

# CHEMICAL KINETICS

## 1. Rate of Reaction :

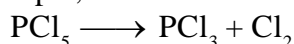
The rate of a reaction means the speed with which the reaction takes place. This is expressed either in terms of decrease in the concentration of a reactant per unit time or increase in the concentration of a product per unit time. Hence the rate of a reaction may be defined as follows :

The rate of reaction is the change in the concentration of any one of the reactants or products per unit time i.e.,

$$\text{Rate of reaction} = \frac{\text{Decrease in the concentration of a reactant}}{\text{Time interval}}$$

$$\text{or} \quad = \frac{\text{Increase in the concentration of a product}}{\text{Time interval}}$$

For example, consider the reaction ,

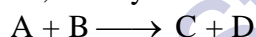


Suppose in a time interval  $\Delta t$ , decrease in concentration of  $\text{PCl}_5$  is  $\Delta [\text{PCl}_5]$  and increase in the concentration of  $\text{PCl}_3$  and  $\text{Cl}_2$  are  $\Delta [\text{PCl}_3]$  and  $\Delta [\text{Cl}_2]$  respectively, where square brackets indicate molar concentrations (moles/litre) of the substances involved. Then we have,

$$\text{Rate of reaction} = -\frac{\Delta[\text{PCl}_5]}{\Delta t} = +\frac{\Delta[\text{PCl}_3]}{\Delta t} = +\frac{\Delta[\text{Cl}_2]}{\Delta t}$$

It may be emphasized that the rate of reaction is always positive. The minus sign along with the first term is used simply to show that the concentration of the reactant ( $\text{PCl}_5$ ) is decreasing while plus sign along with the other two terms is used to show that the concentration of the products ( $\text{PCl}_3$ ) and ( $\text{Cl}_2$ ) is increasing.

In general, for any reaction of the type



$$\text{Rate of reaction} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{\Delta[\text{B}]}{\Delta t} = +\frac{\Delta[\text{C}]}{\Delta t} = +\frac{\Delta[\text{D}]}{\Delta t}$$

## Units of the Rate of Reaction :

Since concentration is usually expressed in moles/litre and the time is taken in seconds or minutes, the unit of the rate of reaction is moles litre<sup>-1</sup> sec<sup>-1</sup> (mol L<sup>-1</sup> s<sup>-1</sup>) or moles litre<sup>-1</sup> min<sup>-1</sup> (mol L<sup>-1</sup> min<sup>-1</sup>).

In case of gaseous reactions, pressures are used in place of molar concentrations. As pressures are expressed in atmospheres, therefore the units of the rate of reaction are atm min<sup>-1</sup> or atm s<sup>-1</sup> etc. The relationship between partial pressure of a gas in a reaction mixture

and its molar concentration follows from the relationship  $PV = nRT$  i.e.  $\frac{n}{V} = \frac{P}{RT}$

Where partial pressure,  $P = \frac{\text{No. of moles of the gas}}{\text{Total no. of moles}} \times \text{Total pressure}$

## Average Rate and Instantaneous Rate of Reaction :

A difficulty arises in stating the rate of reaction as above. This is because according to the Law of Mass Action, the rate of reaction depends upon the molar concentrations of reactants which keep on decreasing with the passage of time (while those of the products keep on increasing). Therefore, the rate of reaction does not remain constant throughout.

Thus the rate of reaction as defined above is the 'average rate of reaction' during the time interval chosen.

To know the rate of reaction at any instant of time during the course of a reaction, we introduce the term 'instantaneous rate of reaction' which may be defined as follows :

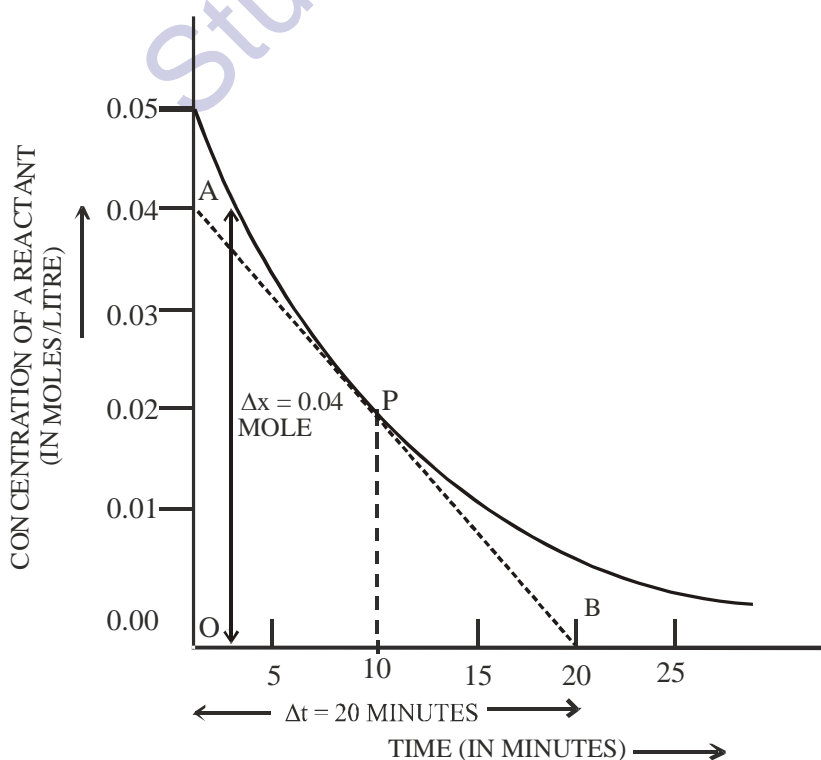
The rate of reaction at any instant of time is the rate of change of concentration (i.e. change of concentration per unit time) of any one of the reactants or products at that particular instant of time.

To express the instantaneous rate of reaction, as small interval of time ( $dt$ ) is chosen at that particular instant of time during which the rate of reaction is supposed to be almost constant. Suppose the small change in concentration is  $dx$  in the small interval of time  $dt$ . Then

the rate of reaction at that instant is given by  $\frac{dx}{dt}$ .

## Measurement of the Rate of Reaction :

In order to measure the rate of a reaction, the progress of the reaction is followed by studying the concentration of one of the reactants or products at different intervals of time. the most common practice to do so is to withdraw small amount of the reaction mixture ( $2\text{ cm}^3$  or  $5\text{ cm}^3$ ) at different intervals of time, cool it down immediately to nearly  $0^\circ\text{C}$  to arrest the reaction (called freezing the reaction) and then find out the concentration of the reactant or the product by suitable method usually by titration against a suitable reagent. However, this method is not preferred when some observable property like volume, pressure, optical rotation etc. changes with time and can be observed directly at different intervals of time without stopping the reaction. it is important to mention that except concentration, all other factors (like temperature etc.) which affect the rate of the reaction are kept constant during the kinetic study of the reaction.



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If concentration of one of the reactants is studied at different intervals of time and these values are plotted against the corresponding times, a graph of the type shown in figure is obtained.

### Calculation of instantaneous rate of reaction :

To know the rate of the reaction at any time  $t$ , a tangent is drawn to the curve at the point corresponding to that time figure and it is extended on either side so as to cut the axes, say at the points A and B. then

$$\begin{aligned} \text{Rate of reaction} &= \frac{\text{Change in the concentration}}{\text{Time}} \\ &= \frac{\Delta x}{\Delta t} = \frac{OA}{OB} \text{ Slope of the tangent} \end{aligned}$$

Thus the slope of the tangent gives the rate of reaction.

For example, from the (figure) in the present case, at time  $t = 10$  minutes,  $\Delta x = 0.04$  mole and  $\Delta t = 20$  minutes  $= 20 \times 60 = 1200$  seconds, therefore, rate of reaction at the end of 10 minutes will be  $0.04/1200 = 3.33 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ .

### Calculation of the average rate of reaction :

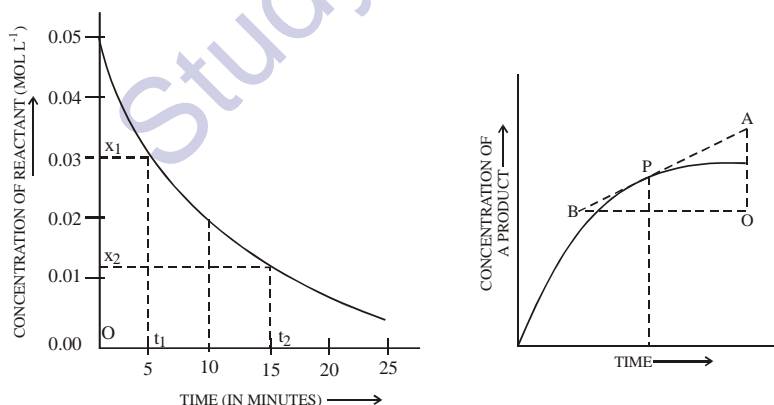
To calculate the average rate of reaction between any two instants of time say  $t_1$  and  $t_2$ , the corresponding concentrations  $x_1$  and  $x_2$  are noted from the graph. Then

$$\text{Average rate of reaction} = \frac{x_2 - x_1}{t_2 - t_1}$$

For example, from the (figure) between the time interval 5 to 15 minutes,

$$\text{Average rate} = \frac{0.03 - 0.012}{15 - 5} = \frac{0.018}{10} = 0.0018 \text{ and mol L}^{-1} \text{ min}^{-1}$$

If concentration of one of the products is plotted against time, the type of curve obtained and the rate of reaction at any instant of time are calculated as shown in the figure.



#### Illustration 1 :

*In a reaction the concentration of a reactant (A) changes from  $0.200 \text{ mol litre}^{-1}$  to  $0.150 \text{ mol litre}^{-1}$  in 10 minutes. What is the average rate of reaction during this interval?*

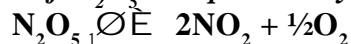
**Solution :**

$$\begin{aligned} \Delta[A] &= [A]_{\text{final}} - [A]_{\text{initial}} \\ &= [0.150 - 0.200] \\ &= -0.050 \text{ mol litre}^{-1} \\ \Delta t &= 10 \text{ minutes} \end{aligned}$$

$$\text{Average rate of reaction} = \frac{-\Delta[A]}{\Delta t} = \frac{0.50}{10} = 0.005 \text{ mol litre}^{-1} \text{ min}^{-1}$$

**Illustration 2 :**

*Decomposition of  $N_2O_5$  is expressed by the equation ,*



*If in a certain time interval, rate of decomposition of  $N_2O_5$  is  $1.8 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$ , what will be the rates of formation of  $NO_2$  and  $O_2$  during the same interval ?*

**Solution :**

The rate expression for the decomposition of  $N_2O_5$  is

$$-\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \frac{\Delta[NO_2]}{\Delta t} = 2 \times \frac{\Delta[O_2]}{\Delta t}$$

So 
$$\frac{\Delta[NO_2]}{\Delta t} = 2 \frac{\Delta[N_2O_5]}{\Delta t} = 2 \times 1.8 \times 10^{-3}$$
$$= 3.6 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$$

and 
$$\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \times 1.8 \times 10^{-3}$$
$$= 0.9 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$$

[Rate is always positive and hence  $= \frac{\Delta[N_2O_5]}{\Delta t}$  is taken positive.]

**Illustration 3 :**

*If the decomposition of nitrogen (V) oxide  $2N_2O_5 \rightarrow 4NO_2 + O_2$ , following a first order kinetics.*

- (i) Calculate the rate constant for a 0.04 M solution, if the instantaneous rate is  $1.4 \times 10^{-6} \text{ mol L s}^{-1}$ .
- (ii) Also calculate the rate of reaction when the concentration of  $N_2O_5$  is 1.20 M.
- (iii) What concentration of  $N_2O_5$  would give a rate of  $2.45 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ ?

**Solution :**

- (i) As the given reaction is of first order, therefore,

$$\text{Rate} = k[N_2O_5]$$

or 
$$k = \frac{\text{rate}}{[N_2O_5]} = \frac{1.4 \times 10^{-6}}{0.04} \quad [M = \text{conc. in mol L}^{-1}]$$
$$= 3.5 \times 10^{-5} \text{ s}^{-1}$$

- (ii) Now if the concentration of  $N_2O_5$  is 1.20 M, then

$$\begin{aligned} \text{rate} &= k[N_2O_5] \\ &= 3.5 \times 10^{-5} \times 1.20 = 4.2 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

- (iii) To obtain concentration of  $N_2O_5$  when the rate is  $2.45 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ , we note that

$$[N_2O_5] = \frac{\text{Rate}}{k} = \frac{2.45 \times 10^{-5}}{3.5 \times 10^{-5}} = 0.7 \text{ mol L}^{-1} \text{ or } 0.7 \text{ M}$$

**Factors Affecting the Reaction Rate :**

The rate of any particular reaction depends upon the following factors:

- (i) **Concentration of the reactants :** Greater the concentrations of the reactants, faster is the reaction. Conversely, as the concentrations of the reactants decrease, the rate of reactions also decreases.
- (ii) **Temperature :** The rate of reaction increases with increase of temperature. In most of the cases, the rate of reaction becomes nearly double for 10 K rise of temperature. In some cases, reactions do not take place at room temperature but take place at higher temperature.

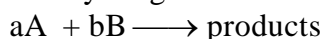
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- (iii) **Presence of Catalyst :** A catalyst generally increases the speed of a reaction without itself being consumed in the reaction. In case of reversible reactions, a catalyst helps to attain the equilibrium quickly without disturbing the state of equilibrium.
- (iv) **Surface area of the reactants :** For a reaction involving a solid reactant or catalyst, the smaller is the particle size, i.e., greater is the surface area, the faster is the reaction.
- (v) **Presence of light :** Some reactions do not take place in the dark but take place in the presence of light e.g.,  $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$ . Such reactions are called “photochemical reactions”.  
**Now we shall discuss the quantitative effect of concentration and temperature on the rate of reaction. The study of quantitative effect of concentration on the rate of reaction leads to the introduction of a number of new terms such as order of reaction, specific reaction rate (rate constant) and molecularity of reaction. It also leads to the study of mechanism of the reactions. These different aspects are discussed in the following sections.**

## 2. Molecularity and Order :

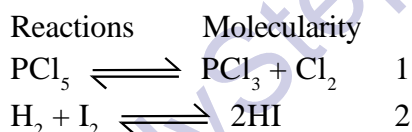
Single step reaction is called *elementary* reaction while a reaction occurring in two or more steps is called *complicated* or *consecutive* reaction. Each step of a complicated reaction is an elementary reaction.

The minimum number of molecules, atoms or ions of reactants required for an elementary reaction to occur is indicated by the sum of the stoichiometric coefficients of the reactant(s) in the chemical equation, is known molecularity of the reaction. Thus for an elementary reaction represented by the general chemical equation .



$$\text{molecularity} = a + b$$

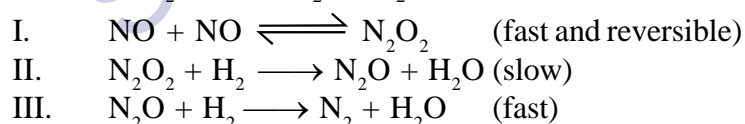
Examples:



A complicated reaction has no molecularity of its own but molecularity of each of the steps involved in its mechanism.

For example :

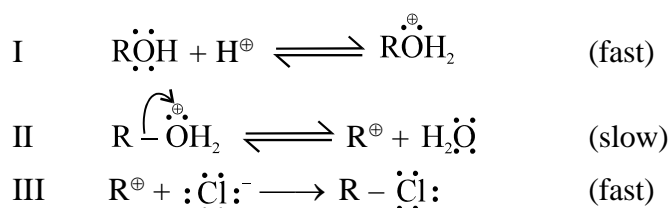
The reaction :  $2\text{NO} + 2\text{H}_2 \rightleftharpoons \text{N}_2 + 2\text{H}_2\text{O}$ , takes place in the sequence of following three steps .



The molecularity of each step involved in mechanism is 2 i.e., each step is bimolecular. So as regards the molecularity of the reaction under consideration we simply say that the reaction has mechanism and each step involved in it is bimolecular

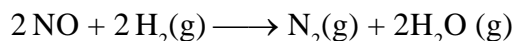
However, there is another view also , according to which molecularity of a complicated reaction is taken to be equal to the number of molecules, atoms or ions of reactant(s) and/or intermediates coming into contact and colliding simultaneously in the slowest step i.e. the rate-determining step (RDS) of the reaction.

For example the reaction  $\text{ROH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{RCl} + \text{H}_2\text{O}$ , which actually is a nucleophilic substitution reaction



Here the step II is the slowest step and hence the R.D.S. the molecularity of which is one. Therefore, the mechanism is called unimolecular nucleophilic substitution ( $S_N1$ ) and the reaction is said to follow  $S_N1$  mechanism.

The mathematical equation showing the relation of rate of reaction with concentration of reactant(s) is called rate-law of the reaction. For example, the kinetic experiment carried on the reaction.



has shown that :

- (i) rate increases 4 - fold when conc. of NO is doubled keeping the conc. of  $\text{H}_2$  constant
- (ii) rate gets just doubled when conc. of  $\text{H}_2$  is doubled keeping that of NO constant, and
- (iii) rate increases 8 - fold when concentrations of both NO and  $\text{H}_2$  are doubled simultaneously. These experimental rate data fit into following equation.

$$\text{Rate} \propto [\text{NO}]^2[\text{H}_2]$$

This equation is called experimentally observed “Rate law” of the reaction.

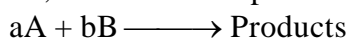
**Order of reaction is defined as the sum of the powers of the concentration terms appearing in experimentally observed rate law.**

Thus for the reaction (reduction of nitric oxide by hydrogen) considered above .

$$\text{Order w.r.t. NO} = 2 \qquad \text{Order w.r.t. H}_2 = 1$$

$$\text{Overall order} = 2 + 1 = 3$$

In general , let a reaction represented by the chemical equation:



obeys the following rate law.

$$\text{Rate} \propto [\text{A}]^m [\text{B}]^n, \text{ or } \text{Rate} = k[\text{A}]^m [\text{B}]^n$$

Where  $k$  = rate constant of reaction, a constant at constant temp and is actually the rate of reaction when conc. of each reactant is equal to unity  $k$  is also called **velocity constant** or **specific reaction rate**.

**Note that  $m$  and  $n$  are experimental quantities which may or may not be equal to the respective stoichiometric coefficients.**

**Also note that if either of A or B is taken in large excess as compared to another, the order w.r.t this reactant will be zero so order =  $m$  (when B is in large excess), and order =  $n$  (when A is large excess) , i.e.,**

$$\text{Rate} = k'[\text{A}]^m, k' = k[\text{B}]^n \text{ another constant, when B is in large excess.}$$

$$\text{Order w.r.t. A} = m$$

$$\text{Order w.r.t. B} = 0$$

$$\text{Rate} = k''[\text{B}]^n, k'' = k[\text{A}]^m = \text{another constant, when A is in large excess.}$$

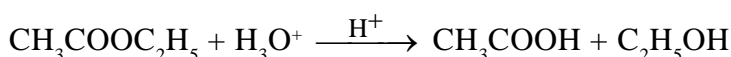
$$\text{Order w.r.t. A} = 0$$

$$\text{Order w.r.t. B} = n$$

$k'$  or  $k''$  is actually known as pseudo rate constant

**Thus, a bimolecular reaction conforms to the first - order when one of the reactants is taken in large excess and the reaction is said to be pseudo unimolecular or pseudo first order.**

An example of this is the hydrolysis of ester by dil. acid i.e.



The reaction is originally of second - order obeying the kinetics.

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

But the reaction is usually carried out taking dilute aqueous solution of ester and acid (HCl) such that in the reaction mixture water exists in large excess as compared to ester or better to say, water has almost its maximum concentration of  $55.5 \text{ mole L}^{-1}$ . So there is no appreciable change in the concentration of water and the same remains practically constant.

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$k[\text{H}_2\text{O}]$  becomes another constant ( $k'$ ) called pseudo rate constant and reactions obeys the following 1st order kinetics

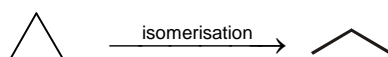
$$\text{Rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5]$$

Thus, the molecularity of the above reaction is 'two' but its order is 'one'.

In the light of the above concept one may define order of reaction as “**the number of molecules of the reactant(s) whose concentration alters during the chemical change is the order of reaction**”.

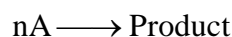
### Distinction between Molecularity and Order

- (i) Molecularity is a theoretical property while order is an experimental property.
- (ii) Molecularity concerns to mechanism, order concerns to kinetics
- (iii) Molecularity is always a whole number and never zero while order may be any number zero, fractional and integral.
- (iv) Molecularity is invariant but order may vary with change in experimental condition. As for example, the isomerisation of cyclo - propane represented by the chemical equation given below is a first order reaction at high cyclo propane pressure and is a second order reaction at low cyclo propane pressure.



- (v) Reactions of higher molecularity is rare since the chance of coming into contact and colliding simultaneously decreases as the number of molecules involved in collision increases.

#### Unit of rate constant



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

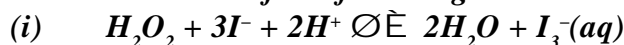
$$\frac{[\text{conc.}]}{\text{sec}} = k[\text{conc.}]^n$$

$$k = [\text{conc.}]^{1-n} \text{sec}^{-1}$$

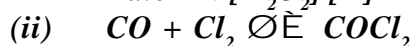
$$= [\text{mole/litre}]^{1-n} \text{sec}^{-1}$$

#### Illustration 4 :

*State the order w.r.t. each reactant, order of overall reaction and units of rate constant in each of the following reactions*

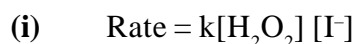


$$\text{Rate} = k [\text{H}_2\text{O}_2] [\text{I}^-]$$



$$\text{Rate} = k[\text{CO}]^2[\text{Cl}_2]^{1/2}$$

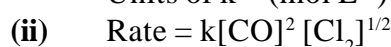
#### Solution :



Order w.r.t.  $\text{H}_2\text{O}_2 = 1$ ; Order w.r.t.  $\text{I}^- = 1$

Overall order = 2

$$\text{Units of } k = (\text{mol L}^{-1})^{1-2} \text{s}^{-1} = \text{mol}^{-1} \text{L s}^{-1}$$



Order w.r.t. to  $\text{CO} = 2$ ; Order w.r.t.  $\text{Cl}_2 = \frac{1}{2}$

Overall order = 2.5



**Illustration 5 :**

For the reaction,  $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$   
at 300 K following data are obtained

expt. No.	Initial Concentration		Initial rate
	[NO]	[Cl <sub>2</sub> ]	
1.	0.010	0.010	$1.2 \times 10^{-4}$
2.	0.010	0.020	$2.4 \times 10^{-4}$
3.	0.020	0.020	$9.6 \times 10^{-4}$

Write rate law for the reaction. What is the order of the reaction? Also calculate the specific rate constant.

**Solution :**

Let the rate law for the reaction be

$$\text{Rate} = k[\text{NO}]^x[\text{Cl}_2]^y$$

From Expt. (1),  $1.2 \times 10^{-4} = k[0.010]^x[0.010]^y$  ..... (i)

From Expt. (2),  $2.4 \times 10^{-4} = k[0.010]^x[0.020]^y$  ..... (ii)

Dividing Eq. (ii) by Eq. (i),

$$\frac{2.4 \times 10^{-4}}{1.2 \times 10^{-4}} = \frac{[0.020]^y}{[0.010]^y}$$

$$2 = 2^y$$

$$y = 1$$

From Expt. (2),  $2.4 \times 10^{-4} = k[0.010]^x[0.020]^y$  ..... (ii)

From Expt. (3),  $9.6 \times 10^{-4} = k[0.020]^x[0.020]^y$  ..... (iii)

Dividing Eq. (iii) by Eq. (ii),

$$\frac{9.6 \times 10^{-4}}{2.4 \times 10^{-4}} = \frac{[0.020]^x}{[0.010]^y}$$

$$4 = 2^x$$

$$x = 2$$

Order of reaction =  $x + y = 2 + 1 = 3$

Rate law for the reaction is,  $\text{Rate} = k[\text{NO}]^2[\text{Cl}_2]$

Considering Eq. (i) (again),  $1.2 \times 10^{-4} = k[0.010]^2[0.010]$

$$k = \frac{1.2 \times 10^{-4}}{[0.010]^3} = 1.2 \times 10^2 \text{ mol}^{-2} \text{ litre}^2 \text{ sec}^{-1}$$

**Illustration 6 :**

For the hypothetical reaction,  $2\text{A} + \text{B} \rightarrow \text{products}$

The following data are obtained :

Expt No.	Initial conc. of (A) (mol L <sup>-1</sup> )	initial conc. of (B) (mol L <sup>-1</sup> )	initial rate (mol L <sup>-1</sup> s <sup>-1</sup> )
1.	0.10	0.20	$3 \times 10^2$
2.	0.30	0.40	$3.6 \times 10^3$
3.	0.30	0.80	$1.44 \times 10^4$
4.	0.10	0.40	.....
5.	0.20	0.60	.....
6.	0.30	1.20	.....

Find out how the rate of the reaction depends upon the concentration of A and B and fill in the blanks.



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### Solution :

From Expt (2) and (3), it is clear that when concentration of A is kept constant and that of B is doubled, the rate increases four times. This shows that the reaction is of second order with respect to B.

Similarly, from Expt. (1) and (2), it is observed that when concentration of A is increased three times and that of B two times, the rate becomes twelve times. Hence, the reaction is first order with respect to A.

