Ex.22** Prove with the help of the following data that hydrolysis of  $\text{H}_2\text{O}_2$  is a first order reaction. Initial concentration in the reaction 25.0.

<b>Sol.</b>	<b>Time, t</b>	<b>10</b>	<b>20</b>	<b>30</b>
	<b>(in minutes)</b>			
	<b>V</b>	<b>20.0</b>	<b>15.7</b>	<b>12.5</b>

For a first order reaction,  $k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$  ;      Here,  $a = 25$

$$k_1 \text{ at } t = 10 \text{ minutes} = \frac{2.303}{10} \log \frac{25}{20} = \frac{2.303}{10} \times 0.0969 = 2.23 \times 10^{-2}$$

$$k_1 \text{ at } t = 20 \text{ minutes} = \frac{2.303}{20} \log \frac{25}{15.7} = \frac{2.303}{20} \times 0.2020 = 2.32 \times 10^{-2}$$

$$k_1 \text{ at } t = 30 \text{ minutes} = \frac{2.303}{30} \log \frac{25}{12.5} = \frac{2.303}{30} \times 0.3010 = 2.31 \times 10^{-2}$$

Constant value of  $k$  shows that hydrolysis of  $\text{H}_2\text{O}_2$  in aqueous medium is a first order reaction.

**Ex.23** The rate constant for an isomerization reaction,  $A \longrightarrow B$ , is  $2.5 \times 10^{-3} \text{ min}^{-1}$ . If the initial concentration of A is 1M, calculate the rate of reaction after 1 hr.

**Sol.** As,  $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$ , for first order reaction

$$\Rightarrow 2.5 \times 10^{-3} = \frac{2.303}{60} \log \frac{1}{(a-x)}$$

$$\therefore (a-x) = 0.8607$$

$$\text{The rate after 60 minutes} = k(a-x) = 2.5 \times 10^{-3} \times 0.8607 = 2.1518 \times 10^{-3}$$

**Ex.24** The rate of a first order reaction is  $0.08 \text{ mol L}^{-1}$  at 20 min. and  $0.06 \text{ mol L}^{-1}$  at 40 min. after start of reaction. Find the half-life of reaction.

**Sol.** As, rate =  $k[A]$

$$0.08 = k[A]_{10}$$

$$0.06 = k[A]_{20}$$

$$\therefore \frac{[A]_{10}}{[A]_{20}} = \frac{0.08}{0.06} = \frac{4}{3}$$

For first order reaction :

$$t = 2.303 \log \frac{[A]_{10}}{[A]_{20}}$$

$$\text{when } t = (40 - 20) = 20 \text{ min.}$$

$$\therefore 20 = \frac{2.303}{k} \log \frac{4}{3}$$

$$\therefore k = \frac{2.303}{20} \log \frac{4}{3} = 0.0144 \text{ min}^{-1}$$

$$\therefore t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0144} = 48.13 \text{ min}$$

**Ex.25** Radioactive decay of an atomic nucleus is a first order reaction. Half-life period of radium [ ${}_{88}\text{Ra}^{226}$ ] is 1590 years. Find out its decay constant.

**Sol.**  $t_{1/2} = \frac{0.693}{k_1} = \frac{0.693}{t_{1/2}} = \frac{0.693}{1590} = 4.358 \times 10^{-4} \text{ Y}^{-1}$

□

## SECOND ORDER REACTION

	A	+	A	$\longrightarrow$	Product
	A	+	B	$\longrightarrow$	Product
At t = 0	a		a		0
At t = t	(a - x)		(a - x)		x
At t = $t_1$	(a - $x_1$ )		(a - $x_1$ )		$x_1$
At t = $t_2$	(a - $x_2$ )		(a - $x_2$ )		$x_2$

As per rate law,  $\frac{dx}{dt} = k_2[A]^n = k_2[A]^2 = k_2[A][B]$

$$\therefore \left( \frac{dx}{dt} \right) = k_2 (a-x)^2 \quad (k_2 = \text{rate constant for second order reaction})$$

$$\text{Also, } k_2 = \frac{1}{t} \left[ \frac{1}{(a-x)} - \frac{1}{a} \right] = \frac{1}{t} \frac{a}{a(a-x)} \quad \text{or} \quad k_2 = \frac{1}{(t_2 - t_1)} \left[ \frac{1}{(a-x_2)} - \frac{1}{(a-x_1)} \right]$$

Where  $(a - x_1)$  and  $(a - x_2)$  are the concentration of the reactant A at time  $t_1$  and  $t_2$  respectively. If reactant

A and B have different concentrations a and b, then  $k_2 = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

when  $a \gg b$  then  $(a - b) \approx a$

$(a - x) \approx a$

Equation reduces to

$$k_2 = \frac{2.303}{t \times a} \log_{10} \frac{b}{a-x}$$

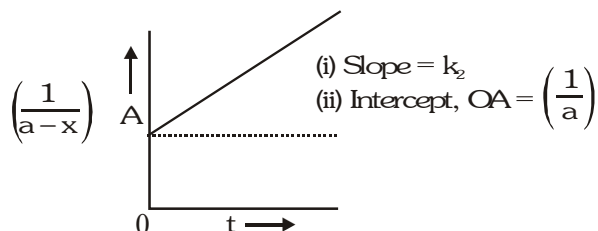
$$\Rightarrow k_2' = k_2 \quad a = \frac{2.303}{t} \log_{10} \left( \frac{b}{b-x} \right) \quad (\text{equation for first order kinetics})$$

This is an example of pseudo first order reaction.

Equation for second order reaction can be rewritten as

$$\frac{a}{(a-x)} = k_2 t + \frac{1}{a}$$

### ◆ Graphical Representation



In general for  $n^{\text{th}}$  order reaction,

$$k_n = \frac{1}{(n-1)t} \left[ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$$

In general for  $n^{\text{th}}$  order reaction,

$$t_{1/2(n)} = \frac{2^{n-1} - 1}{(n-1)k_n(a)^{n-1}} \quad (n \geq 2)$$

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

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

**Ex.26** Initial concentrations of both the reactants of a second order reaction are equal and 60% of the reaction gets completed in 3000 seconds. How much time will be taken in 20% completion of the reaction ?

**Sol.**  $k_2 = \frac{1}{t} \frac{x}{a(a-x)}$

Suppose,  $a = 1$   $k_2 = \frac{1}{3000} \frac{0.6}{1(1-0.6)} = \frac{1}{3000} \frac{0.6}{0.4}$

Now, for 20% completion

$$k_2 = \frac{1}{t} \frac{x}{a(1-x)}$$

$$\frac{1}{3000} \frac{0.6}{0.4} = \frac{1}{t} \frac{(0.2)}{1(1-0.2)}$$

$$\frac{1}{3000} \frac{0.6}{0.4} = \frac{1}{t} \frac{1}{4}$$

$$t = \frac{3000}{0.6} \frac{0.4}{4}$$

$$t = 500 \text{ second}$$

**Ex.27** A second order reaction requires 70 minutes to change the concentration of reactants from 0.08 M to 0.01 M. How much time will it require to become 0.04 M.

**Sol.** For second order reaction

when,  $(a - x) = 0.01$

$$k_2 = \frac{x}{t \cdot a(a - x)}$$

$$k_2 = \frac{0.07}{70 \cdot 0.08 \cdot (0.01)} \quad \dots\dots(1)$$

$(a - x) = 0.04$

$$k_2 = \frac{0.04}{t \cdot 0.08 \cdot (0.04)} \quad \dots\dots(2)$$

From the equation (1) and (2)

$$\frac{0.07}{70 \cdot 0.08 \cdot (0.01)} = \frac{0.04}{t \cdot 0.08 \cdot (0.04)}$$

$$t = 10 \text{ minutes}$$

## 16. THIRD ORDER REACTION :

A reaction is said to be of third order if its rate is determined by the variation of three concentration terms. When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as



**Rate constant of third order reaction**

$$k_3 = \frac{1}{t} \cdot \frac{x(2a - x)}{2a^2(a - x)^2}$$

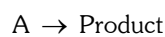
**Half life period**

$$t_{1/2} = \frac{3}{2ka^2}$$

Thus, half life is inversely proportional to the square of initial concentration.



**nth order reaction :**

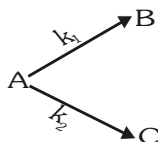


$$k_n t = \frac{1}{n-1} \left\{ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right\} \quad [n \neq 1, n = \text{order}]$$

$$t_{1/2} = \frac{1}{k_n(n-1)} \cdot \left[ \frac{2^{n-1} - 1}{a^{n-1}} \right]$$



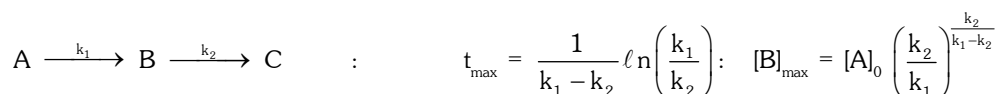
**Side or concurrent reaction :**



$$\ln \frac{[\text{A}]_0}{[\text{A}]_t} = (k_1 + k_2) t \quad ; \quad \frac{[\text{B}]}{[\text{C}]} = \frac{k_1}{k_2}$$



**Consecutive reaction :**



## 17. THRESHOLD ENERGY AND ACTIVATION ENERGY :

For a reaction to take place the reacting molecules must collide together, but only those collisions, in which colliding molecules possess certain minimum energy is called threshold energy ( $E_t$ ).



◆ **Activation energy ( $E_a$ ) :**

The extra energy needed for the reactant molecules to be able to react chemically is known as Activation energy.

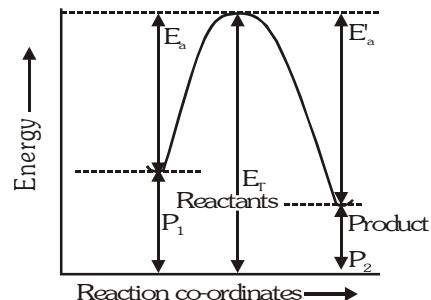
$E_T$  = Threshold energy

$E_a$  = Activation energy of forward reaction

$E'_a$  = activation energy of backward reaction

$P_1$  = Potential energy of reactants

$P_2$  = Potential energy of products



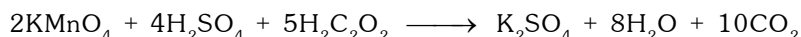
18. **EFFECT OF CATALYST :**

A catalyst is a substance, which increases the rate of reaction without itself being consumed at the end of the reaction, and the phenomenon is called catalysis. There are some catalysts which decrease the rate of reaction and such catalysts are called negative catalyst. Obviously, the catalyst accelerating the rate will be positive catalyst. However, the term positive is seldom used and catalyst itself implies positive catalyst. Catalysts are generally foreign substances but sometimes one of the product formed may act as a catalyst and such a catalyst is called "auto catalyst" and the phenomenon is called **auto catalysis**.

Thermal decomposition of  $\text{KClO}_3$  is found to be accelerated by the presence of  $\text{MnO}_2$ . Here,  $\text{MnO}_2$  (foreign substance) act as a catalyst  $2\text{KClO}_3 + [\text{MnO}_2] \longrightarrow 2\text{KCl} + 3\text{O}_2\uparrow + [\text{MnO}_2]$

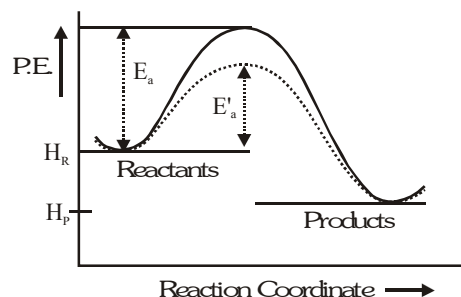
$\text{MnO}_2$  can be received in the same composition and mass at the end of the reaction.

In the permanganate titration of oxalic acid in the presence of bench  $\text{H}_2\text{SO}_4$  (acid medium), it is found that there is slow discharge of the colour of permanganate solution in the beginning but after sometime the discharge of the colour becomes faster. This is due to the formation of  $\text{MnSO}_4$  during the reaction which acts as a catalyst for the same reaction. Thus,  $\text{MnSO}_4$  is an "**auto catalyst**" for this reaction. This is an example of auto catalyst.



□ **General Characteristic of Catalyst**

- ◆ A catalyst does not initiate the reaction, it simply fastens it.
- ◆ Only a small amount of catalyst can catalyse the reaction.
- ◆ A catalyst does not alter the position of equilibrium i.e. magnitude of equilibrium constant and hence  $\Delta G$ . It simply lowers the time needed to attain equilibrium. This mean if a reversible reaction in absence of catalyst completes to go to the extent of 75% till attainment of equilibrium, and this state of equilibrium is attained in 20 minutes then in presence of a catalyst also the reaction will go to 75% of completion before the attainment of equilibrium but the time needed for this will be less than 20 minutes.
- ◆ A catalyst drives the reaction through a different route for which energy barrier is of shortest height and Hence,  $E_a$  is of lower magnitude. That is, the function of the catalyst is to lower down the activation energy.



$E_a$  = Energy of activation in absence of catalyst.

$E'_a$  = Energy of activation in presence of catalyst.

$E_a - E'_a$  = Lowering of activation energy by catalyst.

If  $k$  and  $k_{\text{cat}}$  be the rate constant of a reaction at a given temperature  $T$ , and  $E_a$  and  $E'_a$  are the activation energies of the reaction in absence and presence of catalyst, respectively, the

$$\frac{k_{\text{cat}}}{k} = \frac{Ae^{-E'_a/RT}}{Ae^{-E_a/RT}}$$

$$\frac{k_{\text{cat}}}{k} = Ae^{(E_a - E'_a)/RT}$$

Since  $E_a$ ,  $E'_a$  is +ve, so  $k_{\text{cat}} > k$ . The ratio  $\frac{k_{\text{cat}}}{k}$  gives the number of times the rate of reaction will increase by the use of catalyst at a given temperature and this depends upon  $E_a - E'_a$ . Greater the value of  $E_a - E'_a$ , more number of times  $k_{\text{cat}}$  is greater than  $k$ .

The rate of reaction in the presence of catalyst at any temperature  $T_1$  may be made equal to the rate of reaction in absence of catalyst but we will have to raise the temperature. Let, this temperature be  $T_2$ , then

$$e^{-E'_a/RT_1} = e^{-E_a/RT_2}$$

or 
$$\frac{E'_a}{T_1} = \frac{E_a}{T_2}$$

**Ex.28** A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in presence of catalyst at the same rate, the temperature required is 400K. Calculate the activation energy of the reaction if the catalyst lowers the activation energy barrier by 40 kJ/mol.