Thus the rate law for the reaction is :

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

**Fill in the blanks :** Substituting the values of Expt. (1) in the rate equation,

$$3 \times 10^2 = k[0.10][0.20]^2$$

or 
$$k = \frac{3 \times 10^2}{[0.10][0.20]^2} = 7.5 \times 10^4 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

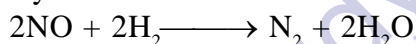
Expt.(4): 
$$\begin{aligned} \text{Rate} &= k[0.10][0.40]^2 \\ &= 7.5 \times 10^4 \times 0.10 \times 0.40 \times 0.40 \\ &= 1.2 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

Expt (5) : 
$$\begin{aligned} \text{Rate} &= k[0.20][.60]^2 \\ &= 7.5 \times 10^4 \times 0.20 \times 0.60 \times 0.60 \\ &= 5.4 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

Expt (6) : 
$$\begin{aligned} \text{Rate} &= k[0.30][1.20]^2 \\ &= 7.5 \times 10^4 \times 0.30 \times 1.20 \times 1.20 \\ &= 3.24 \times 10^4 \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

### 3. Rate Law and Mechanism :

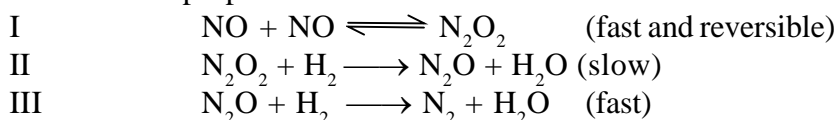
As already mentioned in the reaction:



Obeys the following third order kinetics

$$\text{Rate} \propto [\text{NO}]^2 [\text{H}_2]$$

The kinetics is not in tune with chemical equation. As the law of mass action suggests each concentration term should be raised to power 2. Neither experimental facts nor those coming from Law of mass action can be unacceptable to us. Under this condition we are led to believe that the reaction does not occur according to the chemical equation as written. That is the reaction is not elementary but is complicated. In order to explain the observed rate law following mechanism has been proposed.



The step II being the slowest i.e., the rate - determining step (R.D.S.). Note that the rate of formation of  $\text{N}_2$  cannot be faster than the rate of formation of  $\text{N}_2\text{O}$ . So, the rate of overall reaction or rate of formation of  $\text{N}_2$  will be equal to the rate of step II which according to law of mass action may be given as.

$$\text{Rate of overall reaction} = \text{Rate of step II} = k[\text{N}_2\text{O}_2][\text{H}_2]$$

Where  $k$  = rate constant of step II

The conc. of the intermediate ( $\text{N}_2\text{O}_2$ ) may be evaluated by applying law of mass action upon the equilibrium existing in step I as mentioned below.

$$K_c = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \quad \text{or} \quad [\text{N}_2\text{O}_2] = K_c [\text{NO}]^2$$

Putting this in the rate expression, we get

$$\text{Rate} = k_c k_c [\text{NO}]^2 [\text{H}_2] = k_{\text{obs}} [\text{NO}]^2 [\text{H}_2]$$

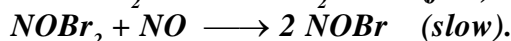
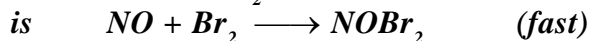
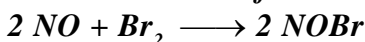
Where  $k_{\text{obs}} = k_c k_c$  = observed rate constant of the reaction

$$\text{Rate} \propto [\text{NO}]^2 [\text{H}_2]$$

This is the same rate - law as observed experimentally.

**Illustration 7 :**

*The possible mechanism for the reaction*



*Establish the rate law.*

**Solution :**

As the slowest step is the rate determining step, therefore the rate law is

$$R = k[\text{NOBr}_2][\text{NO}]$$

Now since  $\text{NOBr}_2$  is an intermediate its concentration can be calculated from step 1 as follows :

$$K = \frac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]} \quad [K = \text{eq. constant}]$$

or  $[\text{NOBr}_2] = K [\text{NO}] [\text{Br}_2]$

Substituting this value in above equation

$$r = k \cdot K [\text{NO}]^2 [\text{Br}_2]$$

or  $\text{rate} = k' [\text{NO}]^2 [\text{Br}_2] \quad [k' = k \cdot K = \text{constant } k']$

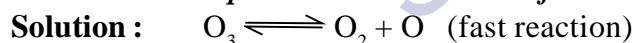
$\therefore \text{Rate} = k' [\text{NO}]^2 [\text{Br}_2]$

**Illustration 8 :**

*Rate law for ozone layer depletion is*

$$\frac{d[\text{O}_3]}{dt} = \frac{K[\text{O}_3]^2}{[\text{O}_2]}$$

*Give the probable mechanism of reaction?*



$\text{Rate} = k [\text{O}_3][\text{O}] \quad \dots [1]$

$$K_c = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} \text{ or } [\text{O}] = K_c \frac{[\text{O}_3]}{[\text{O}_2]}, \quad (\text{equilibrium constant } K_c)$$

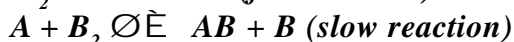
putting the value in (1)

$$\text{From (1) } \text{Rate} = k \cdot [\text{O}_3] \cdot k_c \frac{[\text{O}_3]}{[\text{O}_2]} = k \cdot K_c \cdot \frac{[\text{O}_3]^2}{[\text{O}_2]} = K \cdot \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

$$k = k \times K_c.$$

**Illustration 9 :**

*In hypothetical reaction  $A_2 + B_2 \rightleftharpoons 2AB$  follows the mechanism as given below:*



*Give the rate law and order of reaction.*

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### Solution :

Slowest step is rate determining.

$$\text{Rate} = k[A][B_2] \quad \dots\dots(1)$$

Here [A] should be eliminated.

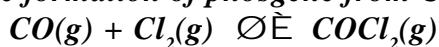
$$K_c = \frac{[A][A]}{[A_2]} = \frac{[A]^2}{[A_2]}$$

$$[A] = K_c^{1/2} [A_2]^{1/2}$$

$$\begin{aligned} \text{From (1). Rate} &= k K_c^{1/2} [A_2]^{1/2} [B_2] \\ &= K [A_2]^{1/2} [B_2] \quad ; \quad [K = k \cdot K_c] \\ \text{Order} &= 1 + 1/2 = 3/2 \end{aligned}$$

### Illustration 10 :

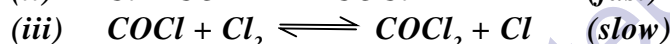
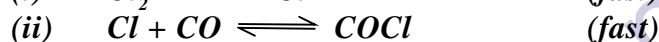
*For the formation of phosgene from CO(g) and chlorine,*



*The experimentally determined rate equation is,*

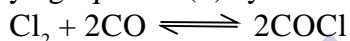
$$\frac{d[COCl_2]}{dt} = k[CO][Cl_2]^{3/2}$$

*Is the following mechanism consistent with the rate equation?*



### Solution :

Multiplying equation (ii) by 2 and adding (i), we get:



$$K = \frac{[COCl]^2}{[Cl_2][CO]^2}$$

$$[COCl] = (K)^{1/2} [Cl_2]^{1/2} [CO] \quad \dots\dots (1)$$

Slowest step is rate determining, hence

$$\text{Rate} = k[COCl][Cl_2] \quad \dots\dots (2)$$

From (1) and (2), we get

$$\text{Rate} = kK^{1/2} [Cl_2]^{1/2} [Cl_2][CO]$$

$$\text{Rate} = k'[Cl_2]^{3/2} [CO] \quad [k' = k \cdot K^{1/2}]$$

Thus, rate law is in accordance with the mechanism.

## 4. Reactions of the First Order :

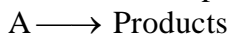
A reaction is said to be of the first order if the rate of the reaction depends upon only on concentration term only. Thus we may have

For the reaction :  $A \longrightarrow \text{Products}$   
Rate of reaction  $\propto [A]$ .

For the reaction :  $2A \longrightarrow \text{Products}$   
Rate of reaction  $\propto [A]$  only.

For the reaction :  $A + B \longrightarrow \text{Products}$   
Rate of reaction  $\propto [A]$  or  $[B]$  only.

Let us consider the simplest case viz.



Suppose we start with 'a' moles per litre of the reactant A. After time t, suppose x moles per litre of it, have decomposed. Therefore, the concentration of A after time t = (a - x) moles per litre. Then according to Law of Mass Action.

Rate of reaction  $\propto (a - x)$

$$\text{i.e., } \frac{dx}{dt} \propto (a - x)$$

$$\text{or } \frac{dx}{dt} = k(a - x) \quad \dots\dots (1)$$

where k is called the rate constant or the specific reaction rate for the reaction of the first order. The expression for the rate constant k may be derived as follows :

Equation (1) may be rewritten in the form

$$\frac{dx}{a - x} = kdt \quad \dots\dots(2)$$

Integrating equation (2), we get  $\int \frac{dx}{a - x} = \int kdt$

$$\text{or } k = \frac{1}{t} \ln \frac{a}{a - x} \quad \dots\dots(3)$$

$$\text{or } k = \frac{2.303}{t} \log \frac{a}{a - x} \quad \dots\dots(4)$$

Equation (4) is sometimes written in another form which is obtained as follows :

If the initial concentration is  $[A]_0$  and the concentration after time t is  $[A]$ , then putting  $a = [A]_0$  and  $(a - x) = [A]$  equation (iv) becomes

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \quad \dots\dots (5)$$

Further, putting  $a = [A]_0$  and  $(a - x) = [A]$  in eqn. (3), we get

$$kt = \ln \frac{[A]_0}{[A]}$$

which can be written in the exponential form as

$$\frac{[A]_0}{[A]} = e^{kt} \quad \text{or} \quad \frac{[A]}{[A]_0} = e^{-kt}$$

$$\text{or } [A] = [A]_0 e^{-kt} \quad \dots\dots (6)$$

### Illustration 11 :

*It was found that cane sugar solution in water was hydrolysed to the extent of 25 per cent in one hour. Calculate the time that will be taken for the sugar to be hydrolysed to the extent of 50 % , assuming that the reaction is of the first order.*

**Solution :**

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

$$\text{Where } \frac{x}{a} = f$$

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$$t_f = \frac{2.303}{k_1} \log \frac{1}{(1-f)} = -\frac{2.303}{k_1} \log(1-f) \quad \dots(1)$$

Putting  $f = 0.25$  at  $t_{0.25} = 1$  hour from the data

$$t_{0.25} = 1 \text{ hr} = \frac{2.303}{k_1} \log(1-0.25) = \frac{2.303}{k_1} \log 4/3 \quad \dots(2)$$

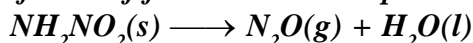
$$\text{Similarly } t_{0.5} = -\frac{2.303}{k_1} \log(1-0.5) = \frac{2.303}{k} \log 2 \quad \dots(3)$$

$$\text{Dividing (iii) by (ii)} \quad \frac{t_{0.5}}{1 \text{ hr}} = \frac{\log 2}{\log 4/3} = 2.4 \text{ hours}$$

Hence time required for 50% hydrolysis = 2.4 hours.

### Illustration 12 :

*The half time of first order decomposition of nitramide is 2.1 hour at 15°C.*



*If 6.2 g of  $\text{NH}_2\text{NO}_2$  is allowed to decompose, calculate*

- (a) *time taken for  $\text{NH}_2\text{NO}_2$  to decompose 99% and*
- (b) *volume of dry  $\text{N}_2\text{O}$  produced at this point measured at STP.*

**Solution :**

For a first-order reaction, rate constant expression is  $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$

$$\text{Initial moles of nitramide} = \frac{6.2}{62} = 0.1$$

$$t = \frac{2.303 \times 2.1}{0.693} \log \frac{0.1}{0.001} = 13.95 \text{ hours}$$

Since, the decomposition is 99 %, so 99 % of the initial moles of  $\text{NH}_2\text{NO}_2$  would be converted to  $\text{N}_2\text{O}$ .

$$\text{Moles of } \text{N}_2\text{O} = \frac{0.1 \times 99}{100}$$

$$\text{Volume of } \text{N}_2\text{O} \text{ at STP} = \frac{0.1 \times 99 \times 22.4}{100} = 2.217 \text{ litre .}$$

### Illustration 13 :

*A drug becomes ineffective after 30 % decomposition. The original concentration of a sample was 5mg/mL which becomes 4.2 mg/mL during 20 months. Assuming the decomposition of first order, calculate the expiry time of the drug in months. What is the half life of the product?*

$$\begin{aligned}
 \text{Solution : } k &= \frac{2.303}{t} \log \left[ \frac{a}{a-x} \right] \\
 &= \frac{2.303}{20} \log_{10} \left( \frac{5}{4.2} \right) \\
 &= 0.00872 \text{ min}^{-1}
 \end{aligned}$$

Expiry time 't' may be calculated as

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x} \qquad 0.00872 = \frac{2.303}{t} \log_{10} \frac{100}{70}$$

$$t = 40.9 \approx 41 \text{ months} \qquad t_{1/2} = \frac{0.693}{0.00872} = 79.4 \text{ months}$$

**Illustration 14 :**

*A first order reaction is 20 % completed in 10 minutes. Calculate the time taken for the reaction to go to 80 % completion.*

**Solution :**

Applying first order equation,

$$k = \frac{2.303}{t} \log_{10} \frac{100}{(100-20)} = \frac{2.303}{10} \log_{10} \frac{100}{80} = 0.0223 \text{ min}^{-1}$$

Again applying first order equation,

$$t = \frac{2.303}{k} \log_{10} \frac{100}{(100-80)} = \frac{2.303}{0.0223} \log_{10} \frac{100}{20} = 72.18$$

**Some Important Characteristics of First Order Reactions :**

(i) Any reaction of the first order must obey equation (5) or (6). This may be tested in any one of the following ways :

(a) **Substitution method :** Starting with a known concentration 'a' or  $[A]_0$ , the concentration of the reactant (a - x) or  $[A]$  at different intervals of time may be noted. For every value of t, the corresponding value of (a - x) i.e.  $[A]$  may be substituted in equation (vi) or (vii). If the values of k thus obtained are nearly constant (within the experimental error), the reaction is of the first order.

(b) **Graphical method :** Equation (6) may be written as

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

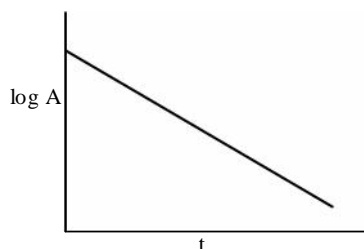
$$\text{or} \quad \log [A] = -\frac{k}{2.303} t + \log [A]_0 \qquad \dots (7)$$

This is the equation of a straight line ( $y = mx + c$ ). Thus if  $\log [A]$  or  $\log (a - x)$  values are plotted against time 't', the graph obtained should be a straight line if the reaction is of the first order.

The intercept made on the y-axis would be ' $\log [A]_0$ ' and the slope of the line would be

equal to  $\left(-\frac{k}{2.303}\right)$  i.e.,  $\text{slope} = -\frac{k}{2.303}$

From this, the value of k can be calculated.



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- (ii) **Half-life Period :** The time taken for any fraction of the reaction to be completed is independent of the initial concentration. For example, let us test the truth of this statement for half of the reaction to be completed. Equation (5) may be written as

$$t = \frac{2.303}{k} \log \frac{a}{a-x} \quad \dots (8)$$

When half of the reaction is completed,  $x = a/2$ . Representing the time taken for half of the reaction to be completed by  $t_{1/2}$  equation (8) becomes

$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{a - \frac{a}{2}} = \frac{2.303}{k} \log 2 = \frac{0.693}{k} \quad \text{i.e.,} \quad t_{1/2} = \frac{0.693}{k}$$

Thus 'a' does not appear in this equation so that  $t_{1/2}$  is independent of a. Similarly, it can be seen that  $t_{1/2}$ ,  $t_{2/3}$  etc. will also be independent of the initial concentration.

The time taken for half of the reaction to be completed i.e., the time in which the concentration of a reactant is reduced to half of its original value is called Half-life period of the reaction.

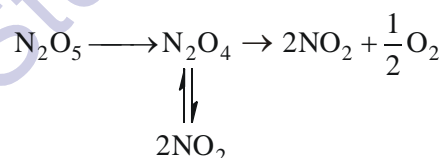
The above result can also be used to test a reaction of the first order. The method is called fractional life method.

- (iii) The units of k are independent of the units in which the concentrations are expressed. This is obvious from equation (5) because in this equation k depends upon the ratio of two

concentrations viz.  $\frac{a}{a-x}$  and the time t. Thus so long as both a and (a - x) are expressed in the same concentration units, the value of k is not affected. The units of k, therefore, depend only upon the units of time 't'. Depending upon whether t is expressed in second, minutes or hours, k would be in  $\text{sec}^{-1}$ ,  $\text{min}^{-1}$  or  $\text{hr}^{-1}$  respectively.

### Examples of the Reactions of First Order

1. **Decomposition of Nitrogen Pentoxide :** The compound, nitrogen pentoxide, is a volatile solid which decomposes in the gaseous state as well as in the form of its solution in an inert solvent like carbon tetrachloride, chloroform etc. according to the equation.



- (i) When the reaction is carried out in the solution,  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  remain in the solution and the volume of oxygen gas collected is noted at different intervals of time. It is obvious that Volume of oxygen gas collected at any time ( $V_t$ )  $\propto V_t$ . Amount of  $\text{N}_2\text{O}_5$  decomposed (x) i.e.,

- (ii) Volume of oxygen gas collected at infinite time ( $V_\infty$ ) (which is done by heating the reaction vessel)  $\left. \begin{array}{l} x \propto V_t \\ a \propto V_\infty \end{array} \right\} \propto \text{Amount of } \text{N}_2\text{O}_5 \text{ initially taken (a)}$

i.e., Substituting these values in the first order equation viz.

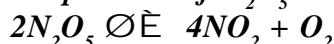
$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{We get} \quad k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

The constancy in the value of k proves the reaction to be of the first order.



**Illustration 15 :**

*For decomposition of  $N_2O_5$  in  $CCl_4$  solution at 320 K*



*show that the reaction is of first order and also calculate the rate constant:*

<i>Time in minutes</i>	<i>10</i>	<i>15</i>	<i>20</i>	<i>25</i>	<i><math>\infty</math></i>
<i>Volume of <math>O_2</math> evolved (in ml)</i>	<i>6.30</i>	<i>8.95</i>	<i>11.40</i>	<i>13.50</i>	<i>34.75</i>

**Solution :**

If the reaction is of first order, it must obey the equation

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

In the above reaction,  $NO_2$  remains in solution and oxygen is liberated and collected at different intervals of time.

Therefore,  $V_t \propto x$                        $V_\infty \propto a$

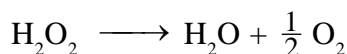
Substituting these values in the first order equation

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

Time	$V_t$	$V_\infty - V_t$	$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$
10	6.30	$34.75 - 6.30 = 28.45$	$k = \frac{2.303}{10} \log \frac{34.75}{28.45} = 0.0198$
15	8.95	$34.75 - 8.95 = 25.80$	$k = \frac{2.303}{15} \log \frac{34.75}{25.80} = 0.0198$
20	11.40	$34.75 - 11.40 = 23.35$	$k = \frac{2.303}{20} \log \frac{34.75}{23.35} = 0.0198$
25	13.50	$34.75 - 13.50 = 21.25$	$k = \frac{2.303}{25} \log \frac{34.75}{21.25} = 0.0198$

Since the value of  $k$  comes out to be constant the reaction, therefore, is of first order. The average value of rate constant is  $0.0198 \text{ min}^{-1}$ .

**Decomposition of Hydrogen Peroxide :** The decomposition of hydrogen peroxide in aqueous solution (catalysed by the presence of finely divided platinum) takes place according to the equation



The kinetics of this reaction may be studied either by the same method as done earlier (i.e. collecting the oxygen gas produced and noting its volume at different intervals of time) or by making use of the fact that  $H_2O_2$  solution can be titrated against  $KMnO_4$  solution. Thus by withdrawing equal amounts of the solution (usually 5 cc) at regular intervals of time and titrating against the same  $KMnO_4$  solution, the amount of  $H_2O_2$  present can be found every time. It is obvious that for the same volume of the reaction solution withdrawn,

$$\left. \begin{array}{l} \text{Volume of } KMnO_4 \text{ solution used} \\ \text{before the commencement of the} \\ \text{reaction i.e. at zero time } (V_0) \end{array} \right\} \propto \left\{ \begin{array}{l} \text{Initial concentration} \\ \text{of } H_2O_2 \text{ (a)} \end{array} \right.$$

i.e.,  $a \propto V_0$

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$$\left. \begin{array}{l} \text{Volume of KMnO}_4 \text{ solution used} \\ \text{at any instant of time } t (V_t) \end{array} \right\} \propto \left\{ \begin{array}{l} \text{Amount of H}_2\text{O}_2 \\ \text{present at that} \\ \text{instant i.e. } (a - x) \end{array} \right.$$

$$(a - x) \propto V_t$$

Substituting these values in the first order equation, we get

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

The decomposition of hydrogen peroxide, as tested by this equation, is found to be of the first order.

### Illustration 16 :

*From the following data show that the decomposition of an aqueous solution of hydrogen peroxide is of first order :*

Time (minutes)	0	10	20	30
V (ml)	46.1	29.8	19.6	12.3

*where V is the volume of potassium permanganate solution in ml required to decompose a definite volume of the peroxide solution.*

### Solution :

It is evident from the given data that at zero time, titre value is proportional to the original concentration of hydrogen peroxide, i.e., a. The titre value at any time t corresponds to undecomposed hydrogen peroxide, i.e., (a - x).

Substituting the value in the equation

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}, \text{ we get}$$

$$(i) \quad k_1 = \frac{2.303}{10} \log \frac{46.1}{29.8} = 4.364 \times 10^{-2}$$

$$(ii) \quad k_1 = \frac{2.303}{20} \log \frac{46.1}{19.6} = 4.276 \times 10^{-2}$$

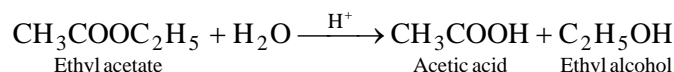
$$(iii) \quad k_1 = \frac{2.303}{30} \log \frac{46.1}{12.3} = 4.404 \times 10^{-2}$$

Since  $k_1$  comes out to be constant in the two cases, the reaction is a first order one with the average value of three.

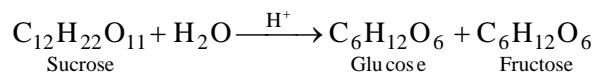
## 5. Pseudo Unimolecular Reactions :

Consider the following acid-catalysed reactions:

(i) Hydrolysis of ethyl acetate



(ii) Inversion of cane-sugar



Both the above reactions are bimolecular but are found to be of the first order, as experimentally it is observed that

For the first reaction, Rate of reaction  $\propto [\text{CH}_3\text{COOC}_2\text{H}_5]$  only

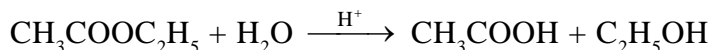
and for the second reaction, Rate of reaction  $\propto [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$  only.

The reason for such a behaviour is obvious from the fact that water is present in such a large excess that its concentration remains almost constant during the reaction.

Such reactions which are not truly of the first order but under certain conditions become reactions of the first order are called pseudo-unimolecular reactions.

**The kinetics of the above reactions have been studied as follows :**

**(a) Hydrolysis of Ethyl acetate**



In this reaction acetic acid is one of the products, the amount of which can be found by titration against standard NaOH solution. But being an acid-catalysed reaction, the acid present originally as catalyst, also reacts with NaOH solution. Hence a little careful thought reveals that for the same volume of reaction mixture withdrawn at different times.

Volume of NaOH solution used in }  $\propto$  { Amount of acid present only as catalyst  
the beginning i.e. at zero time ( $V_0$ ) } (as no  $\text{CH}_3\text{COOH}$  is produced at  $t = 0$ ) ..... (i)

Volume of NaOH solution used }  $\propto$  { Amount of acid present as catalyst  
at any instant of time  $t$  ( $V_t$ ) } + amount of  $\text{CH}_3\text{COOH}$  produced ..... (ii)

Combining results (i) and (ii), we find that

Amount of  $\text{CH}_3\text{COOH}$  produced }  $\propto$  ( $V_t - V_0$ )  
at any instant of time ..... (iii)

But amount of  $\text{CH}_3\text{COOH}$  produced }  $\propto$  { Amount of  $\text{CH}_3\text{COOC}_2\text{H}_5$   
at any instant of time } that has reacted ( $x$ )

Hence  $x \propto (V_t - V_0)$  ..... (iv)

Further

Volume of NaOH solution used after the reaction }  $\propto$  { Amount of acid present as  
has taken place for a long time, say 24 hours or so, } catalyst + Max. amount  
called infinite time ( $V_\infty$ ) } of  $\text{CH}_3\text{COOH}$  produced ..... (v)

Combining results (i) and (v), we find that

Max. amount of  $\text{CH}_3\text{COOH}$  produced  $\propto (V_\infty - V_0)$

But Max. amount of  $\text{CH}_3\text{COOH}$  produced

$\propto$  Initial concentration of  $\text{CH}_3\text{COOC}_2\text{H}_5$  ..... (vi)

Hence,  $a \propto (V_\infty - V_0)$

From equations (iv) and (vi), we have

$$(a - x) \propto (V_\infty - V_0) - (V_t - V_0)$$

or  $(a - x) \propto (V_\infty - V_t)$  ..... (vii)

Substituting the values of  $a$  and  $(a - x)$  from equations (vi) and (vii) in the first order equation, we get

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

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

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### Illustration 17 :

*In an experiment to study hydrolysis of an ester 0.5 M HCl at 300 K was used. 5 cm<sup>3</sup> of the reaction mixture was withdrawn after definite intervals and titrated against 0.2 M NaOH solution. Calculate the rate constant at 300K from the following data.*

<i>t</i> (sec)	0	600	1200	1800	1111
<i>v</i> (cm <sup>3</sup> of NaOH used)	11.5	12.0	12.5	13.0	25.5

### Solution :

From the given data,  $V_0 = 11.5 \text{ cm}^3$ ;  $V_\infty = 25.5 \text{ cm}^3$

$\therefore a \propto V_\infty - V_0 = 25.5 - 11.5 = 14.0$  and  $(a - x) \propto V_\infty - V_t$

Putting the values of  $V_t = 12.0$  at 600 sec.; 12.5 at 1200 sec. and 13.0 at 1800 seconds in the equation

$$k_1 = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}, \text{ we get}$$

$$(i) \quad k_1 = \frac{2.303}{600} \log \frac{14.0}{(25.5 - 12.0)} = \frac{2.303}{600} \log \frac{14.0}{13.5} = 6.061 \times 10^{-5} \text{ s}^{-1}$$

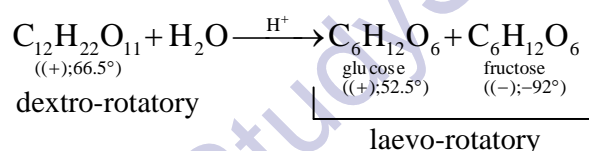
$$(ii) \quad k_1 = \frac{2.303}{1200} \log \frac{14.0}{(25.5 - 12.0)} = \frac{2.303}{1200} \log \frac{14.0}{13.0} = 6.176 \times 10^{-5} \text{ s}^{-1}$$

$$(iii) \quad k_1 = \frac{2.303}{1800} \log \frac{14.0}{(25.5 - 12.0)} = \frac{2.303}{1800} \log \frac{14.0}{12.5} = 6.296 \times 10^{-5} \text{ s}^{-1}$$

The average value of rate constant  $k_1 = 6.177 \times 10^{-5} \text{ s}^{-1}$

### (b) Optical Rotation Method

#### Inversion of Cane Sugar (Sucrose)



In this reaction by the hydrolysis of dextro-rotatory sucrose produces a mixture of glucose (dextro-rotatory) and fructose (laevo rotatory). As laevo rotation of fructose is more therefore the resulting mixture is laevo rotatory.

The kinetics of above reaction is studied by noting the angle of rotation at different intervals of time using polarimeter.

Say angle of rotation at the start of experiment =  $r_0$

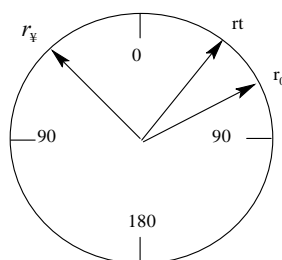
Angle of rotation at any time  $t = r_t$

Angle of rotation at  $\infty$  time =  $r_\infty$

Now, Angle of rotation at any instant of time =  $(r_0 - r_t) \propto$  amount of sucrose hydrolysed

or  $x \propto (r_0 - r_t)$

Similarly, angle of rotation at  $\infty$  time



$$\begin{aligned}
 &= (r_0 - r_\infty) \propto \text{initial conc. of sucrose (a)} \\
 \text{or } &a \propto (r_0 - r_t) \\
 \text{Thus, } &(a - x) \propto (r_0 - r_\infty) - (r_0 - r_t) \\
 &\propto (r_t - r_\infty)
 \end{aligned}$$

$$\text{Hence, } k = 2.303 \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

**Illustration 18 :**

*The optical rotation of sucrose in 0.5 N-hydrochloric acid at 308 K and at various time intervals are given below. Find out the rate constant for the first order hydrolysis of sucrose.*

<b>Time (minutes)</b>	<b>0</b>	<b>10</b>	<b>20</b>	<b>30</b>	<b>60</b>	<b>112</b>
<b>Rotation (degrees)</b>	<b>+32</b>	<b>25.5</b>	<b>20.0</b>	<b>15.5</b>	<b>5.0</b>	<b>-10.50</b>

**Solution :**

Here a, the initial concentration  $\propto (r_0 - r_\infty)$

x, the change in time t  $\propto (r_0 - r_t)$

$$\therefore (a - x) \propto (r_t - r_\infty)$$

Substituting these values for different (a - x) values corresponding to time t from the data in the equation for first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}, \text{ we get}$$

$$(i) \quad k_1 = \frac{2.303}{10} \log \frac{32 - (-10.5)}{25.5 - (-10.5)} = \frac{2.303}{10} \log \frac{42.5}{36.0} = 0.0166 \text{ min}^{-1}$$

$$(ii) \quad k_1 = \frac{2.303}{20} \log \frac{32 - (-10.5)}{20.0 - (-10.5)} = \frac{2.303}{20} \log \frac{42.5}{30.0} = 0.0166 \text{ min}^{-1}$$

$$(iii) \quad k_1 = \frac{2.303}{30} \log \frac{32 - (-10.5)}{15.5 - (-10.5)} = \frac{2.303}{30} \log \frac{42.5}{26.0} = 0.0164 \text{ min}^{-1}$$

$$(iv) \quad k_1 = \frac{2.303}{60} \log \frac{32 - (-10.5)}{5.0 - (-10.5)} = \frac{2.303}{60} \log \frac{42.5}{15.5} = 0.0168 \text{ min}^{-1}$$

Average value of  $k_1 = 0.0166 \text{ min}^{-1}$

## 6. Half life of $n^{\text{th}}$ Order Reaction :

	<b>A <math>\longrightarrow</math> Product</b>	
<b>t = 0</b>	<b>a</b>	<b>0</b>
<b>t = t</b>	<b>a - x</b>	<b>x</b>

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

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

$$\int_0^{a/2} \frac{dx}{(a - x)^n} = \int_0^{t_{1/2}} K dt$$

Let  $a - x = z$

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$$-dx = dz, \text{ when } x = 0, z = a$$

$$\text{When } x = a/2, z = a/2$$

$$\int_a^{a/2} \frac{-dz}{z^n} = \int_0^{t_{1/2}} K dt > \left[ \frac{z^{-n+1}}{-n+1} \right]_a^{a/2} = kt_{1/2}$$

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

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

Therefore for a  $n^{\text{th}}$  order reaction, half life period is inversely related to initial amount

$$t_{1/2} a^{n-1} = \text{constant}$$

## 7. Catalyst :

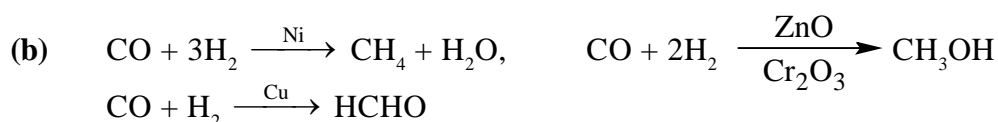
Berzelius used the term catalyst for the first time for the substances which accelerate the rate of chemical reaction. Now the term catalyst has been used for the foreign substances which influence the rate of a reaction and the phenomenon is known as catalysis. Usually two terms are used for catalysis :

**Positive Catalysis :** The phenomenon in which presence of catalyst accelerates the rate of reaction.

**Negative catalysis :** The phenomenon in which presence of catalyst retards the rate of reaction. Such substances are also known as inhibitors or negative catalyst.

### Characteristics Of Catalyst

- (i) A catalyst remains unchanged chemically at the end of reaction, however its physical state may change. e.g.  $\text{MnO}_2$  used as catalyst in granular form for the decomposition of  $\text{KClO}_3$ , is left in powder form at the end of reaction.
- (ii) A catalyst never initiates a chemical reaction. It simply influences the rate of reaction.  
**Exception : combination of  $\text{H}_2$  and  $\text{Cl}_2$  takes place only when moisture (catalyst) is present.**
- (iii) A small quantity of catalyst is sufficient to influence the rate of reaction e.g. 1 g atom of Platinum is sufficient to catalyse 108 litre of  $\text{H}_2\text{O}_2$  decomposition.
- (iv) A catalyst does not influence the equilibrium constant of reaction. It simply helps in attaining equilibrium earlier. It alters the rate of forward & backward reactions equally.
- (v) A catalyst normally does not alter the nature of products in a reaction. However some exceptions are found to this characteristic.



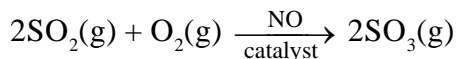
It may therefore be concluded that in some cases nature of products formed depends upon the presence and nature of catalyst used.

- (vi) A catalyst does not make reaction more exothermic
- (vii) Catalyst's activity is more or less specific : A catalyst for one reaction is not necessary to catalyse the another reaction.

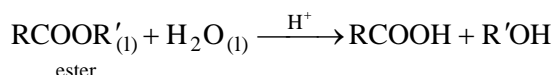
## 8. Types of Catalysis :

1. **Homogeneous catalysis** : The reaction in which catalyst and the reactants have same phase. It includes two types.

(a) **Gaseous phase catalysis** : When reactants and catalyst are in gaseous phase e.g. chamber process for  $\text{H}_2\text{SO}_4$ .

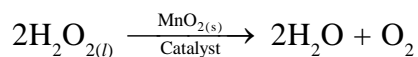


(b) **Solution phase catalysis** : The reactions in which catalyst and reactants are in solution phase or liquid phase of miscible nature.

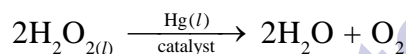


2. **Heterogeneous catalysis** : The reactions in which catalyst and reactants form phase  $\geq 2$ .

(a) **Solid-liquid catalysis** :  $\left. \begin{array}{l} \text{Reactant : Liquid} \\ \text{Catalyst : Solid} \end{array} \right\} \text{Immiscible}$



(b) **Liquid-Liquid catalysis** ::  $\left. \begin{array}{l} \text{Reactant : Liquid} \\ \text{Catalyst : Liquid} \end{array} \right\} \text{Immiscible}$



(c) **Solid-gas catalysis** :  $\left. \begin{array}{l} \text{Reactant : gases} \\ \text{Catalyst : solid} \end{array} \right\} \text{Immiscible}$

Two aspects of solid catalyst are more significant, one is activity and the other is selectivity. Activity is the ability of catalyst to accelerate chemical reactions; the degree of acceleration can be as high as  $10^{10}$  times in certain reactions. Selectivity is the ability of catalyst to direct reaction to yield particular reaction (excluding others). For example, n-heptane selectivity gives toluene in presence of Pt catalyst. Similarly,  $\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{O}_2$  give  $\text{CH}_2 = \text{CHCHO}$  selectivity over Bismuth molybdate catalyst.

## 9. Arrhenius Theory :

In 1889 Arrhenius recognised the temperature dependence of rates or rate constant. He has given an empirical relation which can be written as

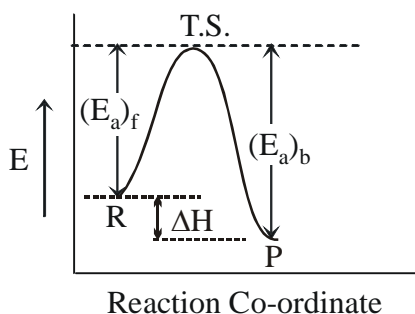
$$k = Ae^{-E_a/RT} \quad \dots\dots (1)$$

k is the rate constant (**of any order other than zero order**), A is the pre-exponential factor,  $E_a$  is the activation energy, R is the universal gas constant and T is the absolute temperature. Activation energy ( $E_a$ ) is the minimum energy required by a reactant at a certain temperature to undergo transformation into product. Arrhenius clearly assumed that reactions occur because of collisions between atoms and molecules of the reactant.

He assumed the activation energy to be the least value of energy which the colliding molecules must possess for the collision to yield a product. If we plot graph between activation energy and progress of a reaction (expressed as reaction co-ordinate), we get a graph as shown in figure.



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The difference between the energies of the reactant and the transition state (TS) is called  $(E_a)_f$ .

$$\Delta H = (E_a)_f - (E_a)_b$$

$A$ , the pre-exponential factor or the frequency factor or the Arrhenius constant is the number of effective collisions occurring per unit time. Effective collision is the number of collisions occurring per unit time in which orientation of the colliding molecules is proper.  $e^{-E_a/RT}$  gives the fraction of the effective collision that have the sufficient activation energy. Therefore the product of  $A$  and  $e^{-E_a/RT}$  gives the number of collisions per unit time that forms the product and is called its number of productive collisions which is the rate constant,  $k$ .

For all practical calculations, we shall assume that  $E_a$  and  $A$  are temperature independent. Both  $A$  and  $E_a$  are characteristics of the reaction.

### Determination of $A$ and $E_a$

#### First Method :

Taking log of both sides of equation (1)

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

Converting (natural log) to common log,  $\log k = \log A - \frac{E_a}{2.303 RT}$

If  $\log k$  is plotted against  $1/T$ , a straight line is obtained which is shown as below:

The slope of this line is given by slope =  $\frac{-E_a}{2.303 R}$

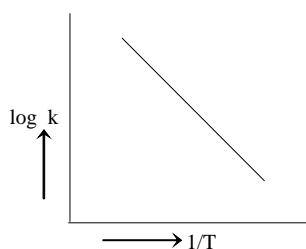
Thus, knowing the slope, the  $E_a$  can be easily calculated. The intercept of the line will give the value of  $\log A$ .

#### Second Method :

The logarithmic form of Arrhenius equation is rearranged as

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

Differentiating with respect to temperature, we get :



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

Integrating with in the limits of temperature  $T_1$  and  $T_2$ , we get

$$\int_{k_1}^{k_2} d \ln k = \int_{T_1}^{T_2} \frac{E_a}{RT^2} dT$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\text{or} \quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \dots (2)$$

Where  $k_1$  and  $k_2$  are rate constants at temperatures  $T_1$  &  $T_2$  respectively. Thus, knowing these values  $E_a$  can be calculated. When the value of  $E_a$  is known, the value of  $A$  can be calculated by substituting its value in equation  $k = Ae^{-E_a/RT}$ . In equation (2), the value of  $R$  has to be inserted in the same unit in which  $E_a$  is desired.

**Temperature Coefficient :** “Temperature coefficient of a chemical reaction is defined as the ratio of rate constants of a reaction at two temperatures differing by  $10^\circ\text{C}$ ”.

$$\therefore \text{Temperature coefficient} = \frac{k_{T+10}}{k_T} \gg 2 \text{ to } 3$$

where  $k_T$  is the rate constant at temperature  $T$  K and  $k_{T+10}$  is the rate constant at temperature  $(T+10)$  K. This ratio generally falls between 2 and 3 which means for most of the chemical reactions, the rate becomes two or three folds for every  $10^\circ\text{C}$  rise in temperature.

**Illustration 19 :**

*The rate of a reaction triple when temperature changes from  $20^\circ\text{C}$  to  $50^\circ\text{C}$ . Calculate energy of activation for the reaction ( $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ).*

**Solution :**

The Arrhenius equation is

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{R \times 2.303} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

Given  $\frac{k_2}{k_1} = 3$  ;  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  $T_1 = 20 + 273 = 293 \text{ K}$

and  $T_2 = 50 + 273 = 323 \text{ K}$

Substituting the given values in the Arrhenius equation,.

$$\begin{aligned} \log_{10} 3 &= \frac{E_a}{8.314 \times 2.303} \left[ \frac{323 - 293}{323 \times 293} \right] \\ E_a &= \frac{2.303 \times 8.314 \times 323 \times 293 \times 0.477}{30} \\ &= 28811.8 \text{ J mol}^{-1} \\ &= 28.8118 \text{ kJ mol}^{-1} \end{aligned}$$

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**Illustration 20 :**

*In Arrhenius equation for a certain reaction, the value of A and  $E_a$  (activation energy) are  $4 \times 10^{13} \text{ sec}^{-1}$  and  $98.6 \text{ kJ mol}^{-1}$  respectively. At what temperature, the reaction will have specific rate constant  $1.1 \times 10^{-3} \text{ sec}^{-1}$  ?*

**Solution :**

According to Arrhenius equation

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

$$\text{or } \log_e k = \log_e A - \frac{E_a}{RT} \log_e e$$

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

$$\text{or } 2.303 \log (1.1 \times 10^{-3}) = 2.303 \log (4 \times 10^{13}) - \frac{98.6 \times 10^3}{8.314 \times T}$$

$$T = \frac{98.6 \times 10^3}{8.314 \times 2.303 \times 16.56} \text{ K} = 311 \text{ K}$$

**Illustration 21 :**

*The rate constant is given by Arrhenius equation*

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

*Calculate the ratio of the catalysed and uncatalysed rate constant at  $25^\circ\text{C}$  if the energy of activation of a catalysed reaction is  $162 \text{ kJ}$  and for the uncatalysed reaction the value is  $350 \text{ kJ}$ .*

**Solution :**

Let  $k_{ca}$  and  $k_{un}$  be the rate constants for catalysed and uncatalysed reactions.

$$2.303 \log_{10} k_{ca} = 2.303 \log_{10} A - \frac{162 \times 10^3}{RT} \quad \text{.....(i)}$$

$$\text{and } 2.303 \log_{10} k_{un} = 2.303 \log_{10} A - \frac{350 \times 10^3}{RT} \quad \text{.....(ii)}$$

Subtracting Eq. (ii) from Eq.(i)

$$\begin{aligned} \log_{10} \frac{k_{ca}}{k_{un}} &= \frac{10^3}{2.303RT} (350 - 162) \\ &= \frac{188 \times 10^3}{2.303 \times 8.314 \times 298} = 32.95 \end{aligned}$$

$$\frac{k_{ca}}{k_{un}} = 8.88 \times 10^{32}$$

**Illustration 22 :**

*At 407 K the rate constant of a chemical reaction is  $9.5 \times 10^{-5} \text{ s}^{-1}$  and at 420 K, the rate constant is  $1.9 \times 10^{-4} \text{ s}^{-1}$ . Calculate the frequency factor of the reaction.*

**Solution :**

The Arrhenius equation is,

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

Given  $k_1 = 9.5 \times 10^{-5} \text{ s}^{-1}$ ;  $k_2 = 1.9 \times 10^{-4} \text{ s}^{-1}$ ;

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ;

$T_1 = 407 \text{ K}$  and  $T_2 = 420 \text{ K}$

Substituting the values in Arrhenius equation.

$$\log_{10} \frac{1.9 \times 10^{-4}}{9.5 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.314} \left[ \frac{420 - 407}{420 \times 407} \right]$$

$$E_a = 75782.3 \text{ J mol}^{-1}$$

Applying now  $\log k_1 = \log A - \frac{E_a}{2.303 RT_1}$

$$\log 9.5 \times 10^{-5} = \log A - \frac{75782.3}{2.303 \times 8.314 \times 407}$$

or  $\log \frac{A}{9.5 \times 10^{-5}} = \frac{75782.3}{2.303 \times 8.314 \times 407}$

$$= 9.7246$$

$$A = 5.04 \times 10^5 \text{ s}^{-1}$$

**Illustration 23 :**

*The energy of activation for a reaction is  $100 \text{ kJ mol}^{-1}$ . Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at  $20^\circ \text{C}$ , other things being equal ?*

**Solution :**

The arrhenius equation is

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

In absence of catalyst,  $k_1 = Ae^{-100/RT}$

In presence of catalyst,  $k_2 = Ae^{-25/RT}$

So  $\frac{k_2}{k_1} = e^{75/RT}$  or  $2.303 \log \frac{k_2}{k_1} = \frac{75}{RT}$

or  $2.303 \log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293}$

or  $\log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293 \times 2.303}$

or  $\frac{k_2}{k_1} = 2.34 \times 10^{13}$

## CHEMICAL KINETICS

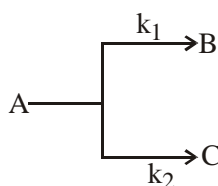
As the things being equal in presence or absence of a catalyst,

$$\frac{k_2}{k_1} = \frac{\text{rate in presence of catalyst}}{\text{rate in absence of catalyst}}$$

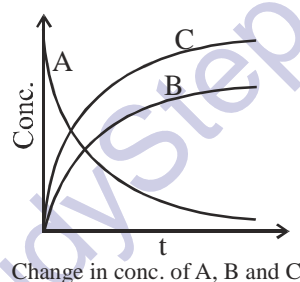
i.e., 
$$\frac{r_2}{r_1} = \frac{k_2}{k_1} = 2.34 \times 10^{13}$$

## 10. Reactions involving Two First Order Parallel Reactions Or Concurrent Reactions :

These are reactions in which a reacting substance do not follow a particular path to give a particular set of products. It follows one or more paths to give different products. For example,



The reactant A follows two different paths to form B and C. (The change in concentration of A, B and C is given in figure below)



Let initial conc. of A =  $a \text{ mol L}^{-1}$  and say the amount transformed in time  $t = x \text{ mol L}^{-1}$ .

If  $y$  and  $z$  be amounts of B and C formed at time  $t$ , then

$$\frac{dx_A}{dt} = \frac{dy_B}{dt} + \frac{dz_C}{dt}$$

Now if the reaction is unimolecular and  $k_1$  and  $k_2$  are rate constants for formation of B and C from A then

$$\text{rate of formation of } y, \quad \frac{dy_B}{dt} = k_1(a - x);$$

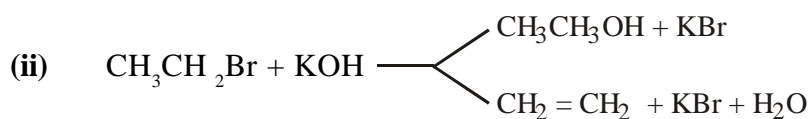
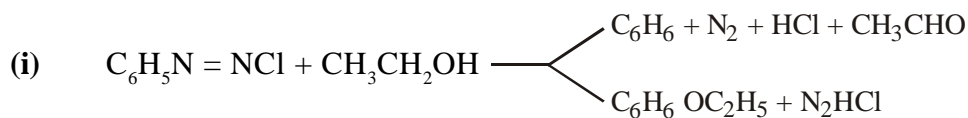
and rate of formation of  $z$ , 
$$\frac{dz_C}{dt} = k_2(a - x)$$

Thus, 
$$\frac{dx_A}{dt} = k_1(a - x) + k_2(a - x) = (k_1 + k_2)(a - x)$$

If  $k_1 + k_2 = k$ , Then 
$$\frac{dx_A}{dt} = k(a - x) \quad (\text{Here } r_f \text{ B} \neq r_f \text{ C})$$

or the rate of reaction will be  $k(a - x)$

### Some examples of side reactions



### Reactions involving opposing or reversible reactions :

Such reactions results in equilibrium. In other words the reactant changes to product and vice versa.

Say we have an opposing reaction in which both forward and backward reactions are first order, viz.,

( $k_1$  and  $k_2$  are rate constant of forward and backward reaction)

Say initial conc. of A and B are a and b mol L<sup>-1</sup> respectively.

If after time t, x moles/L of A change into B, then conc. of A and B will be (a - x) and (b + x) respectively.

The net rate of the reaction would be given as :

Rate =  $k_1(a - x) - k_2(b + x)$  ... (i) [ $\ominus$  both processes occur simultaneously]

When equilibrium is reached, the net rate is zero

Thus,  $k_1(a - x_e) = k_2(b + x_e)$  ( $x_e$  = equilibrium)

$$\text{Hence, } (b + x_e) = \frac{k_1}{k_2} (a - x_e) \quad \text{or} \quad b = \frac{k_1}{k_2} (a - x_e) - x_e$$

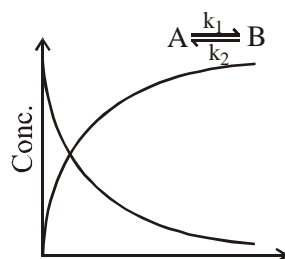
Substituting value of b in eqn. (i)

$$\text{Rate of reaction, } \frac{dx}{dt} = k_1(a - x) - k_2 \left[ \frac{k_1}{k_2} (a - x_e) - x_e + x \right]$$

on solving, we get

$$\text{Rate} = (k_1 + k_2) (x_e - x)$$

After rearranging and integrating the equation, we get an equation similar to first order reaction as shown below.



$$\text{or} \quad \frac{dx}{x_e - x} = (k_1 + k_2) dt \qquad \int_{x_0}^x \frac{dx}{x_e - x} = \int_0^t (k_1 + k_2) dt$$

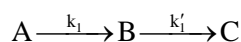
$$\text{or} \quad \log \frac{x_e - x_0}{x_e - x} = (k_1 + k_2) t$$

$$\text{or} \quad (k_1 + k_2) = \frac{1}{t} \log \frac{x_e - x_0}{x_e - x}$$

The equation is similar to first order reaction except that the measured rate constant is now the sum of the forward and the reverse rate constants.

## 11. Consecutive or Sequential Reactions :

**A Typical Example :** In many cases, the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. One of the examples of consecutive reactions involves the following steps.