**Sol.** Let,  $E_a$  and  $E'_a$  be the energy of activation in absence and presence of catalyst for hydrogenation reaction, as  $k = Ae^{-E_a/RT}$

$$k_1 = Ae^{-E_a/R \times 500} \quad (\text{In absence of catalyst})$$

$$k_2 = Ae^{-E'_a/R \times 400} \quad (\text{In presence of catalyst})$$

Given,  $r_1 = r_2$ ; Hence  $k_1 = k_2$

$$e^{-E_a/R \times 500} = e^{-E'_a/R \times 400}$$

$$\Rightarrow \frac{E_a}{R \times 500} = \frac{E'_a}{R \times 400} \quad \text{or} \quad \frac{E_a}{500} = \frac{E_a - 40}{400} \quad (\text{As } E_a - E'_a = 40)$$

$$\therefore E_a = 200 \text{ kJ/mol}^{-1}$$

## 19. DETERMINATION OF ORDER OF REACTION :

### ◆ Integration Method

In this method, value of  $k$  is determined by putting values of initial concentration of reactants and change in concentration with time in kinetic equation of first, second and third order reactions. The equation by which constant value of  $k$  is obtained is called order of that reaction.

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x} \quad (\text{For first order reaction})$$

$$k_2 = \frac{1}{t} \left[ \frac{x}{a(a-x)} \right] \quad (\text{For second order reaction})$$

$$k_3 = \frac{1}{2t} \left[ \frac{x(2a-x)}{a^2(a-x)^2} \right] \quad (\text{For third order reaction})$$

**Ex.29** For a reaction,  $A \rightarrow B$ , it has been found that the order of the reaction is zero with respect to A. Which of the following expression correctly describes the reaction ?

$$[A] \quad k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \quad [B] \quad [A]_0 - [A] = kt \quad [C] \quad t_{1/2} = \frac{0.693}{k} \quad [D] \quad t_{1/2} \propto \frac{1}{[A]_0} \quad \text{Ans. [B]}$$

**Sol.** 
$$-\frac{d[A]}{dt} = k[A]_0, \quad -d[A] = kdt$$

Integrating from  $t = 0$  to  $t = t$

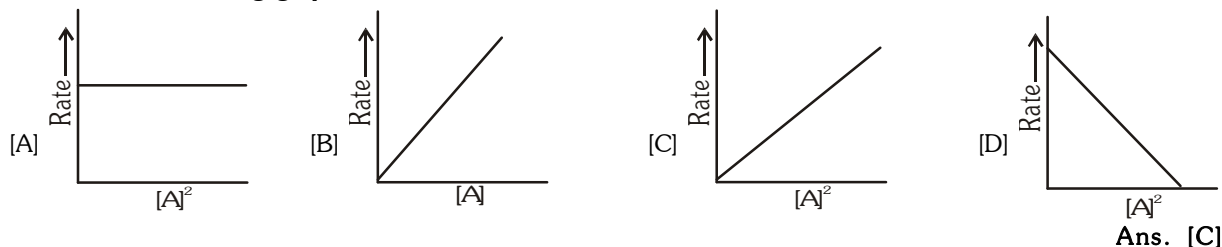
$$[A]_0 - [A] = kt$$

### Graphical Method

If a straight line is obtained on drawing a graph between  $\log(a - x)$  and time then it is first order reaction.

If a straight line is obtained on drawing a graph between  $(a - x)^2$  and  $\frac{dx}{dt}$ , then it is second order reaction.

**Ex.30** Which of the following graphs is for a second order reaction ?



**Sol.** For second order reaction rate vs  $[A]^2$  is a straight line with slope equal to  $k$  rate  $= k[A]^2$

If a straight line is obtained on drawing a graph between  $(a - x)^3$  and  $\frac{dx}{dt}$ , then it is third order reaction.

### Half-life Method

Relation between half-life period of a reaction and initial concentration is as follows :  $t^{1/2} \propto \frac{1}{a^{n-1}}$

For first order reaction (Half life  $\propto a^0$ )

For second order reaction (Half life  $\propto 1/a$ )

For third order reaction (Half life  $\propto 1/a^2$ )

**Ex.31** For a first order reaction,  $t_{0.75}$  is 1386 seconds. Therefore, the specific rate constant is  
 [A]  $10^{-1} \text{ s}^{-1}$  [B]  $10^{-3} \text{ s}^{-1}$  [C]  $10^{-2} \text{ s}^{-1}$  [D]  $10^{-4} \text{ s}^{-1}$

**Ans. [B]**

**Sol.**  $t_{0.75} = 1386 \text{ s} = 2 t_{0.5}$  ;  $t_{0.5} = \frac{1386}{2} = 693 \text{ s}$  ;  $k = \frac{0.693}{693 \text{ s}} = 1 \times 10^{-3} \text{ s}^{-1}$

**Ex.32**  $t_{1/2}$  of first order reactions is given by  $\frac{0.693}{k}$ ,  $t_{3/4}$  would be equal to

[A]  $\frac{0.693}{k}$  [B]  $\frac{0.346}{k}$  [C]  $\frac{1.386}{k}$  [D]  $\frac{0.924}{k}$  **Ans. [C]**

**Sol.**  $t_{3/4} = 2(t_{1/2}) = \frac{2 \times 0.693}{k} = \frac{1.386}{k}$

**Ex.33** The  $t_{1/2}$  of a first order reaction is found to be 2 minutes. The percentage of the reactant left after 360 seconds is :

[A] 12.5 [B] 25 [C] 15 [D] 7.5 **Ans. [A]**

**Sol.** 360 seconds = 6 min = 3 half-lives

$$100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25 \xrightarrow{t_{1/2}} 12.5$$

### Ostwald Isolation Method

This method is used to find out the order of complex reactions. If  $nA$ ,  $nB$  and  $nC$  molecules of substance A, B and C, respectively, are present in a reaction, then  $nA + nB + nC$  will be the order of reaction.

When B and C are in excess, the order of reaction will be  $nA$ .

When A and B are in excess, the order of reaction will be  $nC$ .

When A and C are in excess, the order of reaction will be  $nB$ .

**Ex.34** When the initial concentration of a reaction was doubled, its half life become half, What should be the order of the reaction ?

**Sol.** Rate law for product of a reaction is as follows :

$$\begin{aligned} \text{Rate} &= k[A]^n & \text{and } \frac{t_{0.5}}{t_{0.5}} &= \left[ \frac{2a}{a} \right]^{n-1} \\ 2 &= [2]^{n-1} ; & n - 1 &= 2 \\ n &= 2 \end{aligned}$$

## 20. TEMPERATURE EFFECT :

The rate of reaction is dependent on temperature. This is expressed in terms of temperature coefficient which is a ratio of two rate constants differing by a temperature of 10 . Generally the temperature selected are 298K and 308K. It is mathematically expressed as,

$$\text{Temperature coefficient} = \frac{\text{rate constant at 308K}}{\text{rate constant at 298K}} = \frac{k_{t+10}}{k_t}$$

**The value of temperature coefficient for most of the reactions lies between 2 to 3.**

## 21. ARRHENIUS EQUATION :

Arrhenius derived a mathematical expression to give a quantitative relationship between rate constant and temperature. The expression is

$$k = A.e^{-E_a/RT}$$

(Here, A = frequency factor;  $E_a$  = activation energy ; R = gas constant and T = temperature).

If  $k_1$  and  $k_2$  are rate constants at temperature  $T_1$  and  $T_2$  then

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

**Ex.35** Ethylene oxide is decomposed into  $\text{CH}_4$  and CO. Rate constant for this reaction may be described by

$$\text{the equation } \log k \text{ (s}^{-1}\text{)} = 14.34 - \frac{1.25 \times 10^4}{T}$$

- (i) What will be the energy of activation of this reaction ?
- (ii) What will be the value of k at 670 K ?
- (iii) At what temperature will its half-life period be 25.6 minutes ?

**Sol.** (i) We know,  $\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$  .....(i)

Given,  $\log k \text{ (s}^{-1}\text{)} = 14.34 - \frac{1.25 \times 10^4}{T}$  .....(ii)

Comparing Eqs. (i) and (ii), we get

$$\frac{E_a}{2.303R} = 1.25 \times 10^4$$

(ii)  $E_a = 1.25 \times 10^4 \times 2.303 \times 8.314 \times 10^{-3}$

$\therefore E_a = 239.339 \text{ kJ/mol}$

Substituting the value of T (670 K) in Eq. (ii),

$$\log k \text{ (s}^{-1}\text{)} = 14.34 - \frac{1.25 \times 10^4}{670} = 4.3167$$

$\therefore k = 4.82 \times 10^{-5} \text{ s}^{-1}$

(iii)  $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{256 \times 60} = 0.000451 \text{ sec}^{-1}$

$$\Rightarrow \log 0.000451 \text{ sec}^{-1}$$

$$= 14.34 - \frac{1.25 \times 10^4}{T} \Rightarrow T = 706.79 \text{ K}$$

**Ex.36** The rate constant of forward reaction a reaction increases by 6% when the temperature of the reaction is increased from 300 to 301 K, whereas equilibrium constant increases by 2%. Calculate the activation energy for the forward as well as backward reaction.

**Sol.** According to Arrhenius equation,  $\log \frac{k_2}{k_1} = \frac{E_{a(f)}}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$

If  $k_1 = k$  at 300 K then at 301 K,  $k_2 = k + k \frac{6}{100} = 1.06 k$

$$\therefore \log_{10} \frac{1.06k}{k} = \frac{E_{a(f)}}{2.303 \times 8.314} \left[ \frac{301 - 300}{300 \times 301} \right]$$

$$\therefore E_{a(f)} = \log(1.06) \cdot 2.303 \cdot 8.314 \cdot 300 \cdot 301 = 43753 \text{ J/mol} = 43.753 \text{ kJ/mol}$$

According to van't Hoff equation,  $\log \frac{k_2}{k_1} = \frac{\Delta H^\circ}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$

If  $k_1 = k$  at 300 K,  $k_2 = k + \frac{2}{100} k = 1.02 k$

$$\log_{10} \frac{1.02k}{k} = \frac{\Delta H^\circ}{2.303 \times 8.314} \left( \frac{301 - 300}{300 \times 301} \right)$$

$$\therefore \Delta H = (\log 1.02) \cdot 2.303 \cdot 8.314 \cdot 300 \cdot 301 \text{ J/mol} \\ = 14869 \text{ J mol}^{-1} = 14.87 \text{ kJ/mol}$$

Thus, reaction is endothermic.

For such a reaction,  $\Delta H = E_{a(f)} - E_{a(b)}$

$$\therefore E_{a(b)} = E_{a(f)} - \Delta H = 43.753 - 14.87 \text{ kJ/mol} = 28.883 \text{ kJ mol}^{-1}$$

**Ex.37** Value of rate constant for a first order reaction at 500 K is  $1.60 \cdot 10^{-5} \text{ second}^{-1}$ , whereas at 600 K, it is  $6.36 \cdot 10^{-3} \text{ second}^{-1}$ . Find out the activation energy of the reaction.

**Sol.**  $\log \left( \frac{k_1}{k_2} \right) = \frac{-E_a}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$

$$\log 1.60 \cdot 10^{-5} - \log 6.36 \cdot 10^{-3} = \frac{-E_a}{2.303 \times 8.314} \left[ \frac{1}{500} - \frac{1}{600} \right]$$

$$5.241 - 3.8035 = \frac{E_a}{19.15} \cdot \frac{1}{3000} \quad E_a = 2.5999 \cdot 19.15 \cdot 3000$$

$$E_a = 1.49 \cdot 10^5$$

**Ex.38** An exothermic reaction,  $X \rightarrow Y$ , has an activation energy  $30 \text{ kJ mol}^{-1}$ . If energy change ( $\Delta E$ ) during the reaction is  $-20 \text{ kJ}$ , then the activation energy for the reverse reaction is

[A]  $-30 \text{ kJ}$  [B]  $20 \text{ kJ}$  [C]  $50 \text{ kJ}$  [D]  $10 \text{ kJ}$  **Ans. [C]**

**Sol.**  $\Delta E = E_{a(f)} - E_{a(b)}$  ;  $-20 = 30 - E_{a(b)}$  ;  $E_{a(b)} = 50 \text{ kJ}$

**Ex.39** An endothermic reaction,  $A \rightarrow B$ , has an activation energy as  $x \text{ kJ mol}^{-1}$  of A. If energy change of the reaction is  $y \text{ kJ}$ , the activation energy of reverse reaction is

[A]  $-x$  [B]  $x - y$  [C]  $x + y$  [D]  $y - x$  **Ans. [B]**

**Sol.**  $\Delta E = E_{a(f)} - E_{a(b)}$  ;  $y = x - E_{a(b)}$  ;  $E_{a(b)} = x - y$

**Ex.40** Which of the following relations is correct ?

[A]  $k = A e^{E_a/RT}$  [B]  $\ln k - \ln A = \frac{E_a}{RT}$  [C]  $\ln A - \ln k = \frac{E_a}{RT}$  [D]  $\ln A - \ln k = -\frac{E_a}{RT}$  **Ans. [C]**

**Sol.**  $k = A e^{-E_a/RT}$

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

**Ex.41** Which of the following expression give the effect of temperature on the rate constant ?

[A]  $\ln A = RT \ln E_a - \ln k$

[B]  $\ln k = \ln A - E_a/RT$

[C]  $k = AE_a/RT$

[D] None of these

**Ans. [B]**

**Sol.** The effect of temperature on rate constant is quantitatively given by Arrhenius equation

$$k = Ae^{-E_a/RT} \text{ or } \ln k = \ln A - E_a/RT$$

**Ex.42** The plot of  $\log k$  vs  $\frac{1}{T}$  helps to calculate

[A] Energy of activation

[B] Rate constant of the reaction

[C] Order of the reaction

[D] Energy of activations as well as the frequency factor

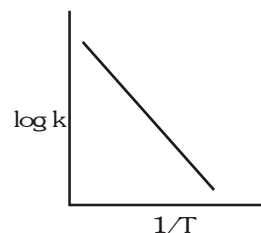
**Ans. [D]**

**Sol.** According to Arrhenius equation :  $\log k = \log A - \frac{E_a}{2.303} \cdot \frac{1}{T}$

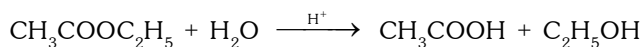
Plot of  $\log k$  vs.  $\frac{1}{T}$  is straight line

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

Intercept =  $\log A$



**Ex.43** The progress of the reaction given below, consider the reaction given below,



the reaction can be followed by measuring the concentration of acid (HCl acid used as catalyst plus acetic acid formed during the reaction) by means of alkali titration. Calculate the volume of alkali (NaOH) needed for the end point that will increase with time.