Let the initial concentration of A be  $[A]_0$  and let after time  $t$ , the concentrations of A, B and C be  $[A]$ ,  $[B]$  and  $[C]$ , respectively. It is obvious that

$$[A]_0 = [A] + [B] + [C] \quad \text{.....(1)}$$

**Differential Rate Law :** The differential rate expressions are

$$-\frac{d[A]}{dt} = k_1[A] \quad \text{.....(2)}$$

$$\frac{d[B]}{dt} = k_1[A] - k'_1[B] \quad \text{.....(3)}$$

$$\frac{d[C]}{dt} = k'_1[B] \quad \text{.....(4)}$$

On integrating equation (2), we get

$$[A] = [A]_0 e^{-k_1 t} \quad \text{.....(5)}$$

Substituting  $[A]$  from equation (5) into equation (3), we get

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k'_1[B]$$

$$\frac{d[B]}{dt} + k'_1[B] = k_1[A]_0 e^{-k_1 t}$$

**Integrated Rate Law :** Multiplying the above expression throughout by  $\exp(k'_1 t)$ , we get

$$\frac{d[B]}{dt} + k'_1[B]e^{k'_1 t} = k_1[A]_0 e^{-(k_1 - k'_1)t}$$

The left side of the above expression is equal to  $d([B]e^{k'_1 t})/dt$ . Hence, the above expression can be written as ,  $d\{[B]e^{k'_1 t}\} = k_1[A]_0 e^{-(k_1 - k'_1)t} dt$

Integrating the above expression with  $[B] = 0$  at  $t = 0$ , we get

$$\begin{aligned}
 [B]e^{k'_1 t} &= k_1[A]_0 \left[ \frac{e^{-(k_1 - k'_1)t}}{-(k_1 - k'_1)} + \frac{1}{k_1 - k'_1} \right] \\
 [B] &= k_1[A]_0 \left[ \frac{e^{-k_1 t}}{-(k'_1 - k_1)} + \frac{e^{-k'_1 t}}{k_1 - k'_1} \right] \\
 [B] &= k_1[A]_0 \left( \frac{k_1}{k'_1 - k_1} \right) \{e^{-k_1 t} - e^{-k'_1 t}\} \quad \text{.....(6)}
 \end{aligned}$$

Substituting equations (5) and (6) in equation (1), we get

$$[A]_0 = [A]_0 e^{-k_1 t} + [A]_0 \left( \frac{k_1}{k'_1 - k_1} \right) (e^{-k_1 t} - e^{-k'_1 t}) + [C]$$

$$\text{or} \quad [C] = [A]_0 \left[ 1 - \frac{1}{k'_1 - k_1} (k'_1 e^{-k_1 t} - k_1 e^{-k'_1 t}) \right] \quad \text{.....(7)}$$



Figure (1) Illustrates the general appearance of the variations of concentrations of A, B and C during the progress of the reaction.

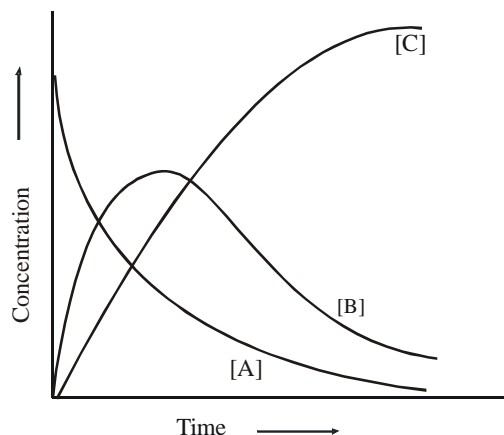


Fig. 1: Typical variations of concentration of A, B and C during the progress of the reaction  $A \rightarrow B \rightarrow C$ . The actual variations on the values of  $k_1$  and  $k'$ .

In general concentration of A decreases exponentially, the concentration of B initially increases upto a maximum and then decreases thereafter, and the concentration of C increases steadily until it reaches its final value  $[A]_0$ , when all A has changed into C.

**Maximum Concentration of B :** Equation (6) is

$$[B] = [A]_0 \left( \frac{k_1}{k'_1 - k_1} \right) \{ e^{-k_1 t} - e^{-k'_1 t} \} \quad \text{.....(6)}$$

At the maximum concentration of B, we have

$$\frac{d[B]}{dt} = 0$$

Hence, differentiating equation (6) with respect to t, we get

$$\frac{d[B]}{dt} = [A]_0 \left( \frac{k_1}{k'_1 - k_1} \right) \{ -k_1 e^{-k_1 t} + k'_1 e^{-k'_1 t} \} \quad \text{.....(8)}$$

Equating equation (8) to zero, we get

$$-k_1 e^{-k_1 t_{\max}} + k'_1 e^{-k'_1 t_{\max}} = 0$$

$$\text{or} \quad \frac{k_1}{k'_1} = e^{(k_1 - k'_1) t_{\max}}$$

$$\text{or} \quad \ln \left( \frac{k_1}{k'_1} \right) = (k_1 - k'_1) t_{\max}$$

$$\text{or} \quad t_{\max} = \frac{1}{k_1 - k'_1} \ln \left( \frac{k_1}{k'_1} \right) \quad \text{.....(9)}$$

substituting equation (9) in equation (6), we get

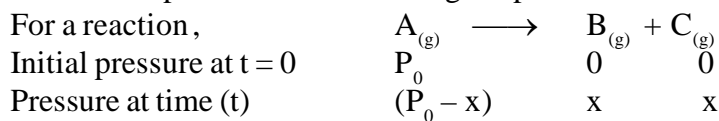
$$[B]_{\max} = [A]_0 \left( \frac{k'_1}{k_1} \right)^{k'_1 / (k_1 - k'_1)} \quad \text{.....(10)}$$

## CHEMICAL KINETICS

### Pressure Change Method :

This method is used for gaseous reactions.

As reaction proceeds there is change in pressure.



(Here  $x$  is no. of moles of A which change to produce)

Thus, total pressure ( $P_t$ ) at time (t) =  $P_0 - x + x + x$

$$\text{or } P_t = P_0 + x, \quad x = P_t - P_0$$

$$a - x = P_0 - (P_t - P_0) = 2P_0 - P_t$$

$$\text{Thus, } k = \frac{2.303}{t} \log \frac{P_0}{(2P_0 - P_t)}$$

### Illustration 24 :

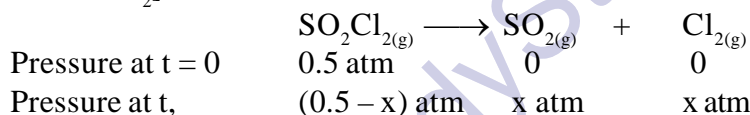
The following rate data was obtained for the first order thermal decomposition of  $SO_2Cl_{2(g)}$  at a constant volume.

Exp.	Time ( $sec^{-1}$ )	Total pressure (atm)
1.	0	0.5
2	100	0.6

Calculate the reaction rate when total pressure is 0.65 atmosphere.

### Solution :

Let us say that the pressure of  $SO_2Cl_2$  decreases by  $x$  atm, then the increase of pressure of  $SO_2$  and  $Cl_2 = x$  atm each. [Q 1 mole of  $SO_2Cl_2$  decomposes to give 1 mole of  $SO_2$  and 1 mole of  $Cl_2$ ].



$$\begin{aligned} \text{Since total pressure } P_T &= P_{SO_2Cl_2} + P_{SO_2} + P_{Cl_2} \\ &= (0.5 - x) + x + x \\ P_T &= 0.5 + x \text{ or } x = P_T - 0.5 \end{aligned}$$

$$\begin{aligned} \text{Hence } P_{SO_2Cl_2} &= 0.5 - (P_T - 0.5) \\ &= 0.5 - P_T + 0.5 = 1.0 - P_T \end{aligned}$$

Since, at  $t = 100$  sec,  $P_T = 0.6$  atm

$$\therefore P_{SO_2Cl_2} = 1.0 - 0.6 = 0.4 \text{ atm}$$

(a) Evaluation of  $k$

$$\begin{aligned} k &= \frac{2.303}{t} \log \frac{\text{Initial pressure}}{\text{Pressure at time } t} \\ &= \frac{2.303}{100} \log \frac{0.5}{0.4} = \frac{2.303}{100} \log 1.25 = \frac{2.303}{100} \times 0.0969 = 2.23 \times 10^{-3} \text{ sec}^{-1} \end{aligned}$$

(b) Rate at  $P_T = 0.65$  atm

$$P_{SO_2Cl_2} \text{ at total pressure of } 0.65 \text{ atm} = 1.0 - 0.65 = 0.35 \text{ atm}$$

$$\text{Rate} = k[N_2O_5] = 2.23 \times 10^{-3} \times 0.35 = 7.8 \times 10^{-4} \text{ atm sec}^{-1}$$

**Illustration 25 :**

**For a homogeneous gaseous phase reaction:  $2A \longrightarrow 3B + C$ , the initial pressure of reactant was  $P^\circ$  while pressure at time 't' was P. Find the pressure after time 2t. Assume I order reaction.**

**Solution :**

	$2A \longrightarrow$	$3B +$	$C$	
Initial Pressure	$P^\circ$	0	0	
Pressure at $t = t$	$P^\circ - 2a$	$3a$	$a$	
Pressure at $t = 2t$	$P^\circ - 2x$	$3x$	$x$	
Given	$P^\circ - 2a + 3a + a = P$			..... (1)
$\therefore$	$P^\circ + 2a = P$			

Now for I order reaction at time t

$$K = \frac{2.303}{t} \log \frac{P^\circ}{P^\circ - 2a} = \frac{2.303}{t} \log \frac{P^\circ}{2P^\circ - P} \quad \text{..... (2)}$$

Let total pressure at  $t = 2t$  be A, then  $P^\circ - 2x + 3x + x = A$  or  $P^\circ + 2x = A$

$$K = \frac{2.303}{2t} \log \frac{P^\circ}{P^\circ - 2x} = \frac{2.303}{2t} \log \frac{P^\circ}{2P^\circ - A} \quad \text{..... (3)}$$

$$K = \frac{2.303}{t} \log \left[ \frac{P^\circ}{2P^\circ - A} \right]^{1/2} \quad \text{..... (4)}$$

By equations (2) and (4)

$$\begin{aligned}
 \left[ \frac{P^\circ}{2P^\circ - P} \right]^2 &= \left[ \frac{P^\circ}{2P^\circ - A} \right] \\
 [2P^\circ - A] \cdot P^\circ &= [2P^\circ - P]^2 \\
 \therefore P^\circ \cdot A &= 2(P^\circ)^2 - (2P^\circ - P)^2 \\
 \therefore A &= 2P^\circ - \frac{(2P^\circ - P)^2}{P^\circ}
 \end{aligned}$$

**Illustration 26 :**

**The decomposition of  $Cl_2O_7$  at 400 K in the gas phase to  $Cl_2$  and  $O_2$  is of I order. After 55 sec at 400 K, the pressure of  $Cl_2O_7$  falls from 0.062 to 0.044 atm. Calculate :**

- (a) The rate constant.  
 (b) Pressure of  $Cl_2O_7$  after 100 sec.

**Solution :**

	$Cl_2O_7 \longrightarrow$	$Cl_2 +$	$\frac{7}{2} O_2$
Mole at $t = 0$	a	0	0
Mole at $t = 55$ sec.	$(a - x)$	x	$7x/2$

- (a) Since Pressure of  $Cl_2O_7$  is given and therefore,  
 $a \propto 0.062$   
 $(a - x) \propto 0.044$

$$\begin{aligned}
 Q \quad K &= \frac{2.303}{t} \log_{10} \frac{0.062}{0.044} \\
 K &= 6.23 \times 10^{-3} \text{ sec}^{-1}
 \end{aligned}$$

- (b) Let at  $t = 100$  sec,  $(a - x) \propto P$

$$\begin{aligned}
 \therefore 6.23 \times 10^{-3} &= \frac{2.303}{100} \log_{10} \frac{0.062}{P} \\
 \therefore P &= 0.033 \text{ atm.}
 \end{aligned}$$

# RADIOACTIVITY

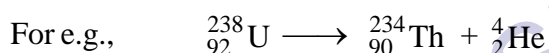
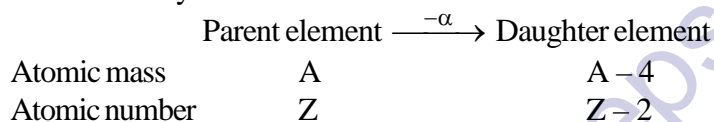
Radioactivity may be defined as a process in which nuclei of certain elements spontaneously disintegrate (transformation into another element by the ejection of  $\alpha$ -or  $\beta$ -particle) at a rate characteristic for each particular active isotope (Becquerel, 1896). All the heavy elements from bismuth (atomic number 83) through uranium and also a few of the lighter elements possess radioactive properties. However, the radioactive property of the different radioactive elements differs widely, e.g. radium atoms have about three million times the activity of uranium atoms. Uranium in the form of potassium uranyl sulphate,  $\text{K}_2\text{UO}_2(\text{SO}_4)_2$  was the first compound found to be radioactive. Radioactive changes are spontaneous. These are not controlled by temperature, pressure or nature of chemical combination.

## Radioactive disintegration

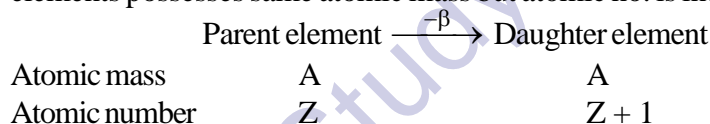
The atomic nuclei of radioactive elements can disintegrate any moment. During disintegration, atoms of new elements having different physical and chemical properties are formed, called daughter elements.

Disintegration occurs by the following processes :

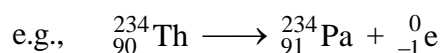
(i)  $\alpha$ -particle emission : When an  $\alpha$ -particle ( ${}^4_2\text{He}$ ) is emitted from the nucleus of parent element, the new element formed called daughter element, possess atomic mass less by 4 unit & atomic number less by 2 units.



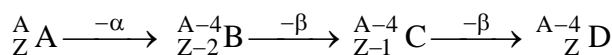
(ii)  $\beta$ -particle emission - When  $\beta$ -particle is emitted from parent element thus formed daughter elements possesses same atomic mass but atomic no. is increased by 1 unit.



- \* Elements having same mass number called isobars. (A - same, Z- different)  
 $\therefore$  daughter element formed by the  $\beta$ -particle emission is an isobar of parent element.



If in a radioactive transformation  $\alpha$  &  $\beta$  both are emitted then atomic mass & atomic number changes accordingly & produces an isotope of the parent element.



(A & D are isotopes)

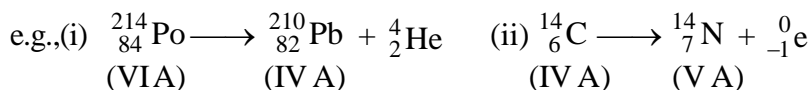
- \* Elements having same no. of protons called isotopes. e.g.,  ${}^{12}_6\text{C}$ ,  ${}^{14}_6\text{C}$  and  ${}^{16}_8\text{O}$ ,  ${}^{17}_8\text{O}$  etc.  
 (A - different, Z- same)
- \* Elements having same no. of neutrons are called isotones. e.g.,  ${}^{14}_6\text{C}$ ,  ${}^{16}_8\text{O}$  &  ${}^{19}_9\text{F}$ ,  ${}^{18}_8\text{O}$  etc.  
 (A - different, Z- different)
- \* Elements having same value of (A - 2Z) are called isodiaphers. e.g.,  ${}^{19}_9\text{F}$ ,  ${}^{39}_{19}\text{K}$   
 (A - different, Z- different, A - 2Z -same)
- \* Elements having same number of electrons are called isoelectronic. e.g.,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$
- \* Compounds having same number of atoms as well as same number of electrons are called isosters.

## 1. Law of Radioactive Disintegration :

- (i) Atoms of all radioactive elements undergo spontaneous disintegration and form new radioactive elements. The disintegration is accompanied by the emission of  $\alpha$ ,  $\beta$ , or  $\gamma$ -rays.
- (ii) The disintegration is at random, i.e. every atom has equal chance for disintegration at any time.
- (iii) The number of atoms that disintegrate per second is directly proportional to the number of remaining unchanged radioactive atoms present at any time. The disintegration is independent of all physical and chemical conditions like temperature, pressure chemical combination etc.

*The two laws of radioactive disintegration can be summed up as below:*

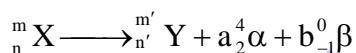
1. **Group displacement law :** The result of  $\alpha$ - and  $\beta$ - particle changes can be summed up in the form of group displacement law. *"In an  $\alpha$ -particle change the resulting element has an atomic weight less by four units and atomic number less by two units and it falls in a group of the periodic table two columns to the left of the original element, and in a  $\beta$ -particle change the resulting element has same atomic weight but its atomic number is increased by one than its parent and hence it lies one column to right".*



2. **Law of radioactive decay :** According to the law of radioactive decay, *the quantity of a radioelement which disappears in unit time (rate of disintegration) is directly proportional to the amount present.*

### **Determination of the number of $\alpha$ -and $\beta$ -particles emitted in a nuclear reaction:**

Consider the following general reaction.



Then,  $m = m' + 4a + 0b$  (i)  $n = n' + 2a - b$  (ii)

Solve for  $a$  and  $b$

Where  $a$  is the number of  ${}_2^4\text{He}$  emitted and  $b$  is the number of  ${}_{-1}^0\beta$  emitted

### **Points to Remember**

1. Rate of decay (activity,  $A$ ) is the number of atoms undergoing decay to unit time; it is represented by  $-\frac{dN_t}{dt}$ .

2. Rate of decay of a nuclide is directly proportional to the number of atoms of that nuclide present at that moment, hence.

$$\frac{dN_t}{dt} \propto N \quad \text{or} \quad \frac{dN_t}{dt} = -\lambda N_t$$

(the negative sign shows that the number of radioactive atoms,  $N_t$  decreases as time  $t$  increases)

3. Rate of decay of nuclide is independent of temperature, so its energy of activation is zero.
4. Since the rate of decay is directly proportional to the amount of the radioactive nuclide present and as the number of undecomposed atoms decreases with increase in time, the rate of decay also decreases with the increase in time.

Various forms of equation for radioactive decay are

$$N_t = N_0 e^{-\lambda t}$$

$$\log N_0 - \log N_t = 2.303\lambda t$$

## CHEMICAL KINETICS

$$\log \frac{N_0}{N_t} = \frac{\lambda t}{2.303}$$

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N_t} \quad \dots\dots (I)$$

Note that the equation (I) is similar to that of first order reaction, hence we can say that radioactive disintegration are examples of first order reactions.

Where  $N_0$  = Initial number of atoms of the given nuclide, i.e. at time 0

$N_t$  = No. of atoms of that nuclide present after t

$\lambda$  = Decay constant

However, unlike first order rate constant (K), the decay constant ( $\lambda$ ) is independent of temperature.

**Decay constant :** The ratio between the number of atoms disintegrating in unit time to the total number of atoms present at that time is called the decay constant of that nuclide.

### Characteristics of decay constant ( )

1. It is characteristic of a nuclide (not of an element)
2. Its units are  $\text{time}^{-1}$
3. Its value is always less than one

**Half-life Period ( $T_{1/2}$  or  $t_{1/2}$ ) :** Rutherford in 1904 introduced a constant known as half-life period of the radio-element for evaluating its radioactivity or for comparing its radioactivity with the activities of other radio-elements. The half-life period of a radio-element is defined as the time required by a given amount of the element of decay to one-half of its initial value.

$$\text{Mathematically, } T_{1/2} = \frac{0.693}{\lambda}$$

**Average Life Period (T) :** Since total decay period of any element is infinity, it is meaningless to use the term total decay period (total life period) for radio elements. Thus the term average life is used which is determined by the following relation.

$$\text{Average life (T)} = \frac{\text{Sum of lives of the nuclei}}{\text{Total number of nuclei}}$$

Relation between average life and half-life . Average life (T) of an element is the inverse of its

decay constant i.e.,  $T = \frac{1}{\lambda}$

Substituting the value of  $\lambda$  in the above equation ,  $T = \frac{T_{1/2}}{0.693} = 1.44T_{1/2}$

Thus, Average life (T) =  $1.44 \times \text{Half-life } (T_{1/2}) = \sqrt{2} \times T_{1/2}$

Thus the average life period of a radioisotope is approximately under-root two times of its half life period.

**Specific activity :** It is the measure of radioactivity of a radioactive substance. It is defined as 'the number of radioactive nuclei which decay per second per gram of radioactive isotope'. Mathematically, if 'm' is the mass of radioactive isotope, then

$$\text{Specific activity} = \frac{\text{Rate of decay}}{m} = \frac{\lambda N}{m} = \lambda \times \frac{\text{Avogadro number}}{\text{Atomic mass in g}}$$

Where N is the number of radioactive nuclei, which undergoes disintegration.

## 2. Radioactivity :

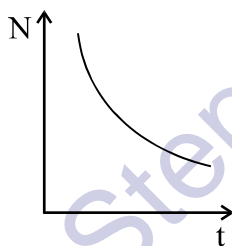
- (a) The phenomenon of spontaneous disintegration of nuclei of unstable atoms is defined as radioactivity.
- (b) Generally it is exhibited by atoms with  $A > 192$  and  $Z > 82$
- (c) It was discovered by Henry Becquerel
- (d) Lead isotope is the stable end product of any natural radioactive series
- (e) Radio activity is a nuclear process and not an atomic process
- (f) Radioactivity is not associated with the electron configuration of the atom.

## 3. Rutherford-Soddy Theory :

- (a) If  $N$  is the number of radioactive nuclei present in a sample at a given instant of time, then the rate of decay at that instant is proportional to  $N$  i.e.,

$$\frac{dN}{dt} = -\lambda N$$

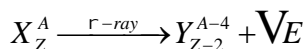
- (b) If  $N_0$  is the number of radioactive nuclei at time  $t = 0$ , then the number of radioactive nuclei at a later time  $t$  is given by,  $N = N_0 e^{-\lambda t}$



- (c) The nuclei of unstable atoms decay spontaneously emitting  $\alpha$ ,  $\beta$  particles and  $\gamma$  rays
- (d) Radioactivity remains unaffected due to the physical and chemical changes of the material.
- (e) Radioactivity obeys the law of probability i.e it is uncertain that when a particular atom will decay.

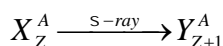
## 4. Soddy-Fajan's Laws :

- (a) During an  $\alpha$ -decay, mass number decreases by 4 units and atomic number by 2 units.



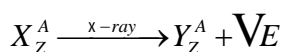
Daughter nucleus will occupy two positions before that of parent nucleus, in periodic table.

- (b) During  $\beta$ -decay mass number of the atom will not change and atomic number increases by 1 unit



Daughter nucleus will occupy one position on the right of that of parent nucleus in periodic table

- (c) During  $\gamma$ -decay, the mass number and atomic number of the nucleus remain unchanged



4.

- (a) Emission of  $\alpha$ -particle means loss of two protons and two neutrons
- (b) Emission of  $\beta$ -particle means loss of an electron.
- (c) Emission of a  $\gamma$ -ray means no change in charge and mass, but only energy changes



## CHEMICAL KINETICS

### 5. Activity (A) :

- (a) The number of atoms of any material decaying per second is defined as the activity of that material.
- (b) Its value depends on the quantity and nature of that material.
- (c) Units of activity –  
fundamental unit – disintegrations per second i.e., Bq  
 $1 \text{ Bq} = 1 \text{ disintegration/s}$
- (d) Practical units: curie and rutherford.  
 $1 \text{ curie} = 3.7 \times 10^{10} \text{ disintegration/second}$   
 $1 \text{ Rutherford} = 10^6 \text{ disintegrations/second}$
- (e) Formulae of activity

$$(i) A = -\frac{dN}{dt} \quad (ii) A = \lambda N \quad (iii) A_0 = \lambda N_0 \quad (iv) A = A_0 e^{-\lambda t} \quad (v) A = \frac{0.693 N_A m}{WT}$$

where  $A_0$  = maximum initial activity;  $A$  = activity after time  $t$ ,  $\lambda$  = decay constant,

$N_A$  = Avogadro number ,

$m$  = mass of material ,

$W$  = atomic weight of material ,

$T$  = half life of material

### 6. Decay Constant ( $\lambda$ ) :

- (a) Decay constant is equal to the reciprocal of that time in which the activity of the material reduces to  $\frac{1}{e}$  or 37 % of its initial activity.

$$(b) \lambda = \frac{-\frac{dN}{dt}}{N} = \frac{\text{No. of atoms decaying per second (Rate of disintegration)}}{\text{No. of atoms remaining after decay}}$$

i.e. The rate of disintegration per atom is defined as decay constant

- (c) Decay constant does not depend on temperature, pressure and volume. It depends on the nature of material.
- (d) Its unit per second.

$$(e) \text{ Decay constant } \left( \lambda = \frac{-\frac{dN}{dt}}{N} \right) \text{ represents the probability of decay per second.}$$

$$(f) \lambda = \frac{2.303}{t} \log_{10} \frac{N_0}{N} = \frac{2.303}{t} \log_{10} \frac{A_0}{A} = \frac{2.303}{t} \log_{10} \frac{M_0}{M}$$

- (g) Its value is equal to the negative of the slope of  $N$ - $t$  curve.
- (h) The decay constant of stable element is zero.

### 7. Half-life ( $T_{1/2}$ ) :

- (a) The time, in which the number of atoms ( $N$ ) reduces to half of its initial value ( $N_0$ ), is defined as the half-life of the element (i.e. half of the atoms decay).  $t = T_{1/2}$ ,  $N = \frac{N_0}{2}$
- (b) The time in which the activity reduces to half of its initial value is defined as half life.

$$\text{At } t = T_{\frac{1}{2}}, \quad A = \frac{A_0}{2}$$

- (c) Its unit is second  
 (d) Formulae of half life

$$(i) \quad T_{\frac{1}{2}} = \frac{0.693}{\lambda} = \frac{\log_e 2}{\lambda}$$

$$(ii) \quad T_{\frac{1}{2}} = \frac{\log_e 2}{\log_{10} \left( \frac{N_0}{N} \right)} = \frac{\log_e 2}{\log_{10} \left( \frac{A_0}{A} \right)} = \frac{\log_e 2}{\log_{10} \left( \frac{M_0}{M} \right)}$$

$$(iii) \quad T_{\frac{1}{2}} = \frac{t}{n} \text{ where } n = \text{No. of half lives}$$

$$(iv) \quad \text{Time of disintegration } t = \frac{T \log_{10} \left( \frac{N_0}{N} \right)}{\log_{10} 2} = \frac{T \log_{10} \left( \frac{N_0}{N} \right)}{0.3010}$$

### 8. Mean life ( $\tau$ ) :

- (a) The time, for which a radioactive material remains active, is defined as mean life of that material :
- (b)  $\tau = \frac{\text{Sum of lives of all atoms}}{\text{total number of atoms present}} = \frac{\int t |dN|}{N_0}$
- (c) The average time taken in decaying by the atoms of an element is defined as its mean life  $\tau$ .
- (d)  $\tau = 1/\lambda$
- (e) Its units are second, minute, hour day, month, year etc.
- (f) Mean life does not depend on the mass of material. It depends on the nature of the material.
- (g) The magnitude of slope of decay curve is equal to the mean life.
- (h) Relation between the mean life and half-life.

$$(i) \quad \tau = \frac{T_{\frac{1}{2}}}{0.693}$$

$$(ii) \quad \tau = 1.44 T_{\frac{1}{2}}$$

$$(iii) \quad \tau > T_{\frac{1}{2}}$$

- (iv) The time, in which the number of radioactive atoms decays to  $1/e$  or 37% of its initial value, is defined as the mean life of that material.

### 9. Important Formulae Related to Law of Disintegration ( $\tau$ ) :

$$(a) \quad N = N_0 e^{-\lambda t}$$

$$(b) \quad A = A_0 e^{-\lambda t}$$

$$(c) \quad M = M_0 e^{-\lambda t}$$

$$(d) \quad \lambda = \frac{2.3027 \log_{10} \left( \frac{N_0}{N} \right)}{t}$$

$$(e) \quad \lambda = \frac{2.3027 \log_{10} \left( \frac{A_0}{A} \right)}{t}$$

$$(f) \quad \lambda = \frac{2.3027 \log_{10} \left( \frac{M_0}{M} \right)}{t}$$

$$(g) \quad \lambda = \lambda_r + \lambda_s$$

## CHEMICAL KINETICS

(h)  $\lambda = \frac{\lambda_r + \lambda_s}{\lambda_r + \lambda_s}$  (When two particles decay simultaneously)

(i)  $N = \frac{N_0}{2^n} = \frac{N_0}{2^{\left(\frac{T}{T_{1/2}}\right)}}$

(j)  $A = \frac{A_0}{2^{\left(\frac{T}{T_{1/2}}\right)}}$

(k)  $M = \frac{M_0}{2^{\left(\frac{T}{T_{1/2}}\right)}}$

### 10. Useful Hints :

(i) Percentage decreases in activity =  $\left[1 - \frac{A}{A_0}\right] \times 100$

(ii) Number of atoms remaining after n half lives  $N = \frac{N_0}{2^n}$

(iii) Number of atoms decayed after time  $t = N_0 - N = N_0 \left[1 - \frac{1}{2^n}\right]$

(iv) The fraction of radioactive material at time T  $= \left[1 - \frac{N}{N_0}\right] = \left[1 - \frac{1}{2^{\frac{T}{T_{1/2}}}}\right]$

(v) Percentage of radioactive material decayed at time T  $= \left[1 - \frac{N}{N_0}\right] \times 100 = \left[1 - \frac{1}{2^{\frac{T}{T_{1/2}}}}\right] \times 100$

(vi) Percentage of radioactive material decayed in n half-lives  $= \frac{N}{N_0} \times 100 = \frac{1}{2^{\frac{T}{T_{1/2}}}} \times 100$

(vii) Fraction of radioactive material decayed in n half lives  $= 1 - \frac{N}{N_0} = \left[1 - \frac{1}{2^n}\right]$

(viii) Percentage of radioactive material decayed in n half lives  $\left[1 - \frac{N}{N_0}\right] \times 100 = \left[1 - \frac{1}{2^n}\right] \times 100$

(ix) Percentage of radioactive material remaining after n half-lives.  $\frac{N}{N_0} \times 100 = \frac{1}{2^n} \times 100$

(x) When decay process is too slow then  $N = N_0 - N_0 \lambda t$  or  $N = -(N_0 \lambda) t + N_0$

(xi) N-t graph is a straight line with -ve slope, for slow decay process.

## 11. Characteristics of $\alpha$ , $\beta$ , and $\gamma$ rays

S.No	Property	$\alpha$ -Particles	$\beta$ -Particles	$\gamma$ -rays
1.	Nature and value of charge	Positive and double of the charge of the proton	Negative and equal to the charge of electron $1.6 \times 10^{-19} \text{ C}$	Uncharged (Neutral)
2.	Nature of particle	Doubly ionized helium atom (2 protons and 2 neutrons)	Electron (or) positron	Electromagnetic waves
3.	Mass	Four times the mass of the proton $(4 \times 1.67 \times 10^{-27} \text{ kg})$	Equal to the mass of electron $9.1 \times 10^{-31} \text{ kg}$	Mass less
4.	Specific charge $\frac{q}{m}$	$\frac{3.2 \times 10^{-19}}{4 \times 1.67 \times 10^{-27}} = 4.79 \times 10^7$	$1.7 \times 10^{11} \text{ C kg}^{-1}$	Uncharged and mass less
5.	Explained by	Tunnel effect	Neutrino hypothesis	Transitions of nuclei into the ground energy level after $\alpha$ and $\beta$ decay
6.	Effect of electric and magnetic fields	Deflected by electric and magnetic fields	Deflected by electric and magnetic fields	Unaffected
7.	Penetrating power	1	100	10000
8.	Ionizing power	100000	100	1
9.	Velocity	Less than the velocity of light $(1.4 \times 10^7 \text{ m/s to } 2.2 \times 10^7 \text{ ms}^{-1})$	Approximately equal to the velocity of light	$3 \times 10^8 \text{ m/s}$
10.	Mutual interaction with matter	Produce heat	Produce heat	Produce the phenomenon of Photoelectric effect, Compton

## 12. $\alpha$ -emission

### (a) Characteristics of $\alpha$ -decay :

- (i) The spectrum of  $\alpha$  -particles is a discrete line spectrum.
- (ii) Spectrum of  $\alpha$  -particles has fine structure i.e. every spectral line consists of a number of fine lines.
- (iii) The  $\alpha$  -emitting nuclei have discrete energy levels i.e energy levels in nuclei are analogous to discrete energy levels in atoms..
- (iv)  $\alpha$  -decay is explained on the basis of tunnel effect.
- (v) Geiger-Muller law -  $\log_e \lambda = A + B \log_e R$  For radioactive series B is same whereas A is different

## CHEMICAL KINETICS

**(b) Range of  $\alpha$ -particles :**

- (i) The maximum distance traversed by  $\alpha$ -particles in air before being finally stopped is defined as the range of  $\alpha$ -particles.
- (ii) The maximum distance traversed by  $\alpha$ -particles before being finally absorbed after ionizing gas molecules, is defined as the range of  $\alpha$ -particles.
- (iii) The range of  $\alpha$ -particles in air is from 2.6cm to 8.6cm.
- (iv) Relations between the range of  $\alpha$ -particles and their energy

$$(I) \quad R = 0.318E^{3/2}$$

$$(II) \quad \log R = \log 0.318 + \frac{3}{2} \log E$$

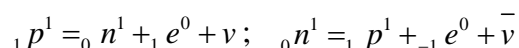
**(c) Size of the nucleus decreases by  $\alpha$  emission**

### 13. Characteristics of $\beta$ -decay :

- (i) The energy spectrum of  $\beta$ -particles is continuous i.e.  $\beta$ -particles of all energies upto a certain maximum are emitted
  - (ii) The number of such  $\beta$ -particles is maximum whose energy is equal to the maximum probable energy i.e. at  $E = E_{mp}$ ,  $N_B = \text{maximum}$ .
  - (iii) There is a characteristic maximum value of energy in the spectrum of  $\beta$ -particles which is known as the end point energy ( $E_0$ )
  - (iv) In  $\beta$ -decay process, a neutron is converted into proton or proton is converted into neutron.
- $${}_0n^1 = {}_1p^1 + {}_{-1}e^0 \quad (\beta^- \text{ Particle}) \qquad {}_1p^1 = {}_0n^1 + {}_1e^0 \quad (\beta^+ \text{ Particle})$$
- (v) The energy of  $\beta$ -particles emitted by the same radioactive material may be same or different.
  - (vi) The number of  $\beta$ -particles with energy  $E = E_0$  (end point energy) is zero.

### 14. Neutrino Hypothesis :

- (a)** According to Pauli, whenever neutron is converted into proton or proton into neutron then this process is accompanied with the emission of a new particle to which he named as neutrino.



**(b) Properties of neutrino :**

- (i) The charge on neutrino is zero
- (ii) The rest mass of neutrino is zero
- (iii) Its spin angular momentum is  $\pm \frac{h}{2}$
- (iv) Its speed is equal to that of light.
- (v) It has finite magnetic moment but the magnitude is very small
- (vi) Its antiparticle is anti-neutrino.
- (vii) The linear momentum vector  $\vec{p}$  and spin vector  $\vec{S}$  are mutually in opposite directions.
- (viii) Its energy is equal to  $(E_{end} - E_s)$ .
- (ix) It does not interact with matter.
- (x) Neutrino was discovered by Pauli and its experimental verification is done by Reines and Cowan.

### 15. (a) Characteristics of $\gamma$ -decay

- (i) The spectrum of  $\gamma$  -rays is a discrete line spectrum.
- (ii) Whenever  $\alpha$  or  $\beta$  - particles is emitted by a nucleus then the daughter nucleus is left in the excited state. It suddenly makes transition in the ground state thereby emitting  $\gamma$  -rays.
- (iii) Knowledge about nuclear energy levels is obtained by  $\gamma$  -spectrum.
- (iv)  $\gamma$  -rays interact with matter as a consequence of which the phenomena of photoelectric effect, Compton effect and pair production happen. (At low energy photoelectric effect and at high energy pair-production are effective).

### 15. (b) Intensity of $\gamma$ -rays in materials

- (i) When  $\gamma$  -rays penetrate matter, then their intensity (a) decreases exponentially with depth (x) inside the matter. The intensity of  $\gamma$  -rays at depth x inside the matter is given by  $I = I_0 e^{-\mu x}$ .
- (ii) The thickness of matter, at which the intensity of  $\gamma$  -rays (I) reduces to half its initial maximum value ( $I_0$ ), is known as its half-value thickness.  $\left( X_{1/2} = \frac{.693}{\mu} \right)$
- (iii) The reciprocal of the distance inside matter, at which the intensity (I) reduces to  $\frac{1}{e}$  or 37 % of its maximum value ( $I_0$ ), is defined as the coefficient of absorption ( $\mu$ ) of that material.
- (iv) Coefficient of absorption
  - (I)  $\mu = -\frac{dI/I}{dx}$
  - (II)  $\mu$  depends on the wavelength of  $\gamma$  -rays ( $\propto \lambda^{-3}$ ) and the nature of absorbing material

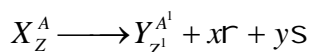
### 16. Radioactive Series :

If parent element is unstable then it will dissociate into daughter element & if this daughter element is still unstable, then it will again dissociate into a new daughter element & process continuous till the formation of a stable element. Series of element obtained from parent element to the finally stable non-radioactive element is known as radioactive disintegration series.

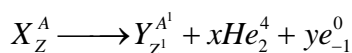
( $4n + 1$ ) is artificial series &  $4n$ , ( $4n + 2$ ), ( $4n + 3$ ) are natural series.

S.No	Series	Name of the series	Initial element	Final element	Nature of series	No of $\alpha$ & $\beta$ Particles emitted
1.	$4n+2$	Uranium series	${}_{92}\text{U}^{238}$	${}_{82}\text{Pb}^{206}$	Natural	8 $\alpha$ , 6 $\beta$
2.	$4n+3$	Actinium series	${}_{92}\text{U}^{235}$	${}_{82}\text{Pb}^{207}$	Natural	7 $\alpha$ , 4 $\beta$
3.	$4n$	Thorium series	${}_{90}\text{Th}^{232}$	${}_{82}\text{Pb}^{208}$	Natural	6 $\alpha$ , 4 $\beta$
4.	$4n+1$	Neptunium series	${}_{93}\text{Np}^{237}$	${}_{83}\text{Bi}^{209}$	Artificial	7 $\alpha$ , 4 $\beta$

## 17. To Calculate no of $\alpha$ -particles and $\beta$ -Particles emitted

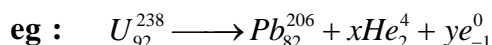


x: no of  $\alpha$ -particles emitted    y: no of  $\beta$ -particles emitted



$$A = A^1 + 4x \qquad x = \frac{A - A^1}{4}$$

$$Z = Z^1 + 2x - y \qquad y = Z^1 - Z + 2x \qquad y = \left( \frac{A - A^1}{2} \right) - (Z - Z^1)$$



$$x = \frac{A - A^1}{4} = \frac{238 - 206}{4} = 8 \alpha \text{ - particles}$$

$$y = \left( \frac{A - A^1}{2} \right) - (Z - Z^1) = \left( \frac{238 - 206}{2} \right) - (92 - 82) = 16 - 10 = 6 \beta \text{ - particles}$$

### Units of radioactivity :

The unit of radioactivity is curie (Ci). It is the quantity of any radioactivity substance which has decay rate of  $3.7 \times 10^{10}$  disintegrations per second.

1 millicurie (mCi) =  $3.7 \times 10^7$  disintegrations per sec.

1 microcurie ( $\mu$ Ci) =  $3.7 \times 10^4$  disintegrations per sec.

There is another unit called rutherford (Rd) which is defined as the amount of a radioactive substance which undergoes  $10^6$  disintegrations per second.

1 milli rutherford =  $10^3$  disintegration per sec.

1 micro rutherford = 1 disintegration per sec.

The SI unit radioactivity is proposed as Becquerel which refers to one dps.

1 curie =  $3.7 \times 10^{10}$  Rutherford

1 curie = 3.7 GBq

Here, G stands for  $10^9$ , i.e., giga.

## 18. Isotopes , Isobars and Isotones :

S.No	Isotopes	Isobars	Isotones
1.	The atoms of the same elements whose charge number (Z) is same but mass number is different are known as isotopes.	The atoms with mass number same and charge number different are known as isobars.	The atoms with same neutron number but A and Z are different are known as isotones
2.	Chemical properties are same	Chemical properties are different	Chemical properties are different
3.	Number of electrons is same	Number of electrons is different	Number of electrons is different
4.	Occupy same place in periodic table	Occupy different places in periodic table	Occupy different places in periodic table.
5.	Example ${}_8O^{16}$ , ${}_8O^{17}$ , ${}_8O^{18}$ ${}_1H^1$ , ${}_1H^2$ , ${}_1H^3$ ${}_{10}Ne^{20}$ , ${}_{10}Ne^{21}$ , ${}_{10}Ne^{22}$	${}_1H^3$ and ${}_2He^3$ ${}_6C^{14}$ and ${}_7N^{14}$ ${}_8O^{17}$ and ${}_9F^{17}$	${}_3Li^7$ and ${}_4Be^8$ ${}_1H^2$ and ${}_2He^3$ ${}_1H^3$ and ${}_2He^4$

## 19. Radioactive Isotopes :

The isotopes of elements which spontaneously decay by emitting radioactive radiations are defined as radioactive isotopes.

They are two types .

- (a) Natural radioactive isotopes                      (b) Artificial radioactive isotopes

(a) **Natural radioactive isotopes :** Those radioactive isotopes which exist naturally are known as natural radioactive isotopes. e.g.  $Th^{232}$ ,  $Pu^{240}$  etc.

(b) **Artificial radioactive isotopes :** Those isotopes, which are prepared artificially by bombarding fundamental particles like  $\alpha, \beta, \gamma, p, n$  etc, no matter, are known as artificial isotopes.

## 20. Uses of Radioactive Isotopes :

(a) **In Medicine :**

- (i) For testing blood chromium-51
- (ii) For testing blood circulation-Sodium-24
- (iii) For detecting brain tumor-Radio mercury-203
- (iv) For detecting fault in thyroid gland-Ratio iodine-131
- (v) For cancer-Cobalt-60
- (vi) For blood-Gold-189
- (vii) For skin diseases-Phosphorous-31

(b) **In Archaeology :**

- (i) For determining age of archaeological sample (Carbon dating) -  $C^{14}$
- (ii) For determining age of meteorites -  $K^{40}$
- (iii) For determining age of earth-Land isotopes

(c) **In Agriculture :**

- (i) For protecting potato crop from earthworm – Cobalt-60
- (ii) For artificial rains  $AgI$
- (iii) As fertilizers-Phosphorous-32

(d) **As tracers :**

Very small quantity of radio isotopes present in a mixture is known as tracer . Tracer technique is used for studying biochemical reactions in trees and animals.

(e) **In industries :**

- (i) For detecting leakage in oil or water pipe lines.
- (ii) For testing machine parts

(f) **In research :**

- (i) In the study of carbon-nitrogen cycle.
- (ii) For determining the age of planets



## 1. Daily Practice Problem Sheet

- In the reaction;  $A + 2B \longrightarrow 3C + D$  which of the following expressions does not describe changes in the concentration of various species as a function of time:  
 (A)  $\frac{d[C]}{dt} = -\frac{3d[A]}{dt}$     (B)  $\frac{3d[D]}{dt} = \frac{d[C]}{dt}$     (C)  $\frac{3d[B]}{dt} = -\frac{2d[C]}{dt}$     (D)  $\frac{2d[B]}{dt} = \frac{d[A]}{dt}$
- Which of the following statement is correct for a reaction  $X + 2Y \longrightarrow \text{products}$  :  
 (A) The rate of disappearance of X = twice the rate of disappearance of Y  
 (B) The rate of disappearance of X = 1/2 rate of appearance of products  
 (C) The rate of appearance of products = 1/2 the rate of disappearance of Y  
 (D) The rate of appearance of products = 1/2 the rate of disappearance of X
- For the reaction,  $4A + B \longrightarrow 2C + 2D$ , The statement not correct is :  
 (A) The rate of disappearance of B is one fourth the rate of disappearance of A  
 (B) The rate of appearance of C is half the rate of disappearance of B  
 (C) The rate of formation of D is half the rate of consumption of A  
 (D) The rates of formation of C and D are equal
- For the reaction  $2A + B \longrightarrow C + D$ ,  $-\frac{d[A]}{dt} = k[A]^2[B]$ . The expression for  $-\frac{d[B]}{dt}$  will be:  
 (A)  $K[A]^2[B]$     (B)  $1/2K[A]^2[B]$     (C)  $K[A]^2[2B]$     (D)  $K[2A]^2[B]$
- Which is correct relation in between  $\frac{dC}{dt}$ ,  $\frac{dn}{dt}$  and  $\frac{dP}{dt}$  where C, n, P, represents concentration, mole and pressure terms for gaseous phase reactant  $A(g) \longrightarrow \text{product}$ .  
 (A)  $-\frac{dC}{dt} = -\frac{1}{V} \frac{dn}{dt} = -\frac{1}{RT} \frac{dP}{dt}$     (B)  $\frac{dC}{dt} = \frac{dn}{dt} = -\frac{dP}{dt}$   
 (C)  $\frac{dC}{dt} = \frac{RT}{V} \frac{dn}{dt} = -\frac{dP}{dt}$     (D) All
- When ammonia is treated with  $O_2$  at elevated temperatures, the rate of disappearance of ammonia is found to be  $3.5 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$  during a measured time interval. Calculate the rate of appearance of nitric oxide and water.
- The following reaction was carried out at  $44^\circ\text{C}$   

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2} O_2$$
 The concentration of  $NO_2$  is  $6.0 \times 10^{-3} \text{ M}$  after 10 minutes of the start of the reaction. Calculate the rate of production of  $NO_2$  over the first ten minutes of the reaction.
- The oxidation of iodide ion by arsenic acid,  $H_3AsO_4$ , is described by the balance equation :  

$$3I^- (aq) + H_3AsO_4 (aq) + 2H^+ (aq) \longrightarrow I_3^- (aq) + H_3AsO_3 (aq) + H_2O (l)$$
 (a) If  $-\Delta[I^-] / \Delta t = 4.8 \times 10^{-4} \text{ M/s}$ , what is the value of  $\Delta[I_3^-] / \Delta t$  during the same time interval ?  
 (b) What is the average rate of consumption of  $H^+$  during that time interval ?
- In a reaction, the rate expression is, rate =  $K[A][B]^{2/3}[C]^0$ , the order of reaction is :  
 (A) 1    (B) 2    (C) 5/3    (D) Zero

- 10.** For the reaction,  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) = 2\text{HBr}(\text{g})$ , the reaction rate =  $K [\text{H}_2] [\text{Br}_2]^{1/2}$ . Which statement is true about this reaction :  
 (A) The reaction is of second order (B) Molecularity of the reaction is 3/2  
 (C) The unit of K is  $\text{sec}^{-1}$  (D) Molecularity of the reaction is 2
- 11.** The dimensions of the rate constant of a second order reaction involves :  
 (A) Neither time nor concentration (B) Time and concentration  
 (C) Time and square of concentration (D) Only time
- 12.** The rate constant for a reaction is  $10.8 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$ . The reaction obeys :  
 (A) First order (B) Zero order (C) Second order (D) Half order
- 13.** Which statement about the order of reaction is correct ?  
 (A) The order of reaction must be a positive integer  
 (B) A second order reaction is also bimolecular  
 (C) The order of reaction increases with increasing temperature.  
 (D) The order of reaction can only be determined by experiment
- 14.** The rate of the reaction  $\text{A} + \text{B} + \text{C} \longrightarrow \text{P}$  is given by :  

$$r = \frac{d[\text{A}]}{dt} = k [\text{A}]^{1/2} [\text{B}]^{1/2} [\text{C}]^{1/4}$$
 The order of the reaction is:  
 (A) 1 (B) 2 (C) 1/2 (D) 5/4
- 15.** Bromomethane is converted to methanol in an alkaline solution :  

$$\text{CH}_3\text{Br}(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{CH}_3\text{OH}(\text{aq}) + \text{Br}^-(\text{aq})$$
 The reaction is first order in each reactant.  
 (a) Write the rate law.  
 (b) How does reaction rate change if the  $\text{OH}^-$  concentration is decreased by factor of 5 ?  
 (c) What is the change in rate if the concentrations of both reactants are doubled ?
- 16.** The oxidation of  $\text{Br}^-$  by  $\text{BrO}_3^-$  in acidic solution is described by the equation  

$$5\text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) \longrightarrow 3\text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$$
 The reaction is first order in  $\text{Br}^-$ , first order in  $\text{BrO}_3^-$ , and second order in  $\text{H}^+$ .  
 (a) Write the rate law  
 (b) What is the overall reaction order ?  
 (c) How does the reaction rate change if the  $\text{H}^+$  concentration is tripled ?  
 (d) What is the change in rate if the concentrations of both  $\text{Br}^-$  and  $\text{BrO}_3^-$  are halved ?
- 17.** For the reaction :  $2\text{A} + \text{B}_2 + \text{C} \longrightarrow \text{A}_2\text{B} + \text{BC}$ , the rate law expression has been determined experimentally to be  $R = k [\text{A}]^2 [\text{C}]$  with,  $k = 3.0 \times 10^{-4} \text{ M}^{-2} \text{ min}^{-1}$ .  
 (i) Determine the initial rate of the reaction, started with concentration  
 $[\text{A}] = 0.1 \text{ M}$ ,  $[\text{B}_2] = 0.35 \text{ M}$  &  $[\text{C}] = 0.25 \text{ M}$   
 (ii) What is the effect on rate of reaction and rate constant on changing the volume to  $1/4^{\text{th}}$  of initial value.
- 18.** For the reaction  $2\text{NO} + \text{Cl}_2 \longrightarrow 2\text{NOCl}$ , it is found that doubling the concentration of both reactants increases the rate by the factor of 8, but doubling the  $\text{Cl}_2$  concentration alone, only doubles the rate. What is the order of the reaction with respect to NO and  $\text{Cl}_2$  ?
- 19.** For the reaction,  $2\text{A} + \text{B} + \text{C} \longrightarrow \text{A}_2\text{B} + \text{C}$   
 the rate =  $k[\text{A}] [\text{B}]^2$  with  $k = 2.0 \times 10^{-6} \text{ M}^{-2} \text{ s}^{-1}$ . Calculate the initial rate of the reaction when  
 $[\text{A}] = 0.1 \text{ M}$ ,  $[\text{B}] = 0.2 \text{ M}$  and  $[\text{C}] = 0.8 \text{ M}$ .