**Sol.**  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$

At  $t = 0$       a                      excess                      0                      0

At  $t = t$       a - x                                      x                      x

At  $t = \infty$       0                                      a                      a

If  $V_0$ ,  $V_t$  and  $V_\infty$  are the volumes of NaOH solution needed for the end point of titration of the reaction mixture at zero time, time  $t$  and at infinity, i.e. after completion of the reaction the condition being achieved by heating the reaction mixture for some time, then

$$V_0 \propto [\text{acid catalyst}]$$

$$V_t \propto [\text{acid catalyst}] + x$$

$$V_\infty \propto [\text{acid catalyst}] + a$$

$$\therefore V_\infty - V_t \propto a - x$$

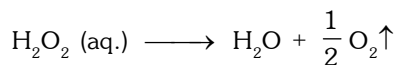
$$V_\infty - V_0 \propto a$$

(since concentration of HCl acid acting as catalyst will remain constant).

The above reaction which is of first order ( actually pseudo unimolecular) will, therefore, obey following equation.

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

Ex.44



At  $t = 0$                       a                      0                      0

At  $t = t$                       a - x                      x                      x

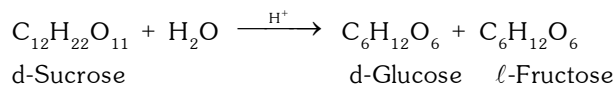
Since  $\text{H}_2\text{O}_2$  acts as a reducing agent towards  $\text{KMnO}_4$ , so concentrations of  $\text{H}_2\text{O}_2$  at various time intervals may be determined by the titration of the reaction mixture against standard  $\text{KMnO}_4$  solution. The titre value will go on decreasing with time. If  $V_0$  and  $V_t$  be the titre values at zero time and any time  $t$  then  $V_0 \propto a$  and  $V_t \propto a - x$

The above reaction being first order, its rate constant may be expressed as

$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

Ex.45

The reaction mentioned below is first order w.r.t. sucrose and zero order w.r.t. water, since water is in large excess as compared to sucrose. That is, it is an example of pseudo unimolecular reaction. Sucrose, glucose and fructose all are optically active substances. Therefore, the progress of the reaction can be followed by measuring angle of rotations of the reaction mixture at various time intervals. During the reaction, angle of rotation goes on decreasing and after sometime there is reversal of the direction of rotation, i.e. from dextro to laevo and Hence, the reaction is called "**inversion of cane sugar**" or inversion of sucrose.



Initially                      a                      Excess                      0                      0

After time  $t$                       a - x                      Constant                      x                      x

At infinity                      0                      Constant                      a                      a

Angle of optical rotation is measured by means of an instrument called polarimeter. Optical rotation is mathematically expressed as,

$$R_{\text{obs}} = \ell \cdot C \cdot [\alpha]_D^t$$

where

$\ell$  = length of the polarimeter tube

$C$  = concentration of test solution

$[\alpha]_D^t$  = specific rotation

For a given sample and polarimeter,  $\ell$  and  $[\alpha]_D^t$  are constant.

$R_{\text{obs}} \propto C$ , or  $R_{\text{obs}} = kC$ ,

If  $r_0$ ,  $r_t$  and  $r_\infty$  be the observed angle of rotations of the sample at zero time, time  $t$  and infinity respectively, and  $k_1$ ,  $k_2$  and  $k_3$  be proportionate in terms of sucrose, glucose and fructose, respectively.

Then,

$$r_0 = k_1 a$$

$$r_t = k_1(a - x) + k_2 x + k_3 x$$

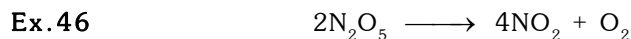
$$r_\infty = k_2 a + k_3 a$$

From these equations it can be shown that

$$\frac{a}{a-x} = \frac{r_0 - r_\infty}{r_t - r_\infty}$$

So, the expression for the rate constant of this reaction in terms of the optical rotational data may be

$$\text{put as } k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$



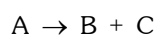
At $t = 0$	$P_0$	0	0
At $t = t$	$P_0 - 2x$	$4x$	$x$
At $t = \infty$	0	$2P_0$	$\frac{1}{2} P_0$

The progress of the reaction can be followed by measuring the pressure of the gaseous mixture in a closed vessel, i.e. at constant volume. The expression for the rate constant in terms of pressure data will be as given below.

$$k = \frac{2.303}{t} \log \frac{P_0}{P_t}, \text{ where } P_t = P_0 - 2x$$

If total pressure after any time  $t$  and at  $\infty$  is given, then it is possible to find  $P_0$  and  $x$  and hence,  $k$  may be calculated.

**Ex.47** Consider a first order reaction,



Assume that A, B and C are gases. The given data is

Time	0	T
Partial pressure of A	$P_1$	$P_2$

And we have to find the rate constant of the reaction.

**Sol.** Since A is a gas assuming it to be ideal, we can state that  $P_A = [A] RT$  [From  $PV = nRT$ ]  
 $\therefore$  At  $t = 0$ ,  $P_1 = [A]_0 RT$  and at  $t = t$ ,  $P_2 = [A]_t RT$ . Thus, the ratio of the concentration of A at two different time intervals is equal to the ratio of its partial pressure at those same time intervals.

$$\therefore \frac{[A]_0}{[A]_t} = \frac{P_1}{P_2}$$

$$\therefore k = \frac{1}{t} \ln \frac{P_1}{P_2}$$

**Ex.48**  $\text{A} \rightarrow \text{B} + \text{C}$

Time	0	t
Total pressure of A + B + C	$P_1$	$P_2$

Find  $k$ .

**Sol.** In this case, we are given total pressure of the system at these time intervals. The total pressure obviously includes the pressure of A, B and C. At  $t = 0$ , the system would only have A. Therefore, the total pressure at  $t = 0$  would be the initial pressure of A.

$\therefore P_1$  is the initial pressure of A. At time  $t$ , let us assume moles of A will decompose to give B and C because of which its pressure is reduced by an amount  $x$  while that of B and C is increased by  $x$  each.

That is :

	$\text{A} \longrightarrow$	$\text{B}$	$+$	$\text{C}$
Initial	$P_1$	0		0
At time $t$	$P_1 - x$	$x$		$x$

$$\therefore \text{Total pressure at time } t = P_1 + x = P_2$$

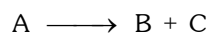
$$\Rightarrow x = P_2 - P_1$$

Now the pressure of A at time  $t$  would be  $P_1 - x = P_1 - (P_2 - P_1) = 2P_1 - P_2$

$$\therefore k = \ln \frac{[A]_0}{[A]_t} = \ln \frac{P_1}{(2P_1 - P_2)}$$



**Ex.49** For the given following first order reaction,



Time	T	$\infty$
Total pressure of A + B + C	$P_2$	$P_3$

Calculate k.

**Sol.** Here  $\infty$  means that the reaction is complete. Now, we have

	A	$\longrightarrow$	B	+	C
At t = 0	$P_1$		0		0
At t = t	$(P_1 - x)$		x		x
At t = $\infty$	0		$P_1$		$P_1$

$$\therefore 2P_1 = P_3$$

$$\Rightarrow P_1 = \frac{P_3}{2}$$

At time t,

$$P_1 + x = P_2$$

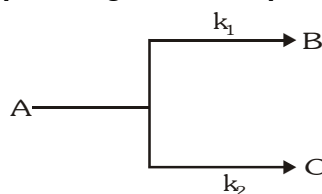
$$\Rightarrow \frac{P_3}{2} + x = P_2 \Rightarrow x = P_2 - \frac{P_3}{2}$$

$$\Rightarrow P_1 - x = \frac{P_3}{2} - (P_2 - \frac{P_3}{2}) = P_3 - P_2$$

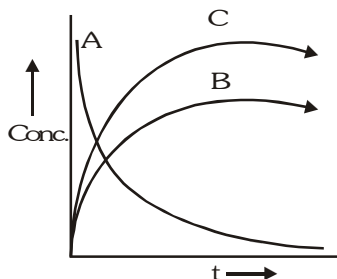
$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]_t} = \frac{1}{t} \ln \frac{P_3/2}{(P_3 - P_2)} = \frac{1}{t} \ln \frac{P_3}{2(P_3 - P_2)}$$

## 22. PARALLEL REACTIONS :

These are reactions in which reaction substances do not follow a particular path to give a particular set of products. It follows one or more paths to give different products, e.g.



The reactant A follows two different paths to form B and C as shown below :

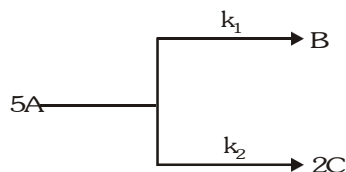


$$\text{Rate} = -\frac{d[A]}{dt} = k_1[A] + k_2[A]$$

$$= k[A] \quad [\text{As, } (k_1 + k_2) = k]$$

$$\% \text{ yield of B} = \frac{k_1}{k_1 + k_2} \times 100$$

**Ex.50** A follows parallel path, first order reaction giving B and C as



If initial concentration of A is 0.25 M, calculate the concentration of C after 5 hours of reaction.

[Given :  $k_1 = 1.5 \times 10^{-5} \text{ s}^{-1}$ ,  $k_2 = 5 \times 10^{-6} \text{ s}^{-1}$ ]

**Sol.**  $k = \frac{2.303}{t} \log \frac{[A]}{[A]_t}$  ( $k = k_1 + k_2 = 1.5 \times 10^{-5} + 5 \times 10^{-6} = 2 \times 10^{-5} \text{ s}^{-1}$ )

$$\Rightarrow 2 \times 10^{-5} = \frac{2.303}{t} \log \frac{0.25}{[A]_t}$$

$$\therefore [A]_t = 0.1744 \text{ M}$$

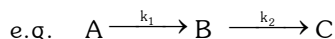
$$\therefore [A]_{\text{decomposed}} = [A]_0 - [A]_t = 0.25 - 0.1744 = 0.0756 \text{ M}$$

$$\text{Fraction of C formed} = \frac{k_2}{(k_1 + k_2)} [A]_{\text{decomposed}} \quad \frac{2}{5} = \frac{5 \times 10^{-6}}{2 \times 10^{-5}} \quad 0.0756 \quad \frac{2}{5} = 7.56 \times 10^{-3} \text{ M}$$

(5 moles of A are used to give 2 moles of C)

## 23. SEQUENTIAL REACTIONS :

These are reactions which proceed from reactants to product through one or more intermediate stages,

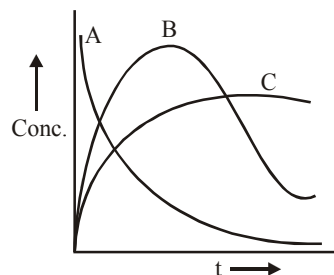


### ◆ Graphical representation

$$\frac{-d[A]}{dt} = k_1[A] \quad \dots\dots\dots(1)$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \quad \dots\dots\dots(2)$$

$$\frac{d[C]}{dt} = k_2[B] \quad \dots\dots\dots(3)$$



Integrating Eq. (1), we get

$$[A] = [A]_0 e^{-k_1 t}$$

Now, we shall integrate Eq. (2) and find the concentration of B related to time t.

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \Rightarrow \frac{d[B]}{dt} + k_2[B] = k_1[A]$$

Substituting [A] as  $[A]_0 e^{-k_1 t}$

$$\Rightarrow \frac{d[B]}{dt} + k_2[B] = k_1[A]_0 e^{-k_1 t} \quad \dots\dots\dots(4)$$

Integration of the above equation is not possible as we are not able to separate the two variables, [B] and t. Therefore, we multiply Eq. (4) by integrating factor  $e^{k_2 t}$ , on both the sides of the equation.

$$\left( \frac{d[B]}{dt} + k_2[B] \right) e^{k_2 t} = k_1[A]_0 e^{(k_2 - k_1)t}$$

We can see that the left hand side of the equation is a differential of  $[B] e^{k_2 t}$ .

$$\therefore \frac{d}{dt} ([B] e^{k_2 t}) = k_1[A]_0 e^{(k_2 - k_1)t}$$

$$d([B]e^{k_2t}) = k_1[A]_0 e^{(k_2-k_1)t} dt$$

Integrating within the limits 0 to t.

$$\begin{aligned} \int d([B]e^{k_2t}) &= k_1[A]_0 \int_0^t e^{(k_2-k_1)t} dt & \Rightarrow [B]e^{k_2t} &= k_1[A]_0 \left[ \frac{e^{(k_2-k_1)t}}{(k_2-k_1)} \right]_0^t \\ \Rightarrow [B]e^{k_2t} &= \frac{k_1[A]_0}{(k_2-k_1)} [e^{(k_2-k_1)t} - 1] & \Rightarrow [B] &= \frac{k_1[A]_0}{(k_2-k_1)} e^{-k_2t} [e^{(k_2-k_1)t} - 1] \\ [B] &= \frac{k_1[A]_0}{k_2-k_1} [e^{-k_1t} - e^{-k_2t}] & \dots\dots\dots(5) \end{aligned}$$

Now, in order to find [C], substitute Eq. (5) in Eq. (3), we get

$$\begin{aligned} \frac{d[C]}{dt} &= \frac{k_1 k_2 [A]_0}{k_2 - k_1} [e^{-k_1t} - e^{-k_2t}] \\ \therefore d[C] &= \frac{k_1 k_2 [A]_0}{k_2 - k_1} [e^{-k_1t} - e^{-k_2t}] dt \end{aligned}$$

On integrating, we get

$$\begin{aligned} \int d[C] &= \frac{k_1 k_2 [A]_0}{(k_2 - k_1)} \int_0^t [e^{-k_1t} - e^{-k_2t}] dt \\ \Rightarrow [C] &= \frac{k_1 k_2 [A]_0}{(k_2 - k_1)} \left[ \left( \frac{e^{-k_1t}}{-k_1} \right)_0^t - \left( \frac{e^{-k_2t}}{-k_2} \right)_0^t \right] \\ \Rightarrow [C] &= \frac{k_1 k_2}{(k_2 - k_1)} [A]_0 \left[ \left( \frac{e^{-k_1t} - 1}{-k_1} \right) - \left( \frac{e^{-k_2t} - 1}{-k_2} \right) \right] \\ \Rightarrow [C] &= \frac{k_1 k_2}{k_2 - k_1} [A]_0 \left[ \left( \frac{1 - e^{-k_1t}}{k_1} \right) - \left( \frac{1 - e^{-k_2t}}{k_2} \right) \right] \\ [C] &= \frac{[A]_0}{k_2 - k_1} [k_2(1 - e^{-k_1t}) - (1 - e^{-k_2t})] \end{aligned}$$

$B_{\max}$  and  $t_{\max}$  : We can also attempt to find the time when [B] becomes maximum. For this, we differentiate

Eq. (5) and find  $\frac{d[B]}{dt}$  and equate it to zero.

$$\begin{aligned} \therefore \frac{d[B]}{dt} &= \frac{k_1[A]_0}{(k_2 - k_1)} [e^{-k_1t}(-k_1) + e^{-k_2t}(k_2)] = 0 \\ \Rightarrow k_1 e^{-k_1t} &= k_2 e^{-k_2t} \\ \frac{k_1}{k_2} &= e^{(k_1-k_2)t}, \text{ taking log of both the sides} \\ \therefore t_{\max} &= \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} & \dots\dots\dots(6) \end{aligned}$$

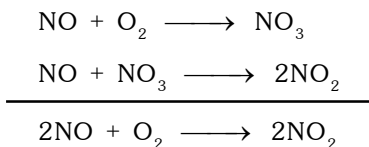
Substituting Eq. (6) in Eq. (5)

$$B_{\max} = [A]_0 \left[ \frac{k_2}{k_1} \right]^{k_2 / (k_1 - k_2)}$$

## 24. HYPOTHESIS OF STEADY STATE :

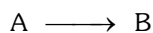
There are many reactions which involve multi steps and the intermediates (one or more) do not appear in the overall equation, e.g.  $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$

Steps involved in the above reaction are

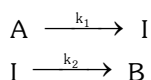


In the above steps,  $\text{NO}_3$  is an intermediate species and do not appear in the overall balanced equation. Usually these intermediates are very reactive and do not accumulate to any significant extent during the reaction.

For hypothetical reaction,



The reaction can proceed in the following steps :

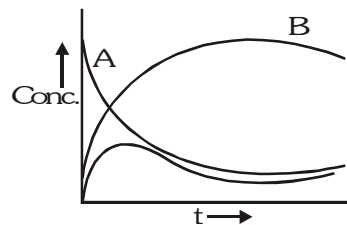


The concentration of the intermediate [I] is much less than the reactant [A] as well as the product [B]. Accordingly the formation of intermediate will start at zero, rises to maximum, and then fall back to zero. If the concentration of intermediate remains small during the reaction, then the curves of reactants, intermediate and product versus  $t$  will be given as below :

From the plot, it is clear that the slope of the curve for intermediate much less than those for reactants A and products B. It is, therefore

good approximation to take  $\frac{d[\text{I}]}{dt} = 0$ , for each reaction intermediate.

**This is steady state (stationary state) approximation.**



## 25. RADIOACTIVITY :

All radioactive decay follows first order kinetics and this is where the similarity ends. This will be explained later in the chapter.

We have measured the rate of reaction in chemical kinetics based on the rate of change of concentration of reactants or products. But this procedure will not work for calculating the rate of a radioactive reaction. This is because most of the time the radioactive substance is a solid. Therefore, its concentration would be a constant with time (assuming it to be pure and that the product does not remain with the reactants). Therefore, the rate of radioactive reactions is measured by calculating the rate of change of number of nuclei of the radioactive substance.

For a radioactive decay  $\text{A} \rightarrow \text{B}$ , the rate of reaction is calculated as

$$\frac{-dN_A}{dt} = \lambda N_A$$

where  $\lambda$  = decay constant of reaction.

$N_A$  = number of nuclei of the radioactive substance at the time when rate is calculated.

As you can see, the above rate law is very much similar to the rate law of a first order chemical reaction, but all other similarities cease here. For example unlike a chemical reaction the decay constant ( $\lambda$ ) does not depend on temperature. Arrhenius equation is not valid for radioactive decay.

$$\frac{-dN_A}{dt} = \lambda N_A$$

Integrating the differential rate law, we get

$$-\int_{N_0}^{N_t} \frac{dN_A}{N_A} = \lambda \int_0^t dt$$

$$\log \frac{N_0}{N_t} = \lambda t$$

where

$N_0$  = number of nuclei of A, at  $t = 0$

$N_t$  = number of nuclei of A, at  $t = t$

$\lambda$  = decay constant

The expression can be rearranged to give

$$N_t = N_0 e^{-\lambda t} \dots\dots\dots(1)$$

This suggest that the number of nuclei of radioactive substance A at any instant of time can be calculated, if we know the number of nuclei at  $t = 0$ , its decay constant and the time.

### ◆ **Half-Life**

Just like a first order reaction, the half-life of radioactive decay is given by

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

[Note : Let us start with 10 nuclei. If the half-life is 5 minutes, then at the end of first 5 minutes, number of nuclei would be 5. Now, what would be the number of nuclei after next 5 minutes ? Will it be 2.5 or 2 or 3 ? We can clearly see that it cannot be 2.5 and if it is 2 or 3 then it cannot be called as half-life. This dilemma can be overcome by understanding that all formula relating to kinetics are only valid when the sample size is very large and in such a large sample size, a small difference of 0.5 will be insignificant. The fact that radioactive decay follows the exponential law implies that this phenomenon is statistical in nature. Every nucleus in a sample of a radionuclide has a certain probability of decaying, but there is no way to know in advance which nuclei will actually decay in a particular time span. If the sample is large enough, i.e. if many nuclei are present - the actual fraction of it that decays in a certain time span will be very close to the probability for any individual nucleus to decay. To say that, a certain radioisotope has a half-life of 5 hr. signifies that every nucleus of this isotope has a 50 percent chance of decaying in every 5 hr. period. This does not mean probability of 100 percent decaying is 10 hr. A nucleus does not have a memory, and its decay probability per unit time is constant until it actually does decay. A half-life of 5 hr. implies a 75 probability of decay in 10 hr., which increases to 87.5% in 15 hr., to 93.75% in 20 hr., and so on, because in every 5 hr. The probability of decay is 50 percent.

### ◆ **Average-Life Time**

Average life time is defined as the life time of a single isolated nucleus. Let us imagine, a single nucleus which decays in 1 second. Assuming 1 second time interval to be very small, the rate of change of nuclei would be  $1/1$  (because  $-dN = 1$  and  $dt = 1$ ). We can also see that since  $\frac{-dN}{dt} = \lambda N$ , for a single isolated nucleus  $N = 1$ ,  $\frac{-dN}{dt} = \lambda$ . Therefore, in this present case,  $\lambda = 1$ .

Now, let us assume, the same nucleus decays in 2 seconds, we can see that  $\frac{-dN}{dt}$ , i.e.  $\lambda$  is equal to  $\frac{1}{2}$ . You will also notice that in the 1<sup>st</sup> case the nucleus survived for 1 second and in the second case it survived for 2 seconds. Therefore, the life time of a single isolated nucleus is  $\frac{1}{\lambda}$ .

$$\therefore t_{av} = \frac{1}{\lambda}$$

◆ **Activity :**

Activity is the rate of decay of a radioactive element. It is represented as 'A' and is equal to  $\lambda N$ . By no means should activity be confused with rate of change of radioactive nuclei represented by  $\frac{-dN}{dt}$ . This is because  $\frac{-dN}{dt}$  talks about the overall change in the number of nuclei in a given instant of time while activity only talks about that change which is decay. For example, if you go to a market with Rs. 50 in your pocket and you spend Rs. 20 in 5 minutes then your rate of change of money in the wallet is Rs. 4/min and in fact the rate of spending the money is also Rs. 4/min. Here, you can see both are same. But if while spending Rs. 20 in 5 minutes, somebody keeps Rs. 10 in your wallet, then the rate of change of money in your wallet would become Rs. 2.5 /min while the rate of spending the money is Rs. 4/min. This implies that as long as the radioactive substance is only decaying the rate of change of nuclei and activity are same and Eq.(1) in terms activity of radioactive substance can be written as  $A_t = A_0 e^{-\lambda t}$ . But if the radioactive substance is also being produced, then  $\frac{dN}{dt}$  = rate of production – activity (of course it's a different matter that rate of production may or may not be a constant).

◆ **Specific Activity**

It is defined as per unit mass of the sample. Let, radioactive sample weighing w g have a decay constant  $\lambda$ . The number of nuclei in the w g would be  $\frac{w}{M} \times N_0$ , where M = molecular weight of the radioactive substance and  $N_0$  = Avogadro's number.

$$\therefore \text{Specific activity} = \frac{\left( \lambda \times \frac{w}{M} \times N_0 \right)}{w} = \frac{\lambda \times N_0}{M}$$

It should be remembered that if a radioactive sample is pure and the product does not remain with reactant, then specific activity is a constant.

◆ **Units of Activity**

The unit of radioactivity of a substance is measured as the rate at which it changes into daughter nucleus. It has been derived on the scale of disintegration of radium.

Let us consider, 1g of radium (atomic mass = 226 and  $t_{1/2} = 1600$  yrs) undergoes decay, then

Rate of decay of radium =  $\lambda$  Number of nuclei of Ra in 1g

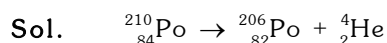
$$= \frac{0.693}{1600 \times 365 \times 24 \times 60 \times 60} \times \frac{1 \times 6.023 \times 10^{23}}{226} = 3.7 \times 10^{10} \text{ dps} = 3.7 \times 10^{10} \text{ becquerel}$$

$$= 1 \text{ curie } (\because 1 \text{ Ci} = 3.7 \times 10^{10} \text{ dps})$$

$$= 3.7 \times 10^4 \text{ Rutherford } (\because 1 \text{ Rd} = 10^6 \text{ dps})$$

The SI unit of activity is dps or Becquerel.

**Ex.51**  $^{210}_{84}\text{Po}$  decays with emission of  $\alpha$ -particle to  $^{206}_{82}\text{Pb}$  with a half-life period of 138.4 days. If 1g of  $^{210}_{84}\text{Po}$  is placed in a sealed tube, how much helium will be accumulated in 69.2 days ? Express the answer in  $\text{cm}^3$  at STP.



Amount of  $^{210}_{84}\text{Po}$  left after 69.2 days can be calculated by applying

$$N = N_0 (1/2)^n$$

$$n = t/t_{1/2} = \frac{69.2}{138.2} = \frac{1}{2}$$

$$\therefore N = 1 \left( \frac{1}{2} \right)^{1/2} = 0.702 \text{ g}$$

Amount of polonium disintegrated =  $1 - 0.7072 = 0.2928$  g

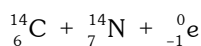
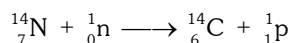
$$\text{Moles of polonium in } 0.2928 \text{ g} = \frac{0.2928}{210}$$

$$\text{Moles of helium atoms formed} = \frac{0.2928}{210}$$

$$\therefore \text{Volume of helium collected} = \frac{0.2928}{210} \times 22400 = 31.23 \text{ cm}^3$$

## 26. CARBON DATING :

The cosmic ray generates neutrons in the atmosphere which bombards the nucleus of atmospheric nitrogen to form radioactive  $^{14}\text{C}$  hence  $^{14}\text{C}$  in the atmosphere has been remaining constant over thousands of years. In living materials, the ratio of  $^{14}\text{C}$  to  $^{12}\text{C}$  remains relatively constant. When the tissue in an animal or plant dies, assimilation of radioactive  $^{14}\text{C}$  ceased to continue. Therefore, in the dead tissue the ratio of  $^{14}\text{C}$  to  $^{12}\text{C}$  would decrease depending on the age of the tissue.



A sample of dead tissue is burnt to give carbon dioxide and the carbon dioxide is analysed for the ratio of  $^{14}\text{C}$  to  $^{12}\text{C}$ . From this data, age of dead tissue (plant or animal) can be determined.

$$\text{Age (t)} = \frac{2.303}{\lambda} \log \frac{N_0}{N}$$

$$\Rightarrow \text{Age} = \frac{2.303}{0.693} t_{1/2} (^{14}\text{C}) \log \left( \frac{N_0}{N} \right)$$

$N_0$  = ratio of  $^{14}\text{C}/^{12}\text{C}$  in living plant

$N$  = ratio of  $^{14}\text{C}/^{12}\text{C}$  in the wood

$$\text{Age} = \frac{2.303}{0.693} t_{1/2} \log \left( \frac{A_0}{A} \right)$$

$A_0$  = Original activity

$A$  = Final activity

$$\text{Also, } N = \left( \frac{1}{2} \right)^n N_0 \Rightarrow \text{where } n = \frac{t}{t_{1/2}}$$

## 27. ROCK DATING :

It is based on the kinetics of radioactive decay. It is assumed that no lead was originally present in the sample and whole of it came from uranium.

Initial no. of mole ( $N_0$ ) =  $[\text{U}] + [\text{Pb}]$

Final no. of mole ( $N$ ) =  $[\text{U}]$

$$\frac{N_0}{N} = \frac{[\text{U}] + [\text{Pb}]}{[\text{U}]} = 1 + \frac{[\text{Pb}]}{[\text{U}]}$$

$$t = \frac{2.303}{\lambda} \log \left[ \frac{N_0}{N} \right]$$

$$\Rightarrow t = \frac{2.303}{\lambda} \log \left[ 1 + \frac{[\text{Pb}]}{[\text{U}]} \right]$$

$$\text{Also, } \left[ 1 + \frac{[\text{Pb}]}{[\text{U}]} \right] = (2)^n \quad \left( n = \frac{t}{t_{1/2}} \right)$$

**Ex.52** A sample of uranium mineral was found to contain  $^{206}\text{Pb}$  and  $^{238}\text{U}$  in the ratio of 0.008 : 1. Estimate the age of the mineral (half-life of  $^{238}\text{U}$  is  $4.51 \times 10^9$  years).