10. A reaction,  $A_2 + B_2 \longrightarrow 2AB$  occurs by the following mechanism ;
- $$\begin{array}{ll} A_2 \longrightarrow A + A & \text{..... (slow)} \\ A + B_2 \longrightarrow AB + B & \text{..... (fast)} \\ A + B \longrightarrow AB & \text{..... (fast)} \end{array}$$
- Its order would be:
- (A) 3/2                      (B) 1                      (C) zero                      (D) 2
11. The chemical reaction,  $2O_3 \longrightarrow 3O_2$  proceeds as follows :
- $$\begin{array}{ll} O_3 \rightleftharpoons O_2 + O & \text{..... (fast)} \\ O + O_3 \longrightarrow 2O_2 & \text{..... (slow)} \end{array}$$
- 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
12. The following two step mechanism has been proposed for the gas-phase decomposition of nitrous oxide ( $N_2O$ ):
- Step I :  $N_2O(g) \longrightarrow N_2(g) + O(g)$
- Step II :  $N_2O(g) + O(g) \longrightarrow N_2(g) + O_2(g)$
- (a) Write the chemical equation for overall reaction.
- (b) Identify any reaction intermediates.
- (c) What is the molecularity of each of the elementary reactions ?
- (d) What is the molecularity of the overall reaction ?
13. What is the order of reaction ,
- $$A_2 + B_2 \longrightarrow 2AB \quad ; \quad \text{having following mechanism}$$
- $$\begin{array}{ll} A_2 \rightleftharpoons A + A & \text{..... (fast)} \\ A + B_2 \longrightarrow AB + B & \text{..... (slow)} \\ A + B \longrightarrow AB & \text{..... (fast)} \end{array}$$
14. The following reaction has a second-order rate law :
- $$H_2(g) + 2ICl(g) \longrightarrow I_2(g) + 2HCl(g) \quad \text{Rate} = k[H_2][ICl]$$
- Devise a possible reaction mechanism.
15. Initial rate data at 25°C are listed in the table for the reaction
- $$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$$
- | Experiment No. | Initial $[NH_4^+]$ | Initial $[NO_2^-]$ | Initial rate of consumption of $NH_4^+$ (M/s) |
|----------------|--------------------|--------------------|---|
| 1.             | 0.24               | 0.10               | $7.2 \times 10^{-6}$                          |
| 2.             | 0.12               | 0.10               | $3.6 \times 10^{-6}$                          |
| 3.             | 0.12               | 0.15               | $5.4 \times 10^{-6}$                          |
- (a) What is the rate law ?
- (b) What is the value of the rate constant ?
- (c) What is the reaction rate when the concentrations are  $[NH_4^+] = 0.39 \text{ M}$  and  $[NO_2^-] = 0.052 \text{ M}$  ?
16. Find :
- (i) rate law expression
- (ii) order of reaction with respect to each reactant and overall order of reaction
- (iii) value and unit of rate constant
- (iv) effect on rate of reaction on changing the volume to  $1/8^{\text{th}}$  of the original.
- For the reaction ,  $A + B + C \longrightarrow \text{product}$

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given :

Experiment No.	[A] <sub>0</sub> 10 <sup>-4</sup> (m/l)	[B] <sub>0</sub> 10 <sup>-2</sup> (m/l)	[C] <sub>0</sub> 10 <sup>-1</sup> (m/l)	Initial rate × 10 <sup>-6</sup> (m/l/s)
1	7	3	5	9
2	7	6	5	12.7
3	7	6	2	12.7
4	14	3	5	4.51

17. Initial rate data at 25°C are listed in the table for reaction ,  $A_2 + B_2 \longrightarrow 2AB$

Experiment No.	[A <sub>2</sub> ] <sub>0</sub> (m/l)	[B <sub>2</sub> ] <sub>0</sub> (m/l)	Initial rate (m/l/s)
1	$1.5 \times 10^{-3}$	$3.2 \times 10^{-4}$	$8.1 \times 10^{-8}$
2	$4.5 \times 10^{-3}$	$9.6 \times 10^{-4}$	$6.56 \times 10^{-6}$
3	$3 \times 10^{-3}$	$1.6 \times 10^{-4}$	$3.24 \times 10^{-7}$

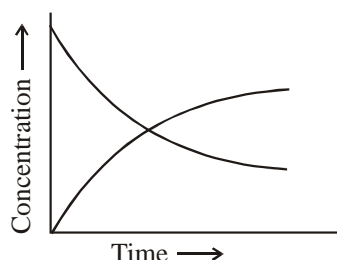
using that , determine

- (i) rate law
  - (ii) order of reaction with respect to A<sub>2</sub> and B<sub>2</sub> and overall order of reaction
  - (iii) value and unit of rate constant
  - (iv) effect on rate of reaction on doubling the volume of container.
18. The data given below are for the reaction of NO and Cl<sub>2</sub> to form NOCl at 295 K.
- | [Cl <sub>2</sub> ] | [NO] | Initial rate (mol litre <sup>-1</sup> sec <sup>-1</sup> ) |
|--------------------|------|---|
| 0.05               | 0.05 | $1 \times 10^{-3}$  |
| 0.15               | 0.05 | $3 \times 10^{-3}$  |
| 0.05               | 0.15 | $9 \times 10^{-3}$  |
- (a) What is the order w.r.t. NO and Cl<sub>2</sub> in the reaction
  - (b) Write the rate expression
  - (c) Calculate the rate constant
  - (d) Determine the reaction rate when conc. of Cl<sub>2</sub> and NO are 0.2 M and 0.4 M respectively.
19. The decomposition of NH<sub>3</sub> on tungsten surface follows zero order kinetics. The half life is 5 minutes for an initial pressure of 70 torr of NH<sub>3</sub>. If the initial pressure had been 0.25 atm , what would the total pressure after 3 minutes ? What is the half life ?
20. 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 .

## 3. Daily Practice Problem Sheet

1. Show that for a first order reaction ,  $R \longrightarrow P$  the concentration of product can be represented as a function of time by ,  $[P] = at + bt^2 + ct^3 + \dots$  and express a , b and c in terms of  $[R]_0$  and K.
2.
  - (i) Substance A decomposes by the first order reaction. Starting initially with  $[A] = 2.00$  M, after 200 minutes  $[A] = 0.25$  M. For this reaction what is  $t_{1/2}$  and k ?
  - (ii) A first order reaction is 40 % complete after 8 min. How long will it take before it is 90 % complete ? What is the value of the rate constant ?

- (iii) For a certain reaction it takes 20 minutes for the initial concentrations of  $34.8 \text{ mol L}^{-1}$  to become  $17.4 \text{ mol L}^{-1}$  and another 20 minutes to become  $8.7 \text{ mol L}^{-1}$ . Calculate the rate constant of the reaction.
- (iv) For a first order reaction in which  $k = 5.48 \times 10^{-1} \text{ sec}^{-1}$ . Find : (a)  $t_{1/3}$  (b)  $t_{2/3}$
3. Show that for a first order reaction
- (i)  $t_{25\%} = 0.415 t_{1/2}$       (ii)  $t_{87.5\%} = 3 t_{1/2}$       (iii)  $t_{90\%} = 3.33 t_{1/2}$   
 (iv)  $t_{99\%} = 6.66 t_{1/2}$       (v)  $t_{99.9\%} = 10 t_{1/2}$       (vi)  $t_{99\%} = 2 t_{90\%}$   
 (vii)  $t_{99.9\%} = 3 t_{90\%}$
4. The solution of  $\text{H}_2\text{O}_2$  of normality 0.73 is catalytically decomposed. What will be the concentration at the end of 45 minute, assuming the decomposition to follow first order rate law if half life is 15 minute ?
5. The change,  $\text{A} \longrightarrow \text{B}$  shows I order :
- (a) How will the rate of reaction change when the concentration of A is tripled ?  
 (b) What will be the change in half life period in doing so ?
6. The virus prepared in a chemical bath shows inactivation process obeying I order. Calculate the rate constant for the viral inactivation if in the beginning 1.5% of the virus is inactivated per minute. Also calculate the time required for its,  
 (a) 50 % inactivation      (b) 80 % inactivation.
7. Show that for I order reaction, the time required for 99.9 % decomposition of the reaction is ten folds to the time required for half of the reaction .
8. The time required for 20 % completion for a reaction is 10 minute for I order reaction. Calculate :  
 (a) specific reaction rate.      (b) Time required for 75 % completion
9. The half life for a I order reaction  $\text{A} \longrightarrow \text{Product}$ , is 10 minute. What % of A remains after  
 (i)  $1/2$  hour      (ii)  $2/3$  hour      (iii) 1 hour
10. The reaction  $\text{SO}_2\text{Cl}_2 \longrightarrow \text{SO}_2 + \text{Cl}_2$  obeys I order kinetics with rate const.  $3.2 \times 10^{-5} \text{ sec}^{-1}$  at  $320^\circ\text{C}$  . What % of  $\text{SO}_2\text{Cl}_2$  will be decomposed on heating gas for 90 minute ?
11. For the first order reaction,  $\text{A} \longrightarrow \text{B}$ , shown in the figure, what is the significance of the point at which the two curves cross each other. How is the slopes of the two curves be related at this point ?



12. A first order gaseous reactions has  $K = 1.5 \times 10^{-6} \text{ sec}^{-1}$  at  $200^\circ\text{C}$  . If the reaction is allowed to run for 10 hour, what percentage of initial concentration would have changed into products. What is the half life period of reaction ?
13. Thermal decomposition of a compound is of first order. If 50 % sample of the compound is decomposed in 120 minute, how long will it take for 90 % of the compound to decompose ?
14. A substance is reduced to one third of its original concentration in 100 minute. Calculate the time in which it will be reduced to one ninth of its original value. Assume I order .

### CHEMICAL KINETICS

15. For the decomposition of  $\text{N}_2\text{O}_5$ , the rate constant is  $6.2 \times 10^{-4} \text{ sec}^{-1}$  at  $45^\circ\text{C}$ . It begins with one mole of  $\text{N}_2\text{O}_5$  in a litre flask, how long would it take for 20%  $\text{N}_2\text{O}_5$  to decompose and how long for 50 % ?
16. In the decomposition of oxalic acid following data were obtained:
 

Time in minute	0	300	600
Pressure in mm	22.0	17.0	13.4

 Determine the rate constant K and half life period, if reaction obeys I order kinetics.
17. Decomposition of  $\text{N}_2\text{O}_5(\text{g})$  into  $\text{NO}_2(\text{g})$  and  $\text{O}_2(\text{g})$  is a first order reaction. If the initial concentration of  $\text{N}_2\text{O}_5(\text{g})$ , i.e.,  $[\text{N}_2\text{O}_5]_0$  is  $0.030 \text{ mol litre}^{-1}$ , what will be its concentration after 30 minute? Rate constant of reaction is  $1.35 \times 10^{-4} \text{ sec}^{-1}$ .
18. For a homogeneous gaseous reaction,  $\text{A} \longrightarrow \text{B} + \text{C} + \text{D}$ , the initial pressure was  $P_0$  while pressure after time t was P. Derive an expression for rate constant K in terms of  $P_0$ , P and t. assume I order reaction.
19. Acetone on heating gives CO and other hydrocarbons at  $600^\circ\text{C}$ . The reaction obeys I order kinetics w.r.t. acetone concentration. The half life period is 81 sec. Calculate the time in which acetone taken in a container at  $600^\circ\text{C}$  reduces its pressure from 0.5 atm to 0.4 atm.
20. Dimethyl ether gaseous phase decomposition is :  
 $\text{CH}_3\text{OCH}_3 \longrightarrow \text{CH}_4 + \text{H}_2 + \text{CO}$  at 750 K having rate constant  $6.72 \times 10^{-3} \text{ min}^{-1}$ . Calculate the time in which initial pressure of 400 mm in closed container becomes 750 mm.
21. The decomposition of  $\text{Cl}_2\text{O}_7$  at 400 K in gaseous phase to  $\text{Cl}_2$  and  $\text{O}_2$  is of I order reaction. After 55 sec at 400 K, the pressure of reaction mixture increase from 0.62 to 1.88 atm. Calculate the rate constant of reaction. Also calculate the pressure of reaction mixture after 100 second.
22. In the vapour phase decomposition of ethylene oxide,  $\text{C}_2\text{H}_4\text{O} \longrightarrow \text{CH}_4 + \text{CO}$  at  $414.5^\circ\text{C}$ , the initial pressure and the pressure after 5 minute were 116.51 mm and 122.56 mm of Hg respectively. If the reaction follows I order kinetics, what must be the pressure after 12 minutes?
23. Calculate the partial pressures of reactants and products, when azomethane decomposes at an initial pressure of 200 mm for 30 minute according to  $(\text{CH}_3)_2\text{N}_2 \longrightarrow \text{C}_2\text{H}_6 + \text{N}_2$ . The rate constant is  $2.5 \times 10^{-4} \text{ sec}^{-1}$ .
24. Rate constant of a first order reaction  $\text{A} \longrightarrow \text{B}$  is  $6.93 \times 10^{-2} \text{ minute}$ . If initial concentration of reactant is 1 M. Then calculate :
  - (i) Initial rate
  - (ii) Rate after 600 seconds
  - (iii) Rate after 75 % of the reaction is completed
  - (iv) Rate after 30 minutes.
25. In a first order reaction concentration of reactant decreases from 10 M to 2.5 M in 500 seconds. Calculate :
  - (i)  $t_{1/2}$  of the reaction
  - (ii) rate of reaction when concentration is 5 M.
26. Rate constant of a first order reaction is  $10^{-3} \text{ sec}$ . Calculate time in seconds when concentration is changing from :
 

(i) 2 M to 0.25 M	(ii) 16 M to 1 M
(iii) 6.4 M to 1.6 M	(iv) 4 M to 0.125 M



## 4. Daily Practice Problem Sheet

1. The following data represent for the decomposition of  $\text{NH}_4\text{NO}_2$  in aqueous solution

Time in minute	10	15	20	25	$\infty$
Volume of $\text{N}_2$ (in mL)	6.25	9.0	11.40	13.65	33.05

- (a) Show that reaction is of I order. (b) Calculate velocity constant.

2. Derive the O. R. for decomposition of  $\text{H}_2\text{O}_2$  from the following data

Time in minute	10	15	20	25	$\infty$
Vol. of $\text{O}_2$ given by $\text{H}_2\text{O}_2$	6.30	8.95	11.40	13.5	35.75

3. Decomposition of diazobenzene chloride was followed at constant temperature by measuring volume of  $\text{N}_2$  evolved at definite intervals of time. Calculate O. R. and rate constant

Time in minute	0	2.0	5.5	7.0	$\infty$
Volume of $\text{N}_2$ in mL	0	10	25	35	163

4. The decomposition of  $\text{N}_2\text{O}_5$  in chloroform was followed by measuring the volume of  $\text{O}_2$  gas evolved;  $2\text{N}_2\text{O}_5 \longrightarrow 2\text{N}_2\text{O}_4 + \text{O}_2(\text{g})$ . The maximum volume of  $\text{O}_2$  gas obtainable was  $100\text{cm}^3$ . In 500 minutes,  $90\text{cm}^3$  of  $\text{O}_2$  were evolved. Calculate the first order rate constant of the reaction.

5. The specific rate constant of the decomposition of  $\text{N}_2\text{O}_5$  is  $0.008\text{ min}^{-1}$ . The volume of  $\text{O}_2$  collected after 20 minute is 16 mL. Find the volume that would be collected at the end of reaction.  $\text{NO}_2$  formed is dissolved in  $\text{CCl}_4$ .

6. Derive order of reaction, for the decomposition of  $\text{H}_2\text{O}_2$  from the following data.

Time in minute	0.	10	20	30
Volume of $\text{KMnO}_4$ needed for $\text{H}_2\text{O}_2$	25	16	10.5	7.09

7. The kinetics of hydrolysis of methyl acetate in excess dilute  $\text{HCl}$  at  $25^\circ\text{C}$  were followed by withdrawing 2 mL of the reaction mixture at intervals of (t), adding 50 mL water and titrating with baryta water. Determine the velocity constant of hydrolysis.

t (in minute)	0	75	119	259	$\infty$
Titre value (in mL)	19.24	24.20	26.60	32.23	42.03

8. The acid catalysed hydrolysis of an organic compound A at  $30^\circ\text{C}$  has half life of 100 minute when carried out in a buffer solution of  $\text{pH} = 5$  and 10 minute when carried out at  $\text{pH} = 4$ . Both the times the half life are independent of the initial concentration of A. If the rate of reaction is given by :  $\text{rate} = k[\text{A}]^m [\text{H}^+]^n$ , what are the values of m and n and also calculate the rate of reaction ?

9. In the inversion of cane sugar in presence of an acid, the following polarimeter readings are obtained

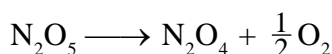
Time in minute	0	30	90	230	$\infty$
Rotation in degree	+46.75	+41.0	+30.75	+12.75	-18.75

Calculate rate constant.



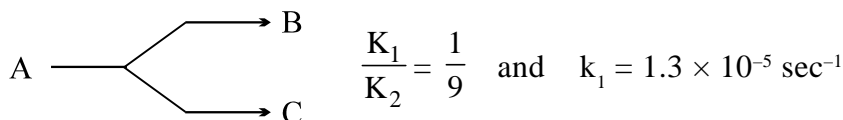
## CHEMICAL KINETICS

10. The inversion of cane sugar proceeds with constant half life of 500 minutes at pH = 5 for any concentration of sugar. However, if pH = 6, the half life changes to 50 minutes. Derive the rate law for inversion of cane sugar.
11. A solution of  $\text{N}_2\text{O}_5$  in  $\text{CCl}_4$  at  $45^\circ\text{C}$  produces 5.02 mL of  $\text{O}_2$  in 1198 sec and 9.58 mL  $\text{O}_2$  after a long time . Calculate rate constant assuming I order for the reaction.



## 5. Daily Practice Problem Sheet

1. An organic compound A decomposes following two parallel first order mechanisms :



Calculate the concentration ratio of C to A, if an experiment is allowed to start with only A for one hour .

2. Trans-1,2-dideuterocyclopropane (A) undergoes a first order decomposition. The observed rate const. at certain temp., measured in terms of disappearance of 'A' was  $1.52 \times 10^{-4} \text{ sec}^{-1}$ . Analysis of products showed that the reaction followed two parallel paths, one leading to dideuteropropane. (B) and the other to cis-1,2-dideuterocyclopropane (C). (B) was found to constitute 11.2 % of the reaction product , independently of extent of reaction . What is the order of reaction for each path and what is the value of the rate constant for the formation of each of the products ?
3. Bicyclohexane was found to undergo two parallel first order rearrangements. At 730 K , the first order rate constant for the formation of cyclohexane was measured as  $1.26 \times 10^{-4} \text{ s}^{-1}$ , and for the formation of methyl cyclopentene the rate constant was  $3.8 \times 10^{-5} \text{ s}^{-1}$ . What is the percentage distribution of the rearrangement products ?
4. For the reaction ,  

$$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+(\text{aq}) \xrightarrow{K_1} [\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}(\text{aq}) \xrightarrow{K_2} [\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$$
 $k_1 = 1.78 \times 10^{-3} \text{ s}^{-1}$  and  $k_2 = 5.8 \times 10^{-5} \text{ s}^{-1}$  for the initial concentration of  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$  is 0.0174 mol/litre at  $0^\circ\text{C}$ . Calculate the value of  $t$  at which the conc. of  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$  is maximum .
5. Two first order reactions proceed at  $25^\circ\text{C}$  at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3 . Find the ratio of the rates of these reactions at  $75^\circ\text{C}$  .
6. The half life of a substance in a first-order reaction is 100 minutes at 323.2 and 15 min at 353.2 K . Calculate the temperature coefficient of the rate constant of this reaction .
7. The activation energy for the reaction ,  $\text{O}_3(\text{g}) + \text{NO}(\text{g}) \longrightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  is 9.6 kJ/mole. Prepare an activation energy plot if  $\Delta H^\circ$  for this reaction is  $-200 \text{ kJ/mole}$ . What is the energy of activation for the reverse reaction ?
8. Which reaction will have the greater temperature dependence for the rate constant-one with a small value of energy of activation (E) or one with a large value of E ?
9. For a chemical reaction the energy of activation is  $85 \text{ J mol}^{-1}$ . If the frequency factor is,  $4.0 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ , what is the rate constant at 400 K ?

10. For the displacement reaction
 
$$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + \text{H}_2\text{O} \longrightarrow [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+} + \text{Cl}^-$$
 the rate constant is given by ,  $\ln [k/(\text{min}^{-1})] = -\frac{11067}{T} + 31.33$ .  
 Evaluate  $k$ ,  $E$  and  $A$  for the chemical reaction at  $25^\circ\text{C}$  .
11. For the reaction ,  $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$ 
 the rate constant is given by ,  $\ln [k(\text{sec}^{-1})] = -\frac{10500}{T} + 33$ .  
 Evaluate  $k$ ,  $E$  and  $A$  for the chemical reaction at  $27^\circ\text{C}$  .
12. For a first order reaction, the rate constant is given by ,  $\ln [k(\text{sec}^{-1})] = -\frac{11400}{T} + 34.7$   
 Evaluate  $k$ ,  $E$  and  $A$  for the chemical reaction at  $27^\circ\text{C}$ .
13. The time required for 20 % completion of a first order reaction at  $27^\circ\text{C}$  is 1.5 times that required for its 30 % completion at  $37^\circ\text{C}$ . If the pre exponential factor for the reaction is  $3 \times 10^9 \text{ sec}^{-1}$ , calculate the time required for 40 % completion at  $47^\circ\text{C}$  and also the energy of activation .
14. The rate constant of a reaction increases by 7 % when its temperature is raised from 300 K to 301 K while its equilibrium constant increases by 3 %. Calculate the activation energy of the forward and reverse reactions.
15. A bottle of milk stored at 300 K sours in 36 hours. When stored in a refrigerator at 275 K it sours in 360 hrs. Calculate the energy of activation of the reaction involved in the souring process.
16. Calculate the ratio of the catalysed and uncatalysed rate constant at  $20^\circ\text{C}$  if the energy of activation of a catalysed reaction is  $20 \text{ kJ mol}^{-1}$  and for the uncatalysed reaction is  $75 \text{ kJ mol}^{-1}$ .
17. A second order reaction where  $a = b$  is 20 % completed in 500 seconds. How long will the reaction take to be 60 % complete.
18. Two reactions of same order have equal pre-exponential factors but their activation energies differs by  $41.9 \text{ J/mole}$ . Calculate the ratios between rate constants of these reactions at 600 K.
19. Rate constant of a reaction changes by 2 % by  $0.1^\circ\text{C}$  rise in temperature at  $25^\circ\text{C}$ . The standard heat of reaction is  $121.6 \text{ kJ mol}^{-1}$ . Calculate  $E_a$  of reverse reaction.
20. The energy of activation and specific rate constant for a first-order reaction at  $25^\circ\text{C}$ 

$$\begin{array}{ccc} 2\text{N}_2\text{O}_5 & \longrightarrow & 2\text{N}_2\text{O}_4 + \text{O}_2 \\ \text{(in CCl}_4\text{)} & & \text{(in CCl}_4\text{)} \end{array}$$
 are  $100 \text{ kJ/mole}$  and  $3.46 \times 10^{-5} \text{ s}^{-1}$  respectively. Determine the temperature at which the half-life of the reaction is 2 hours.
21. In Arrhenius' equation for a certain reaction, the value of  $A$  and  $E$  (activation energy) are  $4 \times 10^{13} \text{ s}^{-1}$  and  $98.6 \text{ kJ mol}^{-1}$  respectively. If the reaction is of first order, at what temperature will its half-life period be ten minutes?
22. Two reactions proceed at  $25^\circ\text{C}$  at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of the second is 2.5. Find the ratio of the rates of these reactions at  $95^\circ\text{C}$  .

### CHEMICAL KINETICS

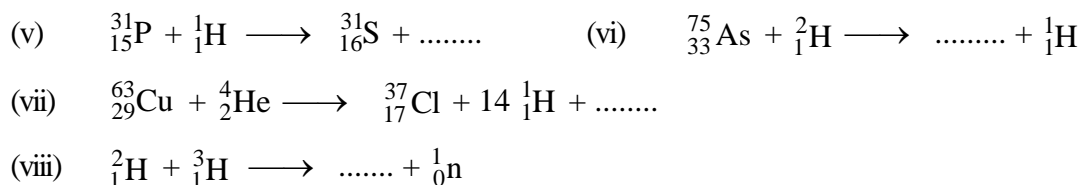
23. What is the energy of activation of a reaction if its rate doubles when the temperature is raised from 290 K to 300 K ?
24. For the reaction  $A + B \longrightarrow C + D$ ;  $\Delta H = + 20 \text{ kJ/mole}$ , the activation energy of the forward reaction is 85 kJ/mole. Calculate the activation energy of the reverse reaction.
25. What is the value of the rate constant, predicted by the Arrhenius's equation if  $T \longrightarrow \infty$  ? Is this value physically reasonable ?
26. The activation energy of a certain uncatalysed reaction at 300 K is  $76 \text{ kJ mol}^{-1}$ . The activation energy is lowered by  $19 \text{ kJ mol}^{-1}$  by the use of catalyst. By what factor, the rate of catalysed reaction is increased ?
27. Given that  $K (\text{sec}^{-1}) = 5 \times 10^{14} e^{-124080/RT}$  where activation energy is expressed in joule. Calculate the temperature at which reaction has  $t_{1/2}$  equal to 25 minute. Assume I order reaction.
28. For the reaction  $A \longrightarrow \text{products}$ , the time for half change is 5000 second at 300K and 1000 second at 310 K. If the reaction obeys first order kinetic, calculate energy of activation .
29. Two reactions of same order have equal exponential factors but their activation energy differ by  $24.9 \text{ kJ mol}^{-1}$ . Calculate the ratio between the rate constant of these reactions at  $27^\circ\text{C}$  [  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$  ]
30. The energy of activation of a I order reaction is  $104.5 \text{ kJ mol}^{-1}$  and pre-exponential factor A in Arrhenius equation is  $5 \times 10^{13} \text{ sec}^{-1}$ . At what temperature will the reaction have half life of 1 minute ?