**Sol.** 
$$t = \frac{2.303}{\lambda} \log \left[ 1 + \frac{^{206}\text{Pb}}{^{238}\text{U}} \right]$$

$$t = \frac{2.303}{0.693} \times t_{1/2} \log \left[ 1 + \frac{^{206}\text{Pb}}{^{238}\text{U}} \right]$$

$$\Rightarrow \text{Ratio by mass } ^{206}\text{Pb} : ^{238}\text{U} = 0.008 : 1$$

$$\text{Ratio by moles } ^{206}\text{Pb} : ^{238}\text{U} = \frac{0.008}{206} : \frac{1}{238} = 0.0092$$

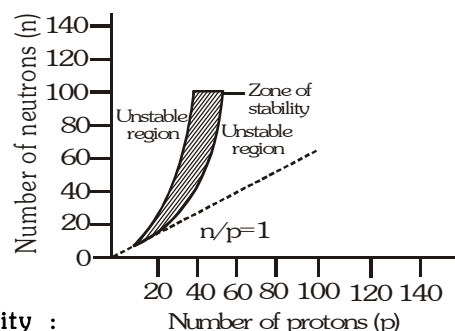
$$\therefore t = \frac{2.303 \times 4.51 \times 10^9}{0.693} \log (1 + 0.0092)$$

$$= \frac{2.303 \times 4.51 \times 10^9}{0.693} \times 0.00397 = \frac{0.0412}{0.693} \times 10^9 = 5.945 \times 10^7 \text{ years}$$

## 28. STABILITY OF NUCLEI WITH RESPECT TO NEUTRON - PROTON RATIO :

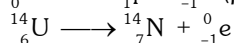
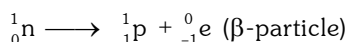
If number of neutrons is plotted against the number of protons, the stable nuclei lie within well-defined region called zone of stability.

All the nuclei falling outside this zone are invariably radioactive and unstable in nature. Nuclei that fall above the stability zone has an excess of neutrons while those lying below have more protons. These nuclei attain stability by making adjustment in n/p ratio.



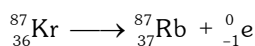
### ◆ When (n/p) ratio is higher than that required for stability :

Such nuclei have tendency to emit  $\beta$ -rays (transforming a neutron into proton).



$$\frac{n}{p}$$

$$1.33 \quad 1$$



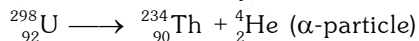
$$\frac{n}{p} :$$

$$\frac{51}{36} \quad \frac{50}{37}$$

### ◆ When (n/p) ratio is lower than that required for stability :

Such nuclei have tendency to increase n/p ratio by adopting any of the following three ways.

- ◆ By emission of an  $\alpha$ -particle (natural radioactivity).

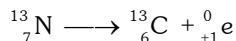


$$\left( \frac{n}{p} \right)$$

$$\left( \frac{146}{92} \right) \quad \left( \frac{144}{90} \right)$$

$$=1.50 \quad =1.60$$

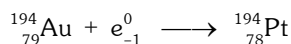
- ◆ By emission of positron



$$\frac{n}{p}$$

$$\frac{6}{7} \quad \frac{7}{6}$$

- ◆ By K-electron capture



$$\left( \frac{n}{p} \right)$$

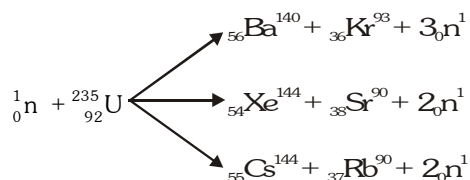
$$\frac{115}{79} \quad \frac{116}{78}$$

$\alpha$ -emission is usually observed in natural radioactive isotopes while emission of positron or K-electron capture is observed in artificial radioactive isotopes. The unstable nuclei continue to emit  $\alpha$  or  $\beta$ -particle until stable nucleus comes into existence.

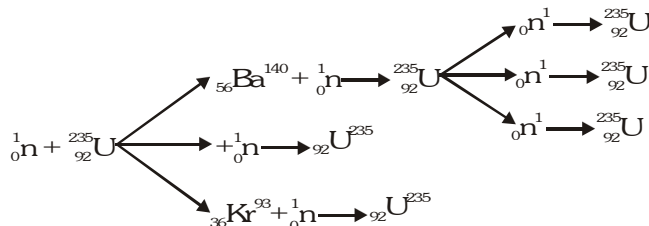


## 29. NUCLEAR FISSION :

It is a nuclear reaction in which heavy nucleus splits into lighter nuclei of comparable masses with release of large amount of energy by bombardment with suitable sub-atomic particles, i.e.



If the neutrons from each nuclear fission are absorbed by other  ${}^{235}_{92}\text{U}$  nuclei, these nuclei split and release even more neutrons. Thus, a chain reaction can occur. A nuclear chain reaction is a self sustaining series of nuclear fissions caused by the previous neutrons released from the previous nuclear reactions.

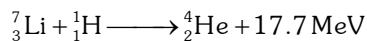
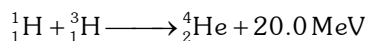
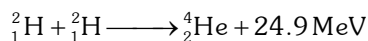
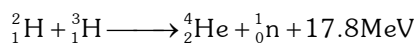


There should be critical amount of the fissionable material to maintain fission chain. This in turn requires, minimum critical mass of the fissionable material. It is the small mass of the fissionable material in which chain reaction can be sustained. If mass is larger than critical mass (supercritical mass), then the number of nuclei that split, multiplies rapidly. An atomic bomb is detonated with small amount of chemical explosive that push together two or more masses of fissionable material to get a supercritical mass.

A nuclear fission reactor is a device that permits a controlled chain nuclear fissions. Control rods made of elements such as boron and cadmium, absorb additional neutrons and can therefore, slow the chain reactions.

## 30. NUCLEAR FUSION :

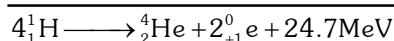
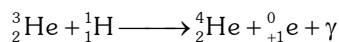
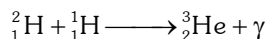
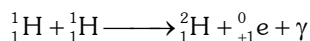
It is a nuclear reaction in which two lighter nuclei are fused together to form a heavier nuclei. To achieve this, colliding nuclei must possess enough kinetic energy to overcome the initial force of repulsion between the positively charged core. At very high temperature of the order of  $10^6$  to  $10^7$  K, the nuclei may have the sufficient energy to overcome the repulsive forces and fuse. Such reactions are therefore also known as thermonuclear reactions.



The energy of fusion process is due to mass defect (converted into binding energy). The high temperature required to initiate such reaction may be attained initially through fission process.

Hydrogen bomb is based on the principle of fusion reactions. Energy released is so enormous that it is about 1000 times that of atomic bomb. In hydrogen bomb, a mixture of deuterium oxide ( $\text{D}_2\text{O}$ ) and tritium oxide ( $\text{T}_2\text{O}$ ) is enclosed in space surrounding an ordinary atomic bomb. The temperature produced by the explosion of the atomic bomb initiates the fusion reaction between  ${}^2_1\text{H}$  and  ${}^3_1\text{H}$  releasing huge amount of energy.

It is believed that the high temperature of stars including the sun is due to fusion reactions. E. Salt Peter in 1953, proposed a proton-proton chain reaction.

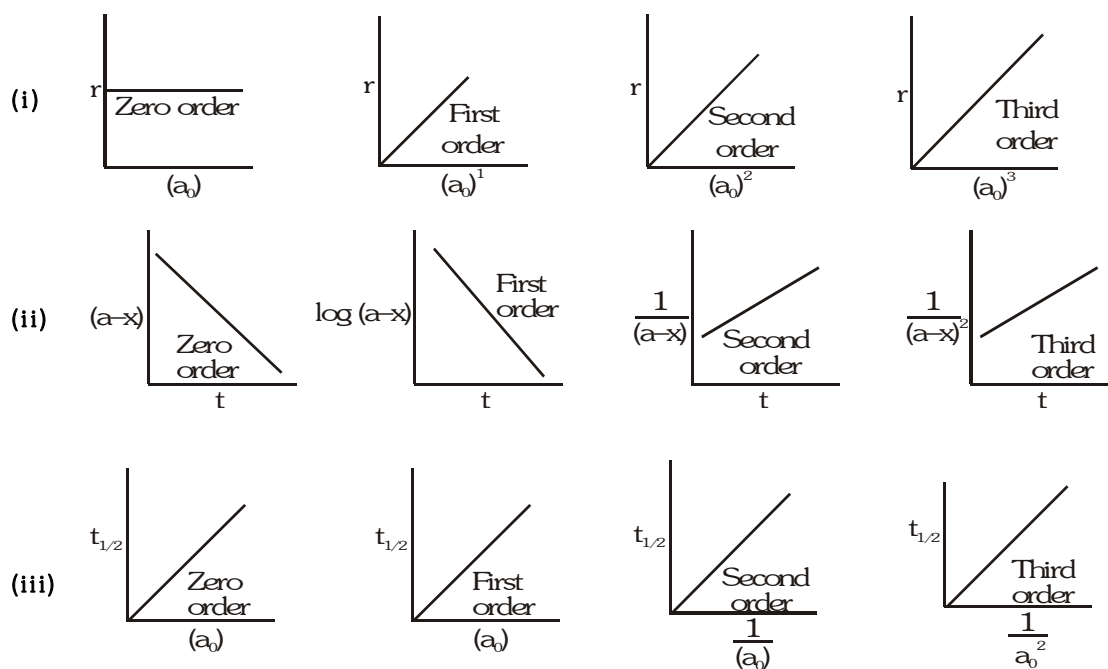


## MEMORY TIPS

1. Expression for rate constants for reaction of different orders.

Type of reaction	Integrated rate equation	Unit of rate constant	Half-life period	$t^{3/4}$ life period
Zero order reaction	$-\frac{d[A]}{dt} = k_0[A]^0$  Differentiation form $\frac{dx}{dt} = k$	Concentration  time <sup>-1</sup>	$t_{1/2} = \frac{a}{2k_0}$	--
First order reaction	$k_1 = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$	time <sup>-1</sup>	$t_{1/2} = \frac{0.693}{K_1}$	$t_{3/4} = 2 \frac{0.693}{k_1} = \frac{1.382}{k_1}$
Second order reaction	$k_2 = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$  Differential form $\frac{dx}{dt} = k(a-x)^2$	Mole <sup>-1</sup> litre time <sup>-1</sup>	$t_{1/2} = \frac{1}{k_2 a}$	$t_{3/4} = \frac{3}{k_2 a}$
Third order reaction	$k_3 = \frac{x \times (2a-x)}{t2a^2(a-x)^2}$  Differential form $\frac{dx}{dt} = k(a-x)^3$	Litre <sup>2</sup> mole <sup>-2</sup> time <sup>-1</sup>	$t_{1/2} = \frac{3}{2k_3 a^2}$	---

2. Some typical linear plots for reactions of different orders :



3. Amount left after  $n$  half-lives =  $\left(\frac{1}{2}\right)^n [A]_0$

$$\text{No. of half-lives} = \frac{\text{Total time}}{t_{1/2}}$$

4. Exponential form of expression for rate constant for reaction of 1<sup>st</sup> order :  $[A] = [A]_0 e^{-kt}$  or  $C_t = C_0 e^{-kt}$

5. 
$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

6. Arrhenius equation for effect of temperature on rate constant,

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

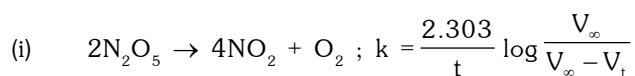
$$\text{on } \log k = \log R - \frac{E_a}{2.303RT}$$

$$\text{Also, } \frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

If  $k_1$  and  $k_2$  are rate constants at temperature  $T_1$  and  $T_2$ , then

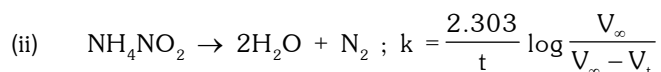
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_1 - T_2}{T_1 T_2} \right]$$

7. Examples of reactions of 1<sup>st</sup> order and their formula for rate constants

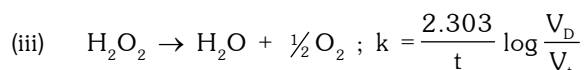


where  $V_\infty$  = volume of  $O_2$  gas collected at infinite time

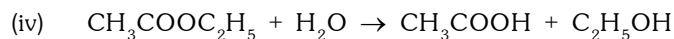
$V_t$  = volume of  $O_2$  gas collected at time  $t$



where  $V_\infty$  and  $V_t$  are volumes of  $N_2$  gas collected after infinity time and after time  $t$  respectively.

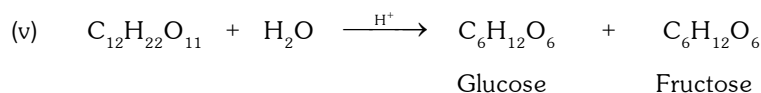


where  $V_D$  and  $V_t$  are the volumes of  $KMnO_4$  solution used for titrating a definite volume of the reaction mixture at  $t = D$  and at time  $t$  respectively.



$$k = \frac{2.303}{t} \log \frac{V_\infty - V_D}{V_\infty - V_t}$$

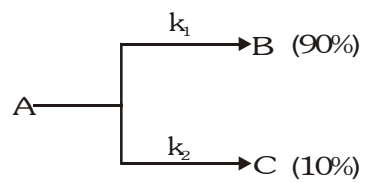
where  $V_D$ ,  $V_t$  and  $V_\infty$  are the volume of  $NaOH$  solution used for titration mixture at zero time, after time  $t$  and after infinity respectively.



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

where  $r_0$ ,  $r_t$  and  $r_\infty$  are the polarimetric reading at zero time, after time  $t$  and after infinity respectively.

8. Rate law equation for reactions involving parallel reaction



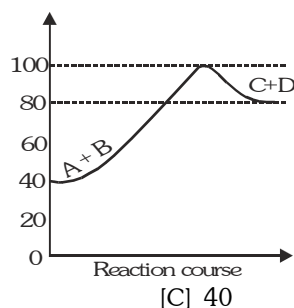
$$\text{Rate} = -\frac{d[A]}{dt} = k_1 [A] + k_2 [A] = [k_1 + k_2] [A]$$

9. Degree of dissociation at any time  $t = (1 - e^{-kt})$
-

# SOLVED OBJECTIVE PROBLEMS

**Ex.1** Find the activation energy [kJ/mol] for the reaction,  $A(g) + B(g) \rightarrow C(g) + D(g)$ .

From the plot given below :



[A] 20

[B] 60

[C] 40

[D] 80

**Sol.**  $E_a = 100 - 40 = 60 \text{ kJ mol}^{-1}$

Hence the answer is [B].

**Ex.2** In an endothermic reaction,  $\Delta H$  represents the enthalpy of reaction in kJ/mol, the minimum value for the energy of activation will be.

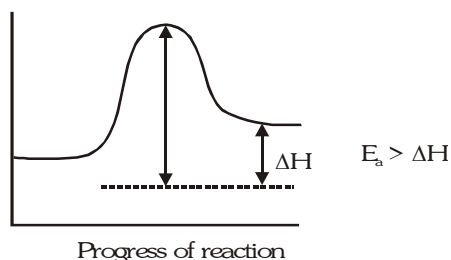
(A) less than  $\Delta H$

(B) zero

(C) more than  $\Delta H$

(D) equal to  $\Delta H$

**Sol.**



Hence, (C) is the correct answer.

**Ex.3** Consider the following first order competing reactions

$A \longrightarrow B, C \longrightarrow D,$

the ratio of  $\frac{k_1}{k_2}$ , if only 25% of A have been reacted whereas 50% of C has been reacted, calculate the

ratio of  $\frac{k_1}{k_2}$

(A) 0.415

(B) 0.246

(C) 2.06

(D) 0.06

**Sol.**  $k_1 = \frac{2.303}{t_1} \log \frac{100}{75}$  for 25% (A) reacted

$k_2 = \frac{2.303}{t_2} \log \frac{100}{50}$  for 50% (C) reacted

$$\therefore \frac{k_1}{k_2} = \frac{t_2}{t_1} \times \frac{0.1249}{0.3010}$$

Since  $t_2 = t_1$

$$\therefore \frac{k_1}{k_2} = \frac{0.1249}{0.3010} = 0.415$$

Hence, (A) is the correct answer.

**Ex.4** For a reaction  $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ . If the reactions are of 1st order then  $\frac{d[B]}{dt}$  is equal to  
 [A]  $-k_2[B]$  [B]  $+k_1[A]$  [C]  $k_1[A] - k_2[B]$  [D]  $k_1[A] + k_2[B]$

**Sol.** Rate of increase in  $[B] = k_1[A]$   
 Similarly rate of decrease in  $[B] = k_2[B]$

$$\text{Thus, } \frac{d[B]}{dt} = k_1[A] - k_2[B]$$

Hence the answer is [C]

**Ex.5** The half life period  $t_{1/2}$  is independent of initial concentration of reactant when the order of reaction is  
 [A] Negative [B] 0 [C] 1 [D] Fractional

**Sol.**  $t_{1/2}$  of a reaction of an order  $n$  is related to initial concentration by the expression

$$t_{1/2} \propto \frac{1}{C_0^{n-1}} \quad (\text{Here, } n = \text{order of reaction})$$

for  $n = 1$ ,  $t_{1/2}$  is independent of concentration term. Hence the answer is [C].

**Ex.6** For a first order reaction,  $A \longrightarrow B$ , the rate of reaction at  $[A] = 0.1 \text{ M}$  is  $1.0 \times 10^{-1} \text{ mol L}^{-1} \text{ min}^{-1}$ . The half-life period for the reaction is

(A) 42 sec (B) 21 sec (C) 20 sec (D) 28 sec

**Sol.**  $r = k[A]$

$$k = \frac{r}{[A]} = \frac{10^{-1}}{0.1} = 1$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1} = 0.693 \text{ min} = 0.693 \times 60 \approx 42 \text{ sec}$$

Hence, (A) is the correct answer.

**Ex.7** A catalyst lowers the activation energy of a reaction from  $30 \text{ kJ mol}^{-1}$  to  $15 \text{ kJ mol}^{-1}$ . The temperature at which the uncatalysed reaction will have the same rate as that of the catalysed at  $27^\circ \text{C}$  is

(A)  $-123^\circ \text{C}$  (B)  $327^\circ \text{C}$  (C)  $-327^\circ \text{C}$  (D)  $+23^\circ \text{C}$

**Sol.**  $\frac{E'_a}{T_1} = \frac{E_a}{T_2} \Rightarrow \frac{15}{300} = \frac{20}{T_2}$

$$\therefore T_2 = 600 \text{ K} = 327^\circ \text{C}$$

Hence, (B) is the correct answer.

**Ex.8**  $\text{SO}_2\text{Cl}_2 \rightleftharpoons \text{SO}_2 + \text{Cl}_2$ , is the first order gas reaction with  $k = 2.2 \times 10^{-5} \text{ sec}^{-1}$  at  $270^\circ \text{C}$ . The percentage of  $\text{SO}_2\text{Cl}_2$  decomposed on heating for 50 minutes is

(A) 1.118 (B) 0.1118 (C) 18.11 (D) 6.39

**Sol.**  $k = \frac{2.303}{t} \log \frac{a}{(a-x)} \Rightarrow \log \frac{a}{(a-x)} = \frac{kt}{2.303}$

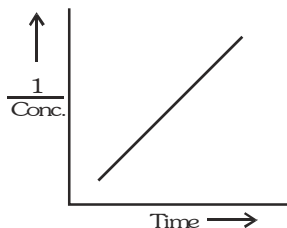
$$\Rightarrow \log \frac{a}{a-x} = \frac{2.2 \times 10^{-5} \times 50 \times 60}{2.303} = 0.0286$$

$$\text{Hence, } \frac{a}{(a-x)} = 1.068 \Rightarrow \frac{a-x}{a} = 0.936$$

$$\Rightarrow 1 - \frac{x}{a} = 0.936 \Rightarrow \frac{x}{a} = 0.068 = 6.39 \%$$

Hence, (D) is the correct answer.

**Ex.9** In the decomposition of  $\text{N}_2\text{O}_5$ , the plot between the reciprocal of concentration of the reactant and the time was found to be linear as shown in figure. Determine the order of reaction.



**Sol.** The reaction is of second order, because for II order,

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \quad \text{or} \quad t = \frac{1}{k} \cdot \frac{x}{a(a-x)}$$

or time (t) vs.  $\frac{1}{\text{conc.}}$  graph is linear

**Ex.10** The inversion of cane sugar proceeds with half-life of 250 minutes at pH = 4 for any concentration of sugar. However, if pH = 5, the half-life changes to 25 minutes. The rate law expression for the sugar inversion can be written as

(A)  $r = k [\text{sugar}]^2 [\text{H}]^6$

(B)  $r = k [\text{sugar}]^1 [\text{H}^+]^0$

(C)  $r = k [\text{sugar}]^1 [\text{H}^+]^1$

(D)  $r = k [\text{sugar}]^0 [\text{H}^+]^1$

**Sol.** At pH = 4, the half-life is 250 minutes for all concentrations of sugar that is  $t_{1/2} \propto [\text{sugar}]^0$ .

The reaction is first order with respect to sugar.

Let, rate =  $k[\text{sugar}]^1 [\text{H}^+]^x$

For  $[\text{H}^+]$   $t_{1/2} \propto [\text{H}^+]^{1-x}$

$\Rightarrow 250 \propto (10^{-4})^{(1-x)}$  .....(1)

At pH = 5, the half life is 25 minutes so  $50 \propto (10^{-5})^{1-x}$  .....(2)

$\therefore 10 = 10^{(1-x)} \Rightarrow (1-x) = 1 \therefore x = 0$

Therefore, rate =  $k [\text{sugar}]^1 [\text{H}^+]^0$

Hence, (B) is the correct answer.

**Ex.11** In a hypothetical reaction  $x \rightarrow y$ , the activation energies for the forward and backward reactions are 13 and 8 kJ/mol respectively. The potential energy of x is 10 kJ/mol, then

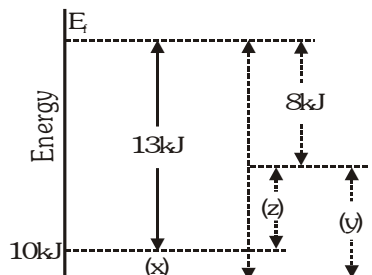
(A) the threshold energy of the reaction is 23 kJ/mol

(B) potential energy of y is 15 kJ

(C) heat of reaction is 5 kJ

(D) the reaction is endothermic

**Sol.**



Hence, (A), (B), (C) and (D) are correct answer.

- Ex.12** The reactions,  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$ , is
- (A) biomolecular reaction (B) second order reaction  
(C) third order reaction (D) none of the above

**Sol.** (A) and (B)

- Ex.13** The activation energies of two reactions are  $E_a$  and  $E_a'$  with  $E_a > E_a'$ . If the temperature of the reacting systems is increased from  $T_1$  and  $T_2$  predict which alternative is correct.  $k_1'$  and  $k_2'$  are rate constants at higher temperature. Assume A being the same for both the reactions.

(A)  $\frac{k_1'}{k_1} = \frac{k_2'}{k_2}$  (B)  $k_1 < k_2$  and  $k_1' < k_2'$  (C)  $k_1 > k_2$  and  $k_1' < k_2'$  (D)  $\frac{k_1'}{k_1} < \frac{k_2'}{k_2}$

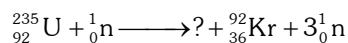
**Sol.** More is energy of activation lesser is rate constant.

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

$$k_1 < k_2 \text{ and } k_1' < k_2'$$

Hence, (B) is the correct answer.

- Ex.14** Fill in the blank :



(A)  ${}_{56}^{141}\text{Ba}$  (B)  ${}_{56}^{139}\text{Ba}$  (C)  ${}_{54}^{139}\text{Ba}$  (D)  ${}_{54}^{141}\text{Ba}$

**Sol.**  $92 + 0 = Z + 36 + 0 \Rightarrow Z = 56$

$$235 + 1 = A + 92 + 3$$

$$\therefore A = 141$$

Missing nucleide is  ${}_{56}^{141}\text{Ba}$

Hence, (A) is the correct answer.

- Ex.15** In the nuclear reaction,  ${}_{92}^{234}\text{U} \longrightarrow {}_{86}^{222}\text{Rn}$ , the number of  $\alpha$  and  $\beta$ -particles lost would be :

(A) 1, 3 (B) 2, 3 (C) 3, 0 (D) 0, 3

**Sol.**  ${}_{92}^{234}\text{U} \longrightarrow {}_{86}^{222}\text{Rn} + x{}_2^4\alpha + y{}_{-1}^0\beta$

$$234 = 222 + 4x \Rightarrow x = 3$$

$$92 = 86 + 2x - y \text{ or } y = 0$$

Hence, (C) is the correct answer.

- Ex.16** The rate constant of a reaction is given by  $k = 3.2 \cdot 10^{10} e^{-\frac{2700}{2.303R}}$

It means that

(A)  $\log k$  vs  $\frac{1}{T}$  will be straight line with slope  $= \frac{-2700}{2.303R}$

(B)  $\log k$  vs  $\frac{1}{T}$  will be a straight line with intercept on  $\log k$  axis  $= \log 3.2 \cdot 10^{10}$

(C) the number of effective collisions are  $3.2 \cdot 10^{10} \text{ cm}^{-3} \text{ sec}^{-1}$

(D) half-life of the reaction increases with increase in temperature

**Sol.** (A) and (B) are correct, (C) is wrong because frequency factor gives total number of collisions and not the effective collision  $\text{cm}^{-3} \text{ sec}^{-1}$ , (D) is wrong because half-life of the reaction decreases with increase in temperature (as reaction becomes faster).

Hence, (A) and (B) are correct answer.



**Ex.17** Two substances x and y are present such that  $[x_0] = 2[y_0]$  and half-life of x is 6 minutes and that of y is 18 minutes. If they start decaying at the same time following first order kinetics how much time later will the concentration of both of them would be same?

- (A) 15 minutes                      (B) 9 minutes                      (C) 5 minutes                      (D) 12 minutes

**Sol.** Amount of x left in  $n_1$  half-lives  $= \left(\frac{1}{2}\right)^{n_1} [x_0]$

Amount of y left in  $n_2$  half-lives  $= \left(\frac{1}{2}\right)^{n_2} [y_0]$

At the end,  $\frac{[x_0]}{2^{n_1}} = \frac{[x_0]}{2^{n_2}}$

$$\Rightarrow \frac{2}{2^{n_1}} = \frac{1}{2^{n_2}}, \{[x_0] = 2[y_0]\}$$

$$\therefore \frac{2^n}{2^n} = 2 \Rightarrow 2^{n_1 - n_2} = (2)^1$$

$$\therefore n_1 - n_2 = 1$$

$$n_2 = (n_1 - 1) \quad \dots(1)$$

Also,  $t = n_1 \cdot t_{1/2(x)}$  ;  $t = n_2 \cdot t_{1/2(y)}$

(Let, concentration of both become equal after time t)

$$\therefore \frac{n_1 \times t_{1/2(x)}}{n_2 \times t_{1/2(y)}} = 1 \Rightarrow \frac{n_1 \times 6}{n_2 \times 18} = 1 \Rightarrow \frac{n_1}{n_2} = 3 \quad \dots(2)$$

From Eqs. (1) and (2), we get

$$n_2 = 0.5, n' = x^{1.5}$$

$$t = 0.5 \cdot 18 = 9 \text{ minutes}$$

Hence (B) is the correct answer.

**Ex.18** Consider a gaseous reaction, the rate of which is given by  $k[x][y]$ , the volume of the reaction vessel containing these gases is suddenly increased to 3<sup>rd</sup> of the initial volume. The rate of reaction relative to the original rate would be

- (A) 9/1                      (B) 1/9                      (C) 6/1                      (D) 1/6

**Sol.** By increasing volume to 3<sup>rd</sup> the concentration will become  $\frac{1}{3}$  times, hence rate  $\frac{1}{9}$  times.

Hence, (B) is the correct answer.

**Ex.19** The rate constant for the reaction,  $2N_2O_5 \longrightarrow 4NO_2 + O_2$ , is  $4.0 \cdot 10^{-5} \text{ sec}^{-1}$ . If the rate of reaction is  $4.80 \cdot 10^{-5} \text{ molL}^{-1} \text{ sec}^{-1}$ , the concentration of  $N_2O_5$  ( $\text{molL}^{-1}$ ) is :

- (A) 1.4                      (B) 1.2                      (C) 0.04                      (D) 0.8

**Sol.**  $r = k [N_2O_5]$

$$\therefore [N_2O_5] = \frac{r}{k} = \frac{4.80 \times 10^{-5}}{4.0 \times 10^{-5}} = 1.2 \text{ molL}^{-1}$$

Hence, (B) is the correct answer.