## 6. Daily Practice Problem Sheet

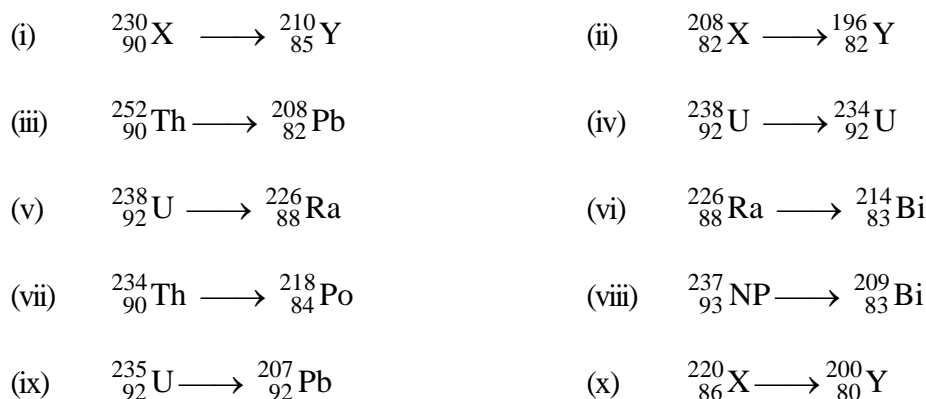
- Q.1 Calculate the number of neutrons in the remaining atom after emission of an alpha particle from  ${}_{92}^{238}\text{U}$  atom.
- Q.2 Radioactive disintegration of  ${}_{88}^{226}\text{Ra}$  takes place in the following manner into RaC.
 
$$\text{Ra} \xrightarrow{-\alpha} \text{Rn} \xrightarrow{-\alpha} \text{RaA} \xrightarrow{-\alpha} \text{RaB} \xrightarrow{-\beta} \text{RaC}$$
 Determine mass number and atomic number of RaC.
- Q.3 A radioactive element A disintegrates in the following manner
 
$$A \xrightarrow{-\alpha} B \xrightarrow{-\beta} C \xrightarrow{-\beta} D$$
 (i) Which one of the elements A, B, C, D are isotopes ?  
 (ii) Which one of the elements A, B, C, D are isobars ?
- Q.4 Write the particles emitted from each nucleides in the following reactions :
 
$$(a) {}_{90}^{231}\text{Th} \xrightarrow{(i)} {}_{91}^{231}\text{Pa} \xrightarrow{(ii)} {}_{89}^{227}\text{Ac} \quad (b) {}_{85}^{217}\text{At} \xrightarrow{(i)} {}_{83}^{213}\text{Bi} \xrightarrow{(ii)} {}_{81}^{209}\text{Tl}$$
- Q.5 An atom has atomic mass 232 and atomic number 90. During the course of disintegration, it emits  $2\beta$ -particles and few  $\alpha$ -particles. The resultant atom has atomic mass 212 and atomic number 82. How many  $\alpha$ -particles are emitted during this process.
- Q.6 In the sequence of the following nuclear reaction
 
$${}_{98}^{238}\text{X} \xrightarrow{-\alpha} \text{Y} \xrightarrow{-\beta} \text{Z} \xrightarrow{-\beta} \text{L} \xrightarrow{n\alpha} {}_{90}^{218}\text{M}$$
 what is the value of n  
 (A) 3 (B) 4 (C) 5 (D) 6

- Q.7** The isotope  $^{235}_{92}\text{U}$  decays in a number of steps to an isotope of  $^{207}_{82}\text{Pb}$ . The groups of particles emitted in this process will be  
 (A)  $4\alpha$ ,  $7\beta$  (B)  $6\alpha$ ,  $4\beta$  (C)  $7\alpha$ ,  $4\beta$  (D)  $10\alpha$ ,  $8\beta$
- Q.8** The  $^{238}_{92}\text{U}$  disintegrates to give 4  $\alpha$ - and 6  $\beta$ - particles. The atomic number of the end product is  
 (A) 92 (B) 96 (C) 84 (D) 90
- Q.9** Following are the atoms having the number of neutrons and protons as given below :
- | Atoms | Protons | Neutron |
|-------|---------|---------|
| A     | 8       | 8       |
| B     | 8       | 9       |
| C     | 8       | 10      |
| D     | 7       | 8       |
| E     | 7       | 9       |
- Select incorrect conclusion(s) :  
 (A) A, B and C, D are isotopes (B) A and D are isotones  
 (C) A and E are isobars (D) A and B are isodiaphers
- Q.10** An alkaline earth element is radioactive. It and its daughter elements decay by emitting there  $\alpha$ -particles in sucession. The daughter element formed wil belong to group -  
 (A) 8 (B) 16 (C) 14 (D) 12
- Q.11**  $^{210}_{84}\text{Po} \longrightarrow ^{206}_{82}\text{Pb} + ^4_2\text{He}$   
 In above reaction, predict the position of Po in the periodic table when lead belongs to IVB group :  
 (A) IIA (B) VIB (C) IV B (D) VB
- Q.12** Radioactive substance of 1 curie is the amount that can produce ..... disintegrations per second.
- Q.13** The last member of  $4n + 1$  series is an isotope of .....
- Q.14** The  $4n$  series starts from Th-232 and ends at  
 (A) Pb-208 (B) Bi-209 (C) Pb-206 (D) Pb-207
- Q.15** Select the wrong statement  
 (A) Nuclear isomers contain the same number of protons and neutrons  
 (B) The decay constant is independent of the amount of the substance taken  
 (C) One curie =  $3.7 \times 10^{10}$  dis/minute  
 (D) Actinium series starts with  $\text{U}^{238}$
- Q.16** The correct starting material and product of different disintegration series are :  
 (A)  $^{232}\text{Th}$ ,  $^{208}\text{Pb}$  (B)  $^{235}\text{U}$ ,  $^{206}\text{Pb}$  (C)  $^{238}\text{U}$ ,  $^{207}\text{Pb}$  (D)  $^{237}\text{Np}$ ,  $^{209}\text{Bi}$
- Q.17** Which of the following is/are correct  
 (A) 1 curie =  $3.7 \times 10^{10}$  d/s (B) 1 rutherford =  $10^6$  d/s  
 (C) 1 becquerel = 1 d/s (D) 1 fermi =  $10^3$  d/s
- Q.18** To which radioactive families do the following nucleides belong ?  
 $^{222}\text{Rn}$ ,  $^{228}\text{Ra}$ ,  $^{207}\text{Pb}$ ,  $^{209}\text{Bi}$ ,  $^{233}\text{Pa}$ .
- Q.19** Balance the following nuclear reactions.
- (i)  $^9_4\text{Be} + ^4_2\text{He} \longrightarrow \dots\dots\dots + ^1_0\text{n}$  (ii)  $^6_3\text{Li} + \dots\dots\dots \longrightarrow ^7_3\text{Li} + ^1_1\text{H}$
- (iii)  $^9_4\text{Be} + \dots\dots\dots \longrightarrow ^8_4\text{Be} + ^1_0\text{n}$
- (iv)  $^{235}_{92}\text{U} + ^1_0\text{n} \longrightarrow ^{141}_{56}\text{Ba} + \dots\dots\dots + 3 ^1_0\text{n}$

## CHEMICAL KINETICS



**Q.20** Calculate  $\alpha$  and  $\beta$  particles emitted during the process.



## 7. Daily Practice Problem Sheet

- The triad of nuclei that represents isotopes is:
 

(A)  ${}_6\text{C}^{14}$ ,  ${}_7\text{N}^{14}$ ,  ${}_9\text{F}^{19}$       (B)  ${}_6\text{C}^{12}$ ,  ${}_7\text{N}^{14}$ ,  ${}_9\text{F}^{19}$

(C)  ${}_6\text{C}^{14}$ ,  ${}_6\text{C}^{13}$ ,  ${}_6\text{C}^{12}$       (D)  ${}_6\text{C}^{14}$ ,  ${}_7\text{N}^{14}$ ,  ${}_9\text{F}^{17}$
- The triad of nuclei that represents isotones is:
 

(A)  ${}_6\text{C}^{12}$ ,  ${}_7\text{N}^{14}$ ,  ${}_9\text{F}^{19}$       (B)  ${}_6\text{C}^{14}$ ,  ${}_7\text{N}^{15}$ ,  ${}_9\text{F}^{17}$

(C)  ${}_6\text{C}^{14}$ ,  ${}_7\text{N}^{14}$ ,  ${}_9\text{F}^{17}$       (D)  ${}_6\text{C}^{14}$ ,  ${}_7\text{N}^{14}$ ,  ${}_9\text{F}^{19}$
- The rate of radioactive disintegration..... with time:
 

(A) Increases      (B) Decreases      (C) Is constant      (D) May increase
- When a radioactive element emits an electron the daughter element formed will have:
 

(A) Mass number one unit less      (B) Atomic number one unit less

(C) Mass number one unit more      (D) Atomic number one unit more
- Decrease in atomic no. is observed during:
 

(A) Alpha emission      (B) Electron capture

(C) Positron emission      (D) all
- Successive emission of an  $\alpha$ -particle and two  $\beta$ -particles by an atom of an element results in the formation of its:
 

(A) Isodiapher      (B) Isomorph      (C) Isotope      (D) Isotherm
- If  $N_0$  is the initial number of nuclei, number of nuclei remaining undecayed at the end of  $n$ th half life is:
 

(A)  $2^{-n} N_0$       (B)  $2^n N_0$       (C)  $n^{-2} N_0$       (D)  $n^2 N_0$
- Which one of the following nuclear reaction is correct:
 

(A)  ${}_6\text{C}^{13} + {}_1\text{H}^1 \longrightarrow {}_7\text{N}^{13} + \beta^- + \gamma$       (B)  ${}_{11}\text{Na}^{23} + {}_1\text{H}^1 \longrightarrow {}_{10}\text{Ne}^{20} + {}_2\text{He}^4$

(C)  ${}_{13}\text{Al}^{23} + {}_0\text{n}^1 \longrightarrow {}_{11}\text{Na}^{23} + {}_{-1}\text{e}^0$       (D)  ${}_{12}\text{Mg}^{24} + {}_2\text{He}^4 \longrightarrow {}_{13}\text{Al}^{27} + {}_0\text{n}^1$

9. The activity of a radionuclide ( $X^{100}$ ) is 6.023 curie. If the disintegration constant is  $3.7 \times 10^4 \text{ sec}^{-1}$ , the mass of radionuclide is:  
 (A)  $10^{-14} \text{ g}$                       (B)  $10^{-6} \text{ g}$                       (C)  $10^{-15} \text{ g}$                       (D)  $10^{-3} \text{ g}$
10. The half life of  $I^{131}$  is 8 day. Given a sample of  $I^{131}$  at  $t = 0$ , we can assert that:  
 (A) No nucleus will decay at  $t = 4$  day  
 (B) No nucleus will decay before  $t = 8$  day  
 (C) All nucleus will decay before  $t = 16$  day  
 (D) A given nucleus may decay at any time after  $t = 0$
11. If 5g of a radioactive substance has  $t_{1/2} = 14 \text{ hr.}$ , 2 g of the same substance will have a  $t_{1/2}$  equal to:  
 (A) 56 hr                      (B) 3.5 hr                      (C) 14 hr                      (D) 28 hr
12. The half life of a radioactive isotope is 2.5 hour. The mass of it that remains undecayed after 10 hour is (If the initial mass of the isotope was 16 g):  
 (A) 32 g                      (B) 16 g                      (C) 4 g                      (D) 1 g
13. The number of  $\alpha$ -and  $\beta$ -particles emitted during the transformation of  ${}_{90}^{232}\text{Th}$  to  ${}_{82}^{208}\text{Pb}$  is respectively:  
 (A) 2, 2                      (B) 4, 2                      (C) 6, 4                      (D) 8, 6
14. If 75% quantity of a radioactive isotope disintegrates in 2 hour, its half life would be:  
 (A) 1 hour                      (B) 45 minute                      (C) 30 minute                      (D) 15 minute
15. A certain radioactive isotope has a half life of 50 day. Fraction of the material left behind after 100 day will be:  
 (A) 50%                      (B) 75%                      (C) 12.5%                      (D) 25%
16. The half life period of a radioactive elements is 140 day. After 560 day, 1 g of the element will reduce to:  
 (A) 0.5 g                      (B) 0.25 g                      (C)  $1/8 \text{ g}$                       (D)  $1/16 \text{ g}$
17. 75% of a first order reaction was completed in 32 minute. When will be 50% of the reaction complete.  
 (A) 24 minute                      (B) 16 minute                      (C) 8 minute                      (D) 4 minute
18. The half life of a radioactive isotope is 1.5 hour. The mass of it that decayed after 6 hour is (the initial mass of the isotope is 32 g):  
 (A) 32 g                      (B) 16 g                      (C) 30 g                      (D) 2 g
19. Half life period of a substance is 1600 minute. What fraction of the substance will remain after 6400 minute:  
 (A)  $1/16$                       (B)  $1/4$                       (C)  $1/8$                       (D)  $1/2$
20. The half life period of a radioactive nuclide is 3 hour. In 9 hour its activity will be reduced by  
 (A)  $1/9$                       (B)  $7/8$                       (C)  $1/27$                       (D)  $1/6$
21. A radioactive isotope having a half life of 3 day was received after 12 day. It was found that there were 3 g of the isotope in the container. The initial weight of the isotope when packed was:  
 (A) 12 g                      (B) 24 g                      (C) 36 g                      (D) 48 g
22. A sample of rock from moon contains equal number of atoms of uranium and lead ( $t_{1/2}$  for U =  $4.5 \times 10^9 \text{ year}$ ). The age of the rock would be:  
 (A)  $4.5 \times 10^9 \text{ year}$                       (B)  $9 \times 10^9 \text{ year}$                       (C)  $13.5 \times 10^9 \text{ year}$                       (D)  $2.25 \times 10^9 \text{ year}$

### CHEMICAL KINETICS

23. Two radioactive elements X and Y have half lives of 50 and 100 minute respectively. Initial sample of both the elements have same no. of atoms. The ratio of the remaining number of atoms of X and Y after 200 minute is:  
 (A) 2 (B) 1/2 (C) 4 (D) 1/4
24. The time in which activity of an element is reduced to 90% of its original value is, (given  $t_{1/2} = 1.4 \times 10^{10}$  yr):  
 (A)  $1.128 \times 10^9$  yr (B)  $2.128 \times 10^9$  yr (C)  $3.128 \times 10^9$  yr (D) None
25. The number of  $\alpha$ - and  $\beta$ - particles emitted in the nuclear reaction  ${}_{90}^{228}\text{Th} \longrightarrow {}_{83}^{212}\text{Bi}$  are:  
 (A)  $4\alpha$  and  $1\beta$  (B)  $3\alpha$  and  $7\beta$  (C)  $8\alpha$  and  $1\beta$  (D)  $4\alpha$  and  $7\beta$
26. Two radioisotopes P and Q of atomic weight 10 and 20 respectively are mixed in equal amount by weight. After 20 day, their weight ratio is found to be 1 : 4. Isotope P has a half life of 10 day. The half life of isotope Q is:  
 (A) Zero (B) 5 day (C) 20 day (D) infinite
27. The radioactivity due to the  $\text{C}^{14}$  isotope ( $t_{1/2} = 6000$  year) of a sample of wood from an ancient tomb was found to be nearly half that of fresh wood; the tomb is, therefore, about:  
 (A) 3000 year old (B) 6000 year old (C) 9000 year old (D) 12000 year old
28. The activity of a radioactive sample drops to 1/64th of its original value in 2hr. The decay constant for the sample is:  
 (A)  $5.775 \times 10^{-4} \text{ sec.}^{-1}$  (B)  $5.775 \times 10^4 \text{ sec.}^{-1}$   
 (C)  $5.775 \times 10^2 \text{ sec.}^{-1}$  (D) None
29. A radioactive element has a half life of  $4.5 \times 10^9$  year. If 80 g of this was taken, the time taken for it to decay to 40 g will be:  
 (A)  $2.25 \times 10^9$  year (B)  $4.50 \times 10^9$  year (C)  $6.75 \times 10^9$  year (D)  $8.75 \times 10^9$  year
30. A certain nuclide has a half life period of 30 minute. If a sample containing 6000 atoms is allowed to decay for 90 minute, how many atoms will remain:  
 (A) 200 atoms (B) 450 atoms (C) 750 atoms (D) 150 atoms
31. A substance is kept for 2 hour and three fourth disintegrates during this period. The half life of the substance is:  
 (A) 2 hour (B) 1 hour (C) 30 minute (D) 4 hour
32. The binding energy of an element is 64 MeV. If BE/nucleon is 6.4, the number of nucleons are:  
 (A) 10 (B) 64 (C) 16 (D) 6
33. The half life of  ${}_{92}\text{U}^{238}$  against  $\alpha$ -decay is  $4.5 \times 10^9$  year. The time taken in year for the decay of 15/16 part of this isotope is:  
 (A)  $9.0 \times 10^9$  (B)  $1.8 \times 10^{10}$  (C)  $4.5 \times 10^9$  (D)  $2.7 \times 10^{10}$
34. A radioactive isotope has a half life of 10 day. If today there are 125g of it left, what was its original weight 40 day earlier:  
 (A) 600 g (B) 1000 g (C) 1250 g (D) 2000 g
35. Radium has atomic weight 226 and half life of 1600 year. The number of disintegration produced per sec. from 1 g are:  
 (A)  $4.8 \times 10^{10}$  (B)  $3.7 \times 10^{10}$  (C)  $9.2 \times 10^6$  (D)  $3.7 \times 10^8$



36. If the amount of radioactive substance is increased three times, the number of atoms disintegrated per unit time would:  
 (A) Be double (B) Be triple (C) Remain one third (D) Not change
37. The half life of a radioactive element is 35 year. If there are  $4 \times 10^6$  nuclei at the start, then after how many year they will be left  $0.5 \times 10^6$ .  
 (A) 35 (B) 70 (C) 105 (D) 140
38. Wooden article and freshly cut tree show activity  $7.6$  and  $15.2 \text{ min}^{-1} \text{ g}^{-1}$  of carbon ( $t_{1/2} = 5760$  year) respectively. The age of the article is:  
 (A) 5760 year (B)  $5760 \times \frac{15.2}{7.6}$  year (C)  $5760 \times \frac{7.6}{15.2}$  year (D)  $5760 \times (15.2 - 7.6)$  year
39. For a radioactive substance with half life period 500 year, the time for complete decay of 100 milligram of it would be:  
 (A) 1000 year (B)  $100 \times 500$  year (C) 500 year (D) Infinite time
40. The decay constant of a radioactive element is defined as the reciprocal of the time interval after which the number of atoms of the radioactive element falls to nearly:  
 (A) 50% of its original number (B) 36.8% of its original number  
 (C) 63.2% of its original number (D) 75% of its original number
41. The radioactive decay rate of a radioactive element is found to be  $10^3$  dps at a certain time. If the half life of element is 1 sec, the decay rate after 1 sec. is..... and after 3 sec. is.....  
 (A) 500, 125 (B) 125, 500 (C)  $10^3$ ,  $10^3$  (D) 100, 10
42. The counting rate observed from a radioactive source at  $t = 0$  seconds was 1600 counts/sec and at  $t = 8$  sec it was 100 counts/sec. The counting rate observed as count per sec at  $t = 6$  sec will be:  
 (A) 400 (B) 300 (C) 200 (D) 150
43. A freshly prepared radioactive source of half life 2 hr. emits radiations of intensity which is 64 times the permissible safe level. The minimum time after which it would be possible to work safely with this source is:  
 (A) 6 hr (B) 12 hr (C) 24 hr (D) 128 hr
44. One mole of A present in a closed vessel undergoes decay as  ${}_Z\text{A}^m \longrightarrow {}_{Z-4}\text{B}^{m-8} + 2 {}_2\text{He}^4$ . The volume of He collected at NTP after 20 days is ( $t_{1/2} = 10$  day):  
 (A) 11.2 litre (B) 22.4 litre (C) 33.6 litre (D) 67.2 litre
45. The number of  $\beta$ -particle emitted during the change  ${}_a\text{X}^c \longrightarrow {}_d\text{Y}^b$  is:  
 (A)  $\frac{a-b}{4}$  (B)  $d + \left[ \frac{a-b}{2} \right] + c$  (C)  $d + \left[ \frac{c-b}{2} \right] - a$  (D)  $d + \left[ \frac{a-b}{2} \right] - c$



## SOLVED PROBLEMS

### SUBJECTIVE

**Problem 1 :**

*Rate of a reaction  $A + B \rightarrow \text{Products}$ ; is given below as a function of different initial concentrations of A and B*

$[A]$ mol/litre	$[B]$ mol litre <sup>-1</sup>	Initial rate mol litre <sup>-1</sup> time <sup>-1</sup>
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

*Determine the order of the reaction with respect to A and with respect to B. What is the half life of A in the reaction ?*

**Solution :**

Let order with respect to A is m and with respect to B is 'n'.

$$\text{Rate} = K[A]^m [B]^n$$

$$0.005 = K [0.01]^m [0.01]^n \quad \dots (i)$$

$$0.010 = K [0.02]^m [0.01]^n \quad \dots (ii)$$

$$0.005 = K [0.01]^m [0.02]^n \quad \dots (iii)$$

Dividing Eq. (i) by (ii), we get

$$\frac{0.005}{0.010} = \left[ \frac{0.01}{0.02} \right]^m \Rightarrow \frac{1}{2} = \left[ \frac{1}{2} \right]^m \quad \therefore m = 1$$

Thus, order with respect to A is one.

Dividing Eq. (i) by (iii), we get

$$\frac{0.005}{0.005} = \left[ \frac{0.01}{0.02} \right]^n \Rightarrow 1 = \left[ \frac{1}{2} \right]^n \quad \therefore n = 0$$

Thus, order with respect to B is zero.

Substituting the values of m and n in Eq. (i), we get

$$0.005 = K [0.01]^1 [0.01]^0 \quad \therefore \frac{0.005}{0.01} = 0.5$$

$$t_{1/2} (\text{Half life period}) = \frac{0.693}{K} = \frac{0.693}{0.5} = 1.386 \text{ time}$$

**Problem 2 :**

*The decomposition of  $Cl_2O_7$  at 440K in the gas phase to  $Cl_2$  and  $O_2$  is a first order reaction.*

- (i) *After 55 seconds at 400 K the pressure of  $Cl_2O_7$  falls from 0.062 to 0.044 atm., calculate that rate constant.*
- (ii) *Calculate the pressure of  $Cl_2O_7$  after 100 sec. of decomposition at this temperature.*

**Solution :**

- (i) In the present equation we may apply the formula

$$K = \frac{2.303}{t} \log \frac{p_0}{p_t} = \frac{2.303}{55} \log \frac{0.062}{0.044} = 6.2364 \times 10^{-3} \text{ sec}^{-1}$$

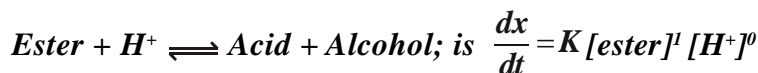
- (ii) Pressure after 100 sec may be calculated as

$$6.2364 \times 10^{-3} = \frac{2.303}{100} \log \frac{0.062}{p_t}$$

$$p_t = 0.0332 \text{ atm}$$

**Problem 3 :**

*Rate law for the following reaction; is*



*What would be the effect on the rate if*

- (i) *Concentration of ester is doubled ?*  
(ii) *Concentration of  $\text{H}^+$  ion is doubled ?*

**Solution :**

The rate law expression in this question, suggests that concentration of acid is nothing to play with velocity.

- (i) When concentration of ester is doubled; velocity of the reaction will become double.  
(ii) When concentration of  $\text{H}^+$  ion is doubled velocity will be unaffected.

**Problem 4 :**

*The reaction  $2\text{A} + \text{B} + \text{C} \rightarrow \text{D} + 2\text{E}$ ; is found to be first order in A; second order in B and zero order in C.*

- (i) *Give the rate law for the above reaction in the form of a differential equation.*  
(ii) *What is the effect on the rate of increasing the concentration of A, B and C two times ?*

**Solution :**

- (i) The rate law according to given information may be given as,  $\frac{dx}{dt} = K[\text{A}]^1[\text{B}]^2[\text{C}]^0$   
(ii) When concentration of A, B and C are doubled then rate will be

$$\frac{dx}{dt} = K[2\text{A}][2\text{B}]^2[\text{C}]^0 = 8K[\text{A}][\text{B}]^2[\text{C}]^0$$

i.e., rate becomes 8 fold, the original rate.