**Ex.20** The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25 °C are  $2 \times 10^{-4} \text{ s}^{-1}$ ,  $114.4 \text{ kJ mol}^{-1}$  and  $6.0 \times 10^{14} \text{ s}^{-1}$  respectively, the value of the rate constant at  $T \rightarrow \infty$  is.

- (A)  $2.0 \times 10^{18} \text{ s}^{-1}$  (B)  $3.6 \times 10^{30} \text{ s}^{-1}$  (C)  $\infty$  (D)  $6.0 \times 10^{14} \text{ s}^{-1}$

**Sol.**  $k = Ae^{-E_a/RT}$

When  $T \rightarrow \infty$

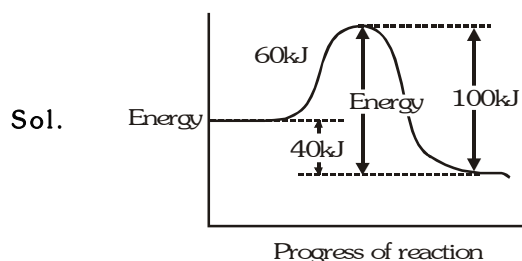
$k \rightarrow A$

$A = 6 \times 10^{14} \text{ s}^{-1}$

Hence, (D) is the correct answer.

**Ex.21** If a reaction  $A + B \rightarrow C$ , is exothermic to the extent of  $40 \text{ kJ/mol}$  and the forward reaction has an activation energy  $60 \text{ kJ/mol}$ , the activation energy for the reverse reaction is

- (A)  $30 \text{ kJ/mol}$  (B)  $40 \text{ kJ/mol}$  (C)  $70 \text{ kJ/mol}$  (D)  $100 \text{ kJ/mol}$



Activation energy for backward reaction =  $100 \text{ kJ}$

Hence, (D) is the correct answer.

**Ex.22** The rate of reaction is doubled for every  $10^\circ\text{C}$  rise in temperature. The increase in reaction rate as a result of temperature rise from  $10^\circ\text{C}$  to  $100^\circ\text{C}$  is.

- (A) 112 (B) 512 (C) 400 (D) 614

**Sol.** Increase in steps of  $10^\circ\text{C}$  has been made 9 times. Hence, rate of reaction should increase  $2^9$  times i.e., 512 times.

Hence, (B) is the correct answer.

**Ex.23.** Van't Hoff equation is

- (A)  $(d/dT) \ln K = (-\Delta E/RT^2)$  (B)  $(d/dT) \ln K = + (E/RT^2)$   
(C)  $(d/dT) \ln K = -(\Delta E/RT)$  (D)  $K = Ae^{-E_a/RT}$

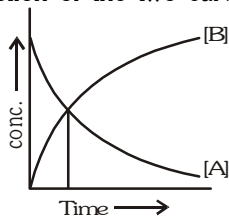
**Sol.** (B) and (D).

**Ex.24** The rate of chemical reaction (except zero order)

- (A) decreases from moment to moment (B) remains constant throughout  
(C) depends upon the order of reaction (D) none of the above

**Sol.** (A) and (C)

**Ex.25** The accompanying figure depicts the change in concentration of species A and B for the reaction  $A \rightarrow B$ , as a function of time the point of intersection of the two curves represents.



- (A)  $t_{1/2}$  (B)  $t_{3/4}$  (C)  $t_{2/3}$  (D) data insufficient to predict

**Sol.** The intersection point indicates that half life of the reactant A is converted into B.

Hence the answer is [A].

## SOLVED SUBJECTIVE PROBLEMS

**Ex.1** For the non-equilibrium process,  $A + B \rightarrow \text{Products}$ , the rate is first order with respect to A and second order with respect to B. If 1.0 mol each of A and B are introduced into a 1 litre vessel, and the initial rate were  $1.0 \times 10^{-2}$  mol/litre-sec, calculate the rate when half of the reactants have been used.

**Sol.**  $\text{Rate}_1 = k [A] [B]^2$   
 $\therefore 10^{-2} = k [1] [1]^2$   
 or  $k = 10^{-2} \text{ litre}^2 \text{ mol}^{-2} \text{ sec}^{-1}$   
 Now  $\text{Rate}_{II} = 10^{-2} \times 0.5 \times (0.5)^2$   
 or New rate =  $1.2 \times 10^{-3} \text{ mol/litre-sec}$

**Ex.2** The energy of activation for a certain reaction is 100 kJ/mol. Presence of catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 25 C, other things being equal ?

**Sol.**  $k = A e^{\frac{-E_a}{RT}}$ ,  $k_1 = A e^{\frac{-100}{RT}}$ ,  $k_2 = A e^{\frac{-25}{RT}}$

$$\therefore \frac{k_1}{k_2} = \frac{e^{\frac{-100}{RT}}}{e^{\frac{-25}{RT}}} = e^{\frac{-75}{RT}}$$

$$\log_e \frac{k_2}{k_1} = \log_e e^{\frac{75}{RT}}$$

$$\therefore \log \frac{k_2}{k_1} = \frac{75}{RT} = \frac{75 \times 10^3}{8.314 \times 298}$$

$$\frac{k_2}{k_1} = 1.4020 \times 10^{13}, \text{ As } r = k(\text{conc})^n$$

$$\frac{r_2}{r_1} = \frac{k_2}{k_1} = 1.4020 \times 10^{13}$$

**Ex.3** Show that for a first order reaction, time required for 99% completion is twice for the time required for the completion of 90% of the reaction.

**Sol.**  $t_{99\%} = \frac{2.303}{k} \log_{10} \frac{100}{100-99} \dots\dots(1)$

( $\because a = 100; x = 99$ )

$t_{90\%} = \frac{2.303}{k} \log_{10} \frac{100}{100-90} \dots\dots (2)$

( $\because a = 100; x = 90$ )

$\therefore$  By Eqs. (1) and (2),

$$\frac{t_{99\%}}{t_{90\%}} = \frac{\log_{10} 100}{\log_{10} 10} = 2$$

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

**Ex.4** For the reaction,  $A + B \longrightarrow C$ , the following data were obtained. In the first experiment, when the initial concentrations of both A and B are 0.1 M, the observed initial rate of formation of C is  $1 \times 10^{-4} \text{ mol litre}^{-1} \text{ minute}^{-1}$ . In second experiment when the initial concentrations of (A) and (B) are 0.1 M and 0.3 M, the initial rate is  $3.0 \times 10^{-4} \text{ mol litre}^{-1} \text{ minute}^{-1}$ . In the third experiment, when the initial concentrations of both A and B are 0.3 M, the initial rate is  $2.7 \times 10^{-3} \text{ mol litre}^{-1} \text{ minute}^{-1}$ .

(a) Write rate law for this reaction.

(b) Calculate the value of specific rate constant for this reaction.

**Sol.** Let, Rate =  $k[A]^x [B]^y$

$$r_1 = 1 \quad 10^{-4} = k(0.1)^x (0.1)^y \quad \dots(1)$$

$$r_2 = 3 \quad 10^{-4} = k(0.1)^x (0.3)^y \quad \dots(2)$$

$$r_3 = 2.7 \quad 10^{-3} = k(0.3)^x (0.3)^y \quad \dots(3)$$

By Eqs. (1) and (2),  $\frac{r_1}{r_2} = \frac{1 \times 10^{-4}}{3 \times 10^{-4}} = \left(\frac{1}{3}\right)^y \therefore y = 1$

By Eqs. (2) and (3),

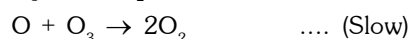
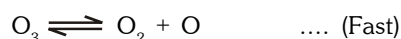
$$\frac{r_2}{r_3} = \frac{3 \times 10^{-4}}{27 \times 10^{-4}} = \left(\frac{1}{3}\right)^x \therefore x = 2$$

$$\therefore \text{Rate} = k[A]^2 [B]^1$$

Also,  $1 \quad 10^{-4} = k (0.1)^2 (0.1)^1$

$$\therefore k = 10^{-1} = 0.1 \text{ L}^2 \text{ mol}^{-1} \text{ min}^{-1}$$

**Ex.5** The chemical reaction,  $2O_3 \rightarrow 3O_2$  proceeds as follows :



The rate law expression should be

[A]  $r = k[O_3]^2$       [B]  $r = k[O_3]^2 [O_2]^{-1}$       [C]  $r = k[O_3][O_2]$       [D] Unpredictable

**Sol.** Rate of reaction ( $r$ ) =  $k [O] [O_3]$

The rate of formation if  $[O]$  depends on first step

$$\therefore \quad \text{Since } K_{eq} = \frac{[O_2][O]}{[O_3]}$$

$$\therefore \quad [O] = K_{eq} \frac{[O_3]}{[O_2]}$$

or  $r = k k_{eq} \frac{[O_3][O_3]}{[O_2]} = k \cdot [O_3]^2 [O_2]^{-1}$

**Ex.6** Disintegration of radium takes place at an average rate of  $1.42 \times 10^{13}$   $\alpha$ -particles per minute. Each  $\alpha$ -particle takes up 2 electrons from the air and becomes a neutral helium atom. After 420 days, the He gas collected was  $0.5 \times 10^{-3}$  L measured at 300 K and 750 mm of mercury pressure. From the above data, calculate Avogadro's number.

**Sol.** No. of  $\alpha$ -particles (or) He formed =  $1.42 \times 10^{13} \text{ min}^{-1}$

$$\therefore \text{No. of He particles formed in 420 days} = 1.42 \times 10^{13} \times 420 \times 1440 = 8.588 \times 10^{18}$$

Also at 27 C and 750 mm ; He = 0.5 mL

Using  $PV = nRT$

$$\frac{750}{760} \times \frac{0.5}{1000} = n \quad 0.0821 \times 300 \quad \Rightarrow \quad n = 2.0 \times 10^{-5} \text{ moles}$$

$$2.0 \times 10^{-5} \text{ moles of He} = 8.588 \times 10^{18} \text{ particles of He}$$

$$\Rightarrow 1 \text{ mole of He} = \frac{8.588 \times 10^{18}}{2.0 \times 10^{-5}} \Rightarrow 4.294 \times 10^{22} \text{ particles}$$

$$\therefore \text{Avogadro's number} = 4.294 \times 10^{22} \text{ particles/mol}$$

**Ex.7** The optical rotations of sucrose in 0.5 N HCl at 35 C at various time intervals are given below. Show that the reaction is of first order :

Time (minutes)	0	10	20	30	40	$\infty$
Rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	-11.1

**Sol.** The inversion of sucrose will be first order reaction if the above data confirm to the equation,

$k_1 = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$  where  $r_0$ ,  $r_t$  and  $r_\infty$  represent optical rotations initially, at the commencement of the reaction after time  $t$  and at the completion of the reaction respectively.

In this case,  $a_0 = r_0 - r_\infty = +32.4 - (-11.1) = +43.5$

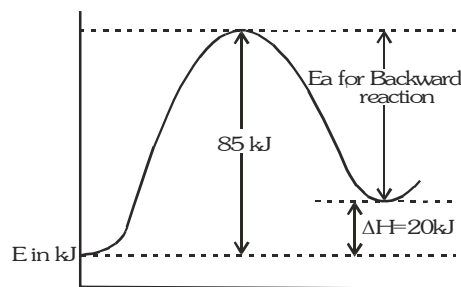
The value of  $k$  at different times is calculated as follows :

Time	$r_t$	$r_t - r_\infty$	$k$
10 min	+28.8	39.9	$\frac{2.303}{10} \log \frac{43.5}{39.9} = 0.008625 \text{ min}^{-1}$
20 min	+25.5	36.6	$\frac{2.303}{20} \log \frac{43.5}{36.6} = 0.008625 \text{ min}^{-1}$
30 min	+22.4	33.5	$\frac{2.303}{30} \log \frac{43.5}{33.5} = 0.008694 \text{ min}^{-1}$
40 min	+19.6	30.7	$\frac{2.303}{40} \log \frac{43.5}{30.7} = 0.008717 \text{ min}^{-1}$

The constancy of  $k_1$  indicates that the inversion of sucrose is a **first order** reaction.

**Ex.8** For  $A + B \rightarrow C + D$ ;  $\Delta H = 20 \text{ kJ mol}^{-1}$  ; the activation energy of the forward reaction is  $85 \text{ kJ/mol}$ . Calculate activation energy of the reverse reaction.

**Sol.**



$$\Delta H \text{ of forward reaction} = 20 \text{ kJ mol}^{-1}.$$

$$\text{Energy of activation for forward reaction (} E_a \text{)} = 85 \text{ kJ mol}^{-1}$$

$$\therefore \text{Energy of activation for backward reaction} = E_a - \Delta H$$

$$= 85 - 20$$

$$= 65 \text{ kJ mol}^{-1}$$

**Ex.9** The reaction given below is observed to be first order with rate constant  $5.26 \times 10^{-3} \text{ sec}^{-1}$ . Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise 0.145 atm and also find the total pressure after 100 sec.



**Sol.**

	$2A(g)$	$\rightarrow$	$4B(g)$	$+$	$C(g)$
Initial	$P_0$		$0$		$0$
At time t	$P_0 - P'$		$2P'$		$P'/2$

$$P_{\text{total}} = P_0 - P' + 2P' + P'/2 = P_0 + \frac{3P'}{2}$$

$$P' = \frac{2}{3} (0.145 - 0.1) = 0.03 \text{ atm}$$

$$k = \frac{2.303}{t} \log \frac{P_0}{P_0 - P'}$$

$$t = \frac{2.303}{5.26 \times 10^{-3}} \log \left( \frac{0.1}{0.07} \right) = 67.82 \text{ sec}$$

$$\text{Also, } k = \frac{2.303}{t} \log \left( \frac{0.1}{P_0 - P'} \right)$$

$$5.26 \times 10^{-3} = \frac{2.303}{100} \log \left( \frac{0.1}{0.1 - P'} \right)$$

$$0.1 - P' = .059$$

$$P' = 0.041$$

$$P_{\text{total}} = 0.1 + \frac{3}{2} (0.041) \approx 0.162 \text{ atm.}$$

**Ex.10** For a reaction  $3A \rightarrow \text{Products}$ , it is found that the rate of reaction doubles if concentration of A is increased four times, calculate order of reaction.

**Sol.** Rate =  $k [\text{Reactant}]^n$  if  $[\text{Reactant}] = a$ ; rate =  $r_1$   
 $r_1 = k[a]^n$  if  $[\text{Reactant}] = 4a$ ; rate =  $2r_1$   
 $2r_1 = k[4a]^n$

$$\therefore \frac{1}{2} = \left[ \frac{1}{4} \right]^n \quad \therefore n = \frac{1}{2}$$

**Ex.11** The amount of  $^{14}_6\text{C}$  isotope in a piece of wood is found to be one fifth of that present in a fresh piece of wood. Calculate the age of the piece of wood (half-life of  $^{14}_6\text{C} = 5577 \text{ year}$ ).

**Sol.**  $t = \frac{2.303}{\lambda} \log \frac{N_0}{N}$

$$\Rightarrow t = \frac{2.303 \times t_{1/2}}{0.693} \log \frac{N_0}{N}$$

$$t = \frac{2.303 \times 5577}{0.693} \log \frac{N_0}{N_0/5} \Rightarrow \frac{2.303 \times 5577}{0.693} \times 0.6989$$

$$= 12.953 \text{ years}$$

**Ex.12** In a reaction,  $2A \rightarrow \text{Products}$ , the concentration of A decreases from 0.5 mol litre<sup>-1</sup> to 0.4 mol litre<sup>-1</sup> in 10 minute. Calculate rate during this interval.

**Sol.** Rate of reaction =  $\frac{1}{2}$  rate of disappearance of A

$$= \frac{1}{2} \left( -\frac{d[A]}{dt} \right) = \frac{1}{2} \left[ \frac{0.5 - 0.4}{10} \right] = 0.005 \text{ mol litre}^{-1} \text{ minute}^{-1}$$

**Ex.13** The time required for 10% completion of first order reaction at 298 K is equal to that required for its 76% completion at 308 K. If the pre-exponential factor for the reaction is  $3.56 \times 10^9 \text{ s}^{-1}$ , calculate its energy of activation.

**Sol.** For first order reactions,

$$t = \frac{2.303}{k} \log \frac{N_0}{N_1}$$

$$\text{At 298 K ; } t = \frac{2.303}{k_{298}} \log \frac{100}{90}$$

$$\text{At 308 K ; } t = \frac{2.303}{k_{308}} \log \frac{100}{76}$$

Since time is same

$$\frac{2.303}{k_{298}} \log \frac{100}{90} = \frac{2.303}{k_{308}} \log \frac{100}{76}$$

$$\text{or } \frac{0.0458}{k_{298}} = \frac{0.1191}{k_{308}}$$

$$\text{or } \frac{k_{308}}{k_{298}} = \frac{0.1191}{0.0458} = 2.60$$

According to Arrhenius equation,

$$2.303 \log \frac{k_{308}}{k_{298}} = \frac{E_a}{8.314} \left[ \frac{1}{298} - \frac{1}{308} \right]$$

$$\text{or } 2.303 \log 2.60 = \frac{E_a}{8.314} \left[ \frac{10}{298 \times 308} \right]$$

$$E_a = 72.93 \text{ kJ}$$

**Ex.14** In a reaction, the decrease in reactant's concentration is 20% in 20 minute and 40% in 40 minute. Calculate order of reaction and rate constant.

**Sol.** For zero order reaction :  $t = \frac{x}{k}$  or  $k = \frac{x}{t}$

$$\text{If } t = t_{20\%} = 20 \text{ minute, } x = 20$$

$$\text{Then } k = \frac{20}{20} = 1 \text{ mol litre}^{-1} \text{ minute}^{-1}$$

$$\text{If } t = t_{40\%} = 40 \text{ minute, } x = 40$$

$$\text{Then } k = \frac{40}{40} = 1 \text{ mol litre}^{-1} \text{ minute}^{-1}; \text{ Thus, reaction is of zero order.}$$

**Ex.15** The rate constant for the decomposition of a certain substance is  $2.80 \times 10^{-3} \text{ m}^{-1} \text{ s}^{-1}$  at 30°C and  $1.38 \times 10^{-1} \text{ m}^{-1} \text{ s}^{-1}$  at 50°C. Evaluate the Arrhenius parameters of the reaction. ( $R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$ )

**Sol.** Energy of activation ( $E_a$ ) and pre-exponential factor A are Arrhenius parameters.

$$k_1 = 2.80 \times 10^{-3} \text{ m}^{-1} \text{ s}^{-1} \text{ at } 303 \text{ K}$$

$$k_2 = 1.38 \times 10^{-1} \text{ m}^{-1} \text{ s}^{-1} \text{ at } 323 \text{ K}$$

$$\text{As } \log_{10} \frac{k_2}{k_1} = \frac{E_a}{R} \left[ \frac{T_2 - T_1}{T_1 \times T_2} \right]$$

$$\therefore E_a = \frac{2.303 R T_1 T_2}{(T_2 - T_1)} \log_{10} \frac{k_2}{k_1}$$

$$E_a = \frac{2.303 \times 8.314 \times 10^{-3} \times 303 \times 323}{(323 - 303)} \log_{10} \left( \frac{1.38 \times 10^{-1}}{2.80 \times 10^{-3}} \right) = 64.91 \text{ kJ mol}^{-1}$$

$$\text{Also, } k = A e^{-E_a/RT}$$

$$\text{or } A = k e^{E_a/RT} = 2.80 \times 10^{-3} e^{64.91 \times 10^3 / 8.314 \times 303} = 4.34 \times 10^8 \text{ s}^{-1}$$

**Ex.16** Calculate the order of reaction for which rate becomes half if volume of container having same amount of reactant is doubled. (Assume gaseous phase reaction)

**Sol.** Rate =  $k[a]^n$

**For Case I :** Let a mole of reactant in vessel of V litre

$$\therefore r_1 = k \left[ \frac{a}{V} \right]^n \quad \dots\dots(1)$$

**For Case II :** The volume is doubled, rate becomes half

$$\therefore \frac{r_1}{2} = k \left[ \frac{a}{2V} \right]^n \quad \dots\dots(2)$$

$\therefore$  By Eqs. (1) and (2),

$$\text{or} \quad 2 = (2)^n$$

$$\therefore n = 1$$

**Ex.17** Rate constant of a first order reaction,  $A \longrightarrow B$ , is  $0.0693 \text{ min}^{-1}$ . Calculate rate (i) at start and (ii) after 20 minutes. Initial concentration of A is 1.0 M.

**Sol.**  $k_1 = 0.0693 \text{ min}^{-1}$

$$t_{\frac{1}{2}} = \frac{0.693}{k_1} = \frac{0.693}{0.0693} = 10 \text{ min}$$

$$\text{Since } C = C_0 \left( \frac{1}{2} \right)^n \quad \left( n = \frac{t}{t_{1/2}} \right)$$

$$n = \frac{20}{10} = 2 \quad C_0 = 1 \text{ M}$$

$$\therefore C = 1 \left( \frac{1}{2} \right)^2 = \frac{1}{4} \text{ M}$$

$$\begin{aligned} \text{Rate of the reaction at the start of the reaction} &= k_1 C_0 \\ &= 10 \quad 0.0693 \quad 1 = 0.693 \text{ M min}^{-1} \end{aligned}$$

$$\text{Rate after 30 min.} = k_1 C = 0.0693 \quad \frac{1}{4} = 17.33 \quad 10^{-3} \text{ M min}^{-1}$$

**Ex.18** Two reactants A and B separately show two chemical reactions. Both reactions are made with same initial concentration of each reactant. Reactant A follows first order kinetics whereas reactant B follows second order kinetics. If both have same half-lives, compare their rates at the start of reactions.

**Sol.** For A : rate =  $k_A [A]$  ... (i)

$$t_{\frac{1}{2}(A)} = \frac{0.693}{k_A} \quad \dots(ii)$$

$$\text{For B : rate} = k_B [B]^2 \quad \dots(iii)$$

$$t_{\frac{1}{2}(B)} = \frac{1}{k_B \times a} \quad \dots(iv)$$

$$\text{Initial rate of A} \quad r_A = k_A a$$

$$\text{Initial rate of B} \quad r_B = k_B a^2$$

$$\therefore \frac{r_A}{r_B} = \frac{k_A \times a}{k_B \times a^2} = \frac{k_A}{k_B \times a} \quad \dots(v)$$

$$\text{If } t_{\frac{1}{2}(A)} = t_{\frac{1}{2}(B)}, \text{ then } \frac{0.693}{k_A} = \frac{1}{k_B \times a}$$

$$\therefore \frac{k_A}{k_B} = 0.693 a$$

$$\therefore \frac{r_A}{r_B} = \frac{0.693 \times a}{a} = 0.693$$



**Ex.19** The rate of a certain reaction depends on concentration according to equation  $-\frac{d[A]}{dt} = \frac{k_1[A]}{1 + k_2[A]}$   
What will be the order of reaction when (i) concentration is very high (ii) very low?

**Sol.** Given,  $-\frac{d[A]}{dt} = \frac{k_1[A]}{1 + k_2[A]} \Rightarrow \frac{-d[A]}{dt} = \frac{k_1}{\frac{1}{[A]} + k_2}$

(i) When [A] is very high  $\frac{1}{[A]}$  is very small, and thus negligible

$$\therefore -\frac{d[A]}{dt} = \frac{k_1}{k_2} = \text{constant}$$

Thus, order of reaction is zero.

(ii) When [A] is very low

$$[1 + k_2[A]] = k'$$

$$\therefore -\frac{d[A]}{dt} = \frac{k_1[A]}{k'} = k''[A]$$

Thus, order of reaction is one.

**Ex.20** Pseudo first order rate for the reaction,  $A + B \longrightarrow \text{Product}$ , when studied in 0.1 M of B is given by  $-\frac{d[A]}{dt} = k[A]$ , where,  $k = 1.25 \times 10^4 \text{ sec}^{-1}$ , calculate the value of second order rate constant.

**Sol.**  $A + B \longrightarrow \text{Product}$

$$-\frac{d[A]}{dt} = k[A] \Rightarrow -\frac{d[A]}{dt} = 1.25 \times 10^4 [A] \quad \dots(i)$$

Assuming the reaction to be of second order

$$-\frac{d[A]}{dt} = k' [A] [B] \Rightarrow -\frac{d[A]}{dt} = k' [A] [0.1] \quad \dots(ii)$$

Dividing Eq. (i) by (ii), we get

$$1 = \frac{1.25 \times 10^4}{k' \times (0.1)}$$

$$\therefore k' = 1.25 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$$

**Ex.21**  $\text{N}_2\text{O}_5$  decomposes according to equation,  $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2} \text{O}_2$

(a) What does  $-\frac{d[\text{N}_2\text{O}_5]}{dt}$  denote? (b) What does  $\frac{d[\text{O}_2]}{dt}$  denote? (c) What are the units of rate of this reaction?

**Sol.** (a) Rate of decomposition of  $\text{N}_2\text{O}_5$ . (b) Rate of formation of  $\text{O}_2$ . (c) Unit of rate =  $\text{mol litre}^{-1} \text{ time}^{-1}$ .

**Ex.22** A first order reaction takes 69.3 minute for 50% completion. How much time will be needed for 80% completion?

**Sol.**  $\therefore k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3} \text{ minute}^{-1} \quad (\because t_{1/2} = 69.3 \text{ min})$

$$k = \frac{2.303}{t} \log \frac{100}{100 - x}$$

Now  $k = \frac{2.303}{t} \log_{10} \frac{100}{20}$ ; [if  $a = 100$ ,  $x = 80$  and  $a - x = 20$ ]

$$\frac{0.693}{69.3} = \frac{2.303}{t} \log_{10} 5 \quad ; \quad t = 160.97 \text{ minute}$$

**Ex.23** The half-life of the nuclide  $^{220}\text{Rn}$  is 693 s. What mass of radon is equivalent to a 1 millicurie (mci) ?

**Sol.**  $t_{1/2} = \frac{0.693}{\lambda} \Rightarrow \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{693} \times 10^{-3} \text{ s}^{-1}$

$$1 \text{ mci} = 3.7 \times 10^7 \text{ disintegration s}^{-1} = -\frac{dN}{dt} \Rightarrow -\frac{dN}{dt} = \lambda N$$

$$N = -\frac{dN/dt}{\lambda} = \frac{3.7 \times 10^7 \text{ s}^{-1}}{10^{-3} \text{ s}^{-1}} = 3.7 \times 10^{10}$$

$$\text{Mass of } ^{220}\text{Rn} = \frac{3.7 \times 10^{10} \times 220}{6.022 \times 10^{23}} = 1.35 \times 10^{-11} \text{ g} = 1.06 \times 10^{-14} \text{ kg}$$

**Ex.24** For the reaction  $A \longrightarrow B + C$

Time  $t$   $\infty$

Total pressure of (B + C)  $P_2$   $P_3$

Calculate k.

**Sol.**

	$A \longrightarrow$	$B$	$+ C$
At $t = 0$	$P_1$	0	0
At $t = t$	$P_1 - x$	x	x
At $t = \infty$	0	$P_1$	$P_1$

$$\therefore 2P_1 = P_3$$

$$\Rightarrow P_1 = \frac{P_3}{2}$$

$$2x = P_2 \Rightarrow x = \frac{P_2}{2}$$

$$\therefore P_1 - x = \frac{P_3}{2} - \frac{P_2}{2} = \frac{P_3 - P_2}{2}$$

$$\therefore k = \frac{1}{t} \ln \frac{[A]_0}{[A]_t} = \frac{1}{t} \ln \frac{P_3}{(P_3 - P_2)}$$

**Ex.25** Derive a relation between  $t_{1/2}$  and temperature for an  $n^{\text{th}}$  order reaction where  $n > 2$  ?

**Sol.**  $\ln k = \ln A - \frac{E_a}{RT}$  (Arrhenius equation) ....(i)

$$t_{1/2} = \frac{(2^{n-1} - 1)}{k(n-1)a_0^{n-1}} \quad \dots\text{(ii)}$$

$$\therefore \ln(t_{1/2}) = \ln \frac{2^{n-1} - 1}{(n-1)a_0^{n-1}} - \ln k \quad \dots\text{(iii)}$$

From the Eqs. (i) and (iii)

$$\ln(t_{1/2}) = \ln \frac{2^{n-1} - 1}{(n-1)a_0^{n-1}} - \ln A + \frac{E_a}{RT}$$

$$\Rightarrow \ln(t_{1/2}) = \ln A + \frac{E_a}{RT}$$

$$\text{where } A = \frac{2^{n-1} - 1}{(n-1)a_0^{n-1}} \times A$$

That is  $t_{1/2}$  decreases with increase in temperature.

A plot of  $t_{1/2}$  vs  $\frac{1}{T}$  gives a straight line with slope  $E_a$ .