**Problem 5 :**

*At  $27^\circ\text{C}$  it was observed, during a reaction of hydrogenation that the pressure of  $\text{H}_2$  gas decreases from 2 atm to 1.1 atm in 75 min. Calculate the rate of reaction (molarity/sec). Given ( $R = 0.082/\text{litre atom } K^{-1} \text{ mole}^{-1}$ )*

**Solution :**

$$\text{Rate} = \frac{\text{Decrease in pressure}}{\text{Time duration}} = \frac{2 - 1.1}{75} = 0.012 \text{ atm/min}$$

$$\text{Rate in atm/sec} = \frac{0.012}{60} = 2 \times 10^{-4} \text{ atm/sec.}$$

Answer is required in molarity per second

$$\therefore PV = nRT$$

$$\frac{P}{RT} = \frac{n}{V}$$

$$\frac{P/\text{sec}}{RT} = \left( \frac{n}{V} \right) / \text{sec}$$

## CHEMICAL KINETICS

$$\left(\frac{n}{V}\right)/\text{sec} = \text{molarity per second}$$

$$\frac{2 \times 10^{-4}}{0.0821 \times 300} = \left(\frac{n}{V}\right)/\text{sec}$$

$$8.12 \times 10^{-6} \text{ . Rate in molarity/sec} = (n/V)/\text{sec}$$

### Problem 6 :

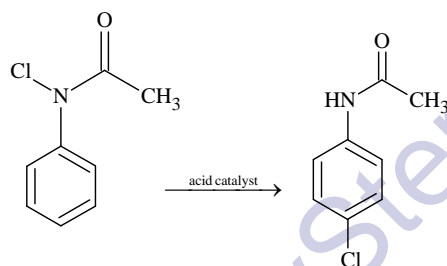
*In presence of an acid N-chloro acetanilide changes slowly into p-chloro acetanilide. Former substance liberated iodine from KI and not the later and hence progress of reaction can be measured by titrating iodine liberated with  $\text{Na}_2\text{S}_2\text{O}_3$  solution, the results obtained were as follows :*

Time (hours)	0	1	2	4	6	8
(a-x) i.e., hypo	45	32	22.5	11.3	3.7	2.9

*show that reaction is unimolecular and find out the fraction of N-chloroacetanilide decomposed after three hours.*

### Solution :

The present reaction is :



Let us apply the kinetics of first order reaction.

$$\text{After 1 hour} \quad K = \frac{2.303}{1} \log \left\{ \frac{45}{32} \right\} = 0.34098 \text{ hour}^{-1}$$

$$\text{After 2 hours} \quad K = \frac{2.303}{2} \log \left\{ \frac{45}{22.5} \right\} = 0.34660 \text{ hour}^{-1}$$

$$\text{After 4 hours} \quad K = \frac{2.303}{4} \log \left\{ \frac{45}{11.3} \right\} = 0.3455 \text{ hour}^{-1}$$

$$\text{After 6 hours} \quad K = \frac{2.303}{6} \log \left\{ \frac{45}{3.7} \right\} = 0.4164 \text{ hour}^{-1}$$

$$\text{After 8 hours} \quad K = \frac{2.303}{8} \log \left\{ \frac{45}{2.9} \right\} = 0.3428 \text{ hour}^{-1}$$

Average value of constant =  $0.3584 \text{ hours}^{-1}$

Since, on applying first order kinetics, we get almost same values of rate constant after different time intervals, hence, the reaction is of first order.

Let us see the fraction decomposed after 3 hours.

$$K = \frac{2.303}{t} \log \left\{ \frac{a}{a-x} \right\}$$

$$0.3584 = \frac{2.303}{3} \log \frac{a}{a-x}$$

$$\therefore \frac{a}{a-x} = 2.98$$

$$\therefore \frac{a-x}{a} = 0.3412$$

$$1 - \frac{x}{a} = 0.3412$$

$$\therefore \frac{x}{a} = 0.658 \text{ [fraction decomposed]}$$

**Problem 7 :**

*For the decomposition of dimethyl ether, A in the Arrhenius equation  $K = Ae^{-E/RT}$  has  $\log A = 13.1003$  and  $E_a$  value of 58.5 kcal. Calculate half life period for first order decomposition at 527°C.*

**Solution :**

Taking logarithm of Arrhenius equation

$K = Ae^{-E/RT}$  we get

$$\log K = \log A - \frac{E}{2.303RT} \quad \dots (i)$$

Given  $A = 1.26 \times 10^{13}$

$E = 58.5 \text{ kcal}$

$T = 527 + 273 = 800 \text{ K}$

Substituting these value in Eq. (i), we get

$$\log K = \log (1.26 \times 10^{13}) - \frac{58.5 \times 10^2}{2.303 \times 1.987 \times 800} = 13.1003 - 15.9799 = -2.8796$$

$$K = 1.3194 \times 10^{-3} \text{ sec}^{-1}$$

$$t_{1/2} = \frac{0.693}{1.3194} \times 10^3 \text{ sec} = 525 \text{ sec}$$

**Problem 8 :**

*For the reaction ,*

*$2\text{NO(g)} + \text{H}_2\text{(g)} \longrightarrow \text{N}_2\text{O(g)} + \text{H}_2\text{O(g)}$  at 900 K, the following data are obtained :*

<i>Initial pressure of NO (atm)</i>	<i>Initial pressure of H<sub>2</sub>(atm)</i>	<i>Rate (atm min<sup>-1</sup>)</i>
0.150	0.400	0.020
0.075	0.400	0.005
0.150	0.200	0.010

*Find the rate law and the value of rate constant.*

**Solution :**

Let order with respect to NO(g) is 'm' and order with respect to H<sub>2</sub>(g) is 'n'

$$\text{Then, Rate} = K[\text{P}_{\text{NO}}]^m [\text{P}_{\text{H}_2}]^n \quad \dots (1)$$

$$0.020 = K [0.15]^m [0.40]^n \quad \dots (2)$$

$$0.005 = K [0.075]^m [0.40]^n \quad \dots (3)$$

$$0.010 = K [0.15]^m [0.2]^n \quad \dots (4)$$

Dividing Eq. (2) by (3), we get

$$\frac{0.020}{0.005} = \left( \frac{0.15}{0.075} \right)^m$$

## CHEMICAL KINETICS

$$m = 2$$

Dividing Eq. (2) by (4), we get  $\frac{0.020}{0.010} = \left(\frac{0.4}{0.2}\right)^n$

$$n = 1$$

$$\text{Rate} = [\text{P}_{\text{NO}}]^2 [\text{P}_{\text{H}_2}]^1$$

Substituting the values of m, n in Eq. (2), we get

$$0.020 = K (0.15)^2 [0.40]$$

$$K = 2.22 \text{ atm}^{-2} \text{ min}^{-1}$$

### Problem 9 :

*10 gram atoms of an  $\alpha$ -active radio isotope are disintegrating in a sealed container. In one hour the helium gas collected at STP is  $11.2 \text{ cm}^3$ . Calculate the half-life of the radio-isotope.*

### Solution :

No. of atoms of helium is  $11.2 \text{ cc at NTP} = \frac{11.2}{22400} \times 6.02 \times 10^{23} = 3.01 \times 10^{20} \text{ atoms}$

Since, helium atom corresponds to  $\alpha$ -particle. Thus, Rate of disintegration =  $3.01 \times 10^{20}$  per hour.

We know, Rate = Rate constant  $\times$  concentration in atom

$$3.01 \times 10^{20} = K \times 10 \times 6.02 \times 10^{23}$$

$$K = 0.05 \times 10^{-3} \text{ hour}^{-1}$$

$$T_{1/2} = \frac{0.693}{K} = \frac{0.693}{0.05 \times 10^{-3}} = 13860 \text{ hours}$$

$$T_{1/2} = \frac{13860}{24 \times 365} = 1.58 \text{ years}$$

### Problem 10 :

*A carbon radio isotope  ${}^A_Z\text{X}$  (half life 10 days) decays to give  ${}^{A-4}_{Z-2}\text{Y}$ . If 1.00 gm atom of  ${}^A_Z\text{X}$  is kept in a sealed tube, how much helium will accumulate in 20 days ? Express the result in  $\text{cm}^3$  at STP.*

### Solution :

Initial concentration ( $N_0$ ) of radio-isotope is 1 gm atom. Concentration remained after 20 days may be calculated as

$$N_t = N_0 \left(\frac{1}{2}\right)^n$$

where  $n = n_0$  of half lives =  $20/10 = 2 = 1\left(\frac{1}{2}\right)^2 = \frac{1}{4}$

Concentration decayed to  $\alpha$ -particles =  $1 - \frac{1}{4} = \frac{3}{4}$  gm atom. An  $\alpha$ -particle takes 2 electron from air and from helium gas. Thus,

$$\text{Helium formed} = \frac{3}{4} \text{ gm atom} = \frac{3}{4} \times 22400 \text{ cc} = 16800 \text{ cc}$$

**Problem 11 :**

*Radioactive decay is a first order process. Radioactive carbon wood sample decays with a half life of 5770 years. What is the rate constant in (years)<sup>-1</sup> for the decay? What fraction would remain after 11540 years?*

**Solution :**

$$K = \frac{0.693}{T_{1/2}} = \frac{0.693}{5770} = 1.201 \times 10^{-4} \text{ year}^{-1}$$

$$K = \frac{2.303}{t} \log \frac{N_0}{N_t}$$

$$1.201 \times 10^{-4} = \frac{2.303}{11540} \log \frac{N_0}{N_t}$$

$$4.002 = \frac{N_0}{N_t}$$

$$\therefore \frac{N_t}{N_0} \text{ (Remaining fraction)} = \frac{1}{4.002}$$

**Problem 11 :**

*A sample of  $^{131}_{53}\text{I}$ , as iodide ion, was administered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4.00 days, 67.7% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable iodide ion had migrated to the thyroid gland? Given  $T_{1/2} \text{ } ^{131}\text{I} = 8 \text{ days}$ .*

**Solution :**

We know,

$$\frac{0.693}{T_{1/2}} = \frac{2.303}{t} \log_{10} \left[ \frac{N_0}{N} \right]$$

$$\frac{0.693}{8} = \frac{2.303}{4} \log_{10} \left[ \frac{N_0}{N} \right]$$

$$\frac{N}{N_0} = 0.707$$

$\Rightarrow$  70.7 % of initial activity is present. Given that 67.7% activity is migrated to thyroid gland.

Thus, weight of I migrated to thyroid gland may be calculated as

$$\frac{67.7}{70.7} \times 100 = 95.75\%$$

$$\text{i.e., } 0.1 \times \frac{95.75}{100} = 0.09575 \text{ mg}$$

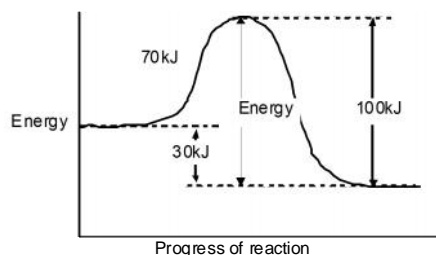
## OBJECTIVE

### Problem 1 :

If a reaction  $A + B \rightarrow C$  is exothermic to the extent of  $30 \text{ kJ/mol}$  and the forward reaction has an activation energy  $70 \text{ kJ/mol}$ , the activation energy for the reverse reaction is

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

**Solution :** (D)



By seeing the curve, activation energy for backward reaction =  $100 \text{ kJ}$

### Problem 2 :

The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at  $25^\circ\text{C}$  are  $3.0 \times 10^{-4} \text{ s}^{-1}$ ,  $104.4 \text{ kJ mol}^{-1}$  and  $6.0 \times 10^{14} \text{ s}^{-1}$  respectively the value of the rate constant as  $T \rightarrow \infty$  is :

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

**Solution :** (B)

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

When  $T \rightarrow \infty$

$K \rightarrow A$

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

### Problem 3 :

The inversion of cane sugar proceeds with half-life of 500 minute at pH 5 for any concentration of sugar. However if pH = 6, the half-life changes to 50 minute. 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)  $r = K[\text{sugar}]^0[\text{H}]^6$       (D)  $r = K[\text{sugar}]^0[\text{H}]^1$

**Solution :** (B)

Since  $t_{1/2}$  does not depend upon the sugar concentration means it is first order respect to sugar concentration.  $t_{1/2} \propto [\text{sugar}]^1$ .

$$t_{1/2} \times a^{n-1} = k$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{[\text{H}^+]_1^{1-n}}{[\text{H}^+]_2^{1-n}}$$

$$\frac{500}{50} = \left( \frac{10^{-5}}{10^{-6}} \right)^{1-n}$$

$$10 = (10)^{1-n}$$

Hence  $n = 0$

**Problem 4 :**

Two substances A and B are present such that  $[A_0] = 4[B_0]$  and half-life of A is 5 minute and that of B is 15 minute. 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 minute      (B) 10 minute      (C) 5 minute      (D) 12 minute

**Solution: (A)**

$$\text{Amount of A left in } n_1 \text{ halves} = \left(\frac{1}{2}\right)^{n_1} [A_0]$$

$$\text{Amount of B left in } n_2 \text{ halves} = \left(\frac{1}{2}\right)^{n_2} [B_0]$$

At the end, according to the question

$$\frac{[A_0]}{2^{n_1}} = \frac{[B_0]}{2^{n_2}} \Rightarrow \frac{4}{2^{n_1}} = \frac{1}{2^{n_2}}, [A_0] = 4[B_0]$$

$$\therefore \frac{2^{n_1}}{2^{n_2}} = 4 \Rightarrow 2^{n_1-n_2} = (2)^2 \therefore n_1 - n_2 = 2$$

$$\therefore n_2 = (n_1 - 2) \quad \dots(1)$$

$$\text{Also } t = n_1 \times t_{1/2(A)} = n_2 \times t_{1/2(B)}$$

(Let concentration of both become equal after time t)

$$\frac{n_1 \times t_{1/2(A)}}{n_2 \times t_{1/2(B)}} = 1 \Rightarrow \frac{n_1 \times 5}{n_2 \times 15} = 1 \Rightarrow \frac{n_1}{n_2} = 3 \quad \dots(2)$$

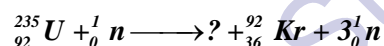
For equation (1) and (2)

$$n_1 = 3, n_2 = 1$$

$$t = 3 \times 5 = 15 \text{ minute}$$

**Problem 5 :**

Fill in the blank



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

**Solution: (A)**

$$92 + 0 = Z + 36 + 0 \Rightarrow Z = 56$$

$$235 + 1 \longrightarrow A + 92 + 3$$

$$\therefore A = 144$$

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

**Problem 6 :**

The rate of a reaction increases 4-fold when concentration of reactant is increased 16 times. If the rate of reaction is  $4 \times 10^{-6} \text{ mole L}^{-1} \text{ s}^{-1}$  when concentration of the reactant is  $4 \times 10^{-4}$ , the rate constant of the reaction will be

- (A)  $2 \times 10^{-4} \text{ mole}^{1/2} \text{ L}^{-1/2} \text{ s}^{-1}$       (B)  $1 \times 10^{-2} \text{ s}^{-1}$   
 (C)  $2 \times 10^{-4} \text{ mole}^{-1/2} \text{ L}^{1/2} \text{ s}^{-1}$       (D)  $25 \text{ mole}^{-1} \text{ L min}^{-1}$

**Solution : (A)**

$$\text{Rate} \propto \sqrt{\text{concentration}}, \text{ Rate} = k\sqrt{\text{concentration}}$$

$$k = \frac{\text{Rate}}{(\text{concen})^{1/2}} = \frac{4 \times 10^{-6}}{(4 \times 10^{-4})^{1/2}} = \frac{4 \times 10^{-6}}{2 \times 10^{-2}} = 2 \times 10^{-4} \text{ mole}^{1/2} \text{ L}^{-1/2} \text{ s}^{-1}$$



## CHEMICAL KINETICS

### Problem 7 :

A catalyst lowers the activation energy of a reaction from  $20 \text{ kJ mole}^{-1}$  to  $10 \text{ kJ mole}^{-1}$ . 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)  $+23^\circ\text{C}$

**Solution : (B)**

$$\frac{E'_a}{T_1} = \frac{E_a}{T_2} = \frac{10}{300} = \frac{20}{T_2} \quad \therefore \quad T_2 = 600 \text{ K} = 327^\circ\text{C}$$

### Problem 8 :

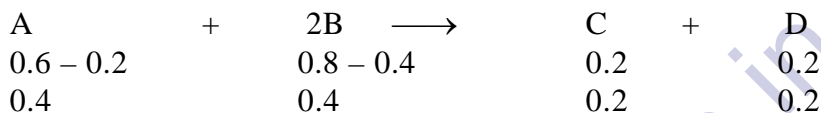
The reaction,  $A(g) + 2B(g) \longrightarrow C(g) + D(g)$  is an elementary process. In an experiment, the initial partial pressure of A and B are  $P_A = 0.60$  and  $P_B = 0.80 \text{ atm}$ . When  $P_C = 0.2 \text{ atm}$  the rate of reaction relative to the initial rate is

- (A)  $1/48$       (B)  $1/24$       (C)  $9/16$       (D)  $1/6$

**Solution : (D)**

$$R_1 = K[A][B]^2 = K[0.6][0.80]^2$$

After reaction



$$\frac{R_2}{R_1} = \frac{K(0.4)(0.4)^2}{(0.6)(0.8)^2} = \frac{1}{6}$$

### Problem 9 :

Thermal decomposition of a compound is of first order. If 50 % of a sample of the compound is decomposed in 120 minutes, show how long will it take for 90 % of the compound to decompose ?

- (A) 399 min      (B) 410 min      (C) 250 min      (D) 120 min

**Solution : (A)**

$$K = \frac{0.6932}{120} \quad \dots(1)$$

$$K = \frac{2.303}{t} \log \frac{a}{0.10a} = \frac{2.303}{t} \log 10 \quad \dots(2)$$

$$\text{Equating (1) and (2)} \quad \frac{0.6932}{120} = \frac{2.303}{t}$$

$$t = 399 \text{ minutes}$$

### Problem 10 :

If concentration are measured in mole/litre and time in minutes, the unit for the rate constant of a  $3^{\text{rd}}$  order reaction are

- (A)  $\text{mol lit}^{-1}\text{min}^{-1}$       (B)  $\text{lit}^2 \text{mol}^{-2} \text{min}^{-1}$       (C)  $\text{lit mol}^{-1}\text{min}^{-1}$       (D)  $\text{min}^{-1}$

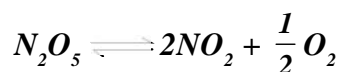
**Solution : (B)**

$$K = [\text{conc.}]^{1-n} \text{min}^{-1}$$

$$\text{For } 3^{\text{rd}} \text{ order reaction} = [\text{mole/litre}]^{1-3} \text{min}^{-1} = \text{lit}^2.\text{mole}^{-2}\text{min}^{-1}$$

**Problem 11 :**

What is the activation energy for the decomposition of  $N_2O_5$  as



If the values of the rate constants are  $3.45 \times 10^{-5}$  and  $6.9 \times 10^{-3}$  at  $27^\circ C$  and  $67^\circ C$  respectively .

- (A)  $102 \times 10^2$  kJ      (B) 488.5 kJ      (C) 112 kJ      (D) 112.5 kJ

**Solution : (D)**

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{6.9 \times 10^{-3}}{3.45 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.31} \left[ \frac{40}{300 \times 400} \right]$$

$$E_a = 112.5 \text{ kJ}$$

**Problem 12 :**

Half life period for a first order reaction is 20 minutes. How much time is required to change the concentration of the reactants from 0.08 M to 0.01M

- (A) 20 minutes      (B) 60 minutes      (C) 40 minutes      (D) 50 minutes

**Solution : (B)**

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

$$\frac{0.6932}{20} = \frac{2.303}{t} \log \frac{0.08}{0.01} = \frac{2.303}{t} \log 8 = \frac{2.303 \times 3 \times \log 2}{t}$$

$$\frac{1}{20} = \frac{3}{t}$$

$$t = 60 \text{ minutes}$$

**Problem 13 :**

The kinetic datas for the reaction:  $2A + B_2 \rightarrow 2AB$  are as given below:

[A]	[B <sub>2</sub> ]	Rate
mol L <sup>-1</sup>	mol L <sup>-1</sup>	mol L <sup>-1</sup> min <sup>-1</sup>
0.5	1.0	$2.5 \times 10^{-3}$
1.0	1.0	$5.0 \times 10^{-3}$
0.5	2.0	$1 \times 10^{-2}$

Hence the order of reaction w.r.t. A and B<sub>2</sub> are, respectively,

- (A) 1 and 2      (B) 2 and 1      (C) 1 and 1      (D) 2 and 2

**Solution : (A)**

$$2.5 \times 10^{-3} = K[0.5]^\alpha [1.0]^\beta \quad \dots(1)$$

$$5 \times 10^{-3} = K[1.0]^\alpha [1.0]^\beta \quad \dots(2)$$

$$1 \times 10^{-2} = K[0.5]^\alpha [2.0]^\beta \quad \dots(3)$$

Dividing equation (1) and (2)

$$\frac{1}{2} = \left[ \frac{1}{2} \right]^\alpha$$

hence  $\alpha = 1$

Dividing equation (1) and (3)

**CHEMICAL KINETICS**

$$\frac{2.5 \times 10^{-3}}{1 \times 10^{-2}} = \left(\frac{1.0}{2.0}\right)^\beta$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^\beta$$

$$\beta = 2$$

**Problem 14 :**

For the first order reaction  $A_{(g)} \rightarrow 2B_{(g)} + C_{(g)}$ , the initial pressure is  $P_A = 90 \text{ mm Hg}$ , the pressure after 10 minutes is found to be 180 mm Hg. The rate constant of the reaction is :

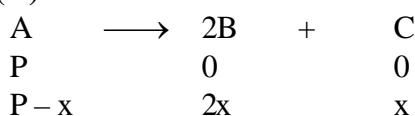
(A)  $1.15 \times 10^{-3} \text{ sec}^{-1}$

(B)  $2.3 \times 10^{-3} \text{ sec}^{-1}$

(C)  $3.45 \times 10^{-3} \text{ sec}^{-1}$

(D)  $6 \times 10^{-3} \text{ sec}^{-1}$

**Solution :** (A)



At equilibrium

$$180 = P - x + 2x + x$$

$$180 = 90 + 2x$$

$$2x = 90, x = 45$$

$$K = \frac{2.303}{t} \log \frac{P}{P-x} = \frac{2.303}{10} \log \frac{90}{90-45} = \frac{2.303}{10} \log 2 = \frac{0.6932}{10}$$

$$= 0.6932 = \frac{0.6932}{60} = 1.1555 \times 10^{-3} \text{ sec}^{-1}$$

## ANSWERS

**Daily Practice Problems 1**

1. (D)

2. (C)

3. (B)

4. (B)

5. (A)

6.  $\frac{\Delta[\text{NO}]}{dt} = 3.5 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$   $\frac{\Delta[\text{H}_2\text{O}]}{dt} = 5.3 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$

7.  $6.0 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$

8. (a)  $1.6 \times 10^{-4} \text{ M/s}$  ; (b)  $3.2 \times 10^{-4} \text{ M/s}$

9. (C)

10. (D)

11. (B)

12. (B)

13. (D)

14. (D)

15. (a)  $\text{Rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$  (b) rate will decrease by factor of 5

(c) rate will increase by factor of 4

16. (a)  $k[\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2$

(b) 4

(c) rate will increase by the factor of 9

(d) rate will decrease by factor of 1/4

17. (i)  $7.5 \times 10^{-7} \text{ M min}^{-1}$  (ii) rate increased by 64 times

18. order w.r.t.  $[\text{NO}] = 2$  ; order w.r.t.  $[\text{Cl}_2] = 1$  19.  $8 \times 10^{-9} \text{ M}^{-2} \text{ s}^{-1}$

20. (i)  $3/2$  (ii)  $\text{atm}^{-1/2} \text{ time}^{-1}$  (iii) increased by 64 times

## Daily Practice Problems 2

1. (B)                      2. (C)                      3. (B)                      4. (C)                      5. (B)                      6. (A)                      7.
- (A)                      8. (B)                      9. (B)                      10. (B)                      11. (B)
12. (a)  $2\text{N}_2\text{O}(\text{g}) \longrightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g})$                       (b) oxygen atom  
(c) (i) unimolecular (ii) bimolecular                      (d) not defined
13.  $3/2$
15. (a)  $\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$                       (b)  $3.0 \times 10^{-4} \text{ M/s}$                       (c)  $6.1 \times 10^{-6} \text{ M/s}$
16. (i)  $r = k[\text{A}]^{-1}[\text{B}]^{1/2}$                       (ii) wrt :  $\text{A} = -1, \text{B} = 1/2, \text{C} = 0$ , overall order  $= -1/2$   
(iii)  $k = \frac{63}{\sqrt{3}} \times 10^{-9}$                       (iv) rate of reaction increases by  $2\sqrt{2}$  times
17. (i)  $k[\text{A}_2]^3[\text{B}_2]$                       (ii) order wrt  $\text{A}_2 = 3$ ; O. wrt  $\text{B}_2 = 1$ , overall order  $= 4$   
(iii)  $k = 7.5 \times 10^3 (\text{mol/lit})^{-3}/\text{sec}$                       (iv) rate of reaction decrease to  $\frac{1}{16}$
18. (a) 2 and 1 (b)  $r = K[\text{Cl}_2]^1[\text{NO}]_2$  (c)  $8 \text{ litre}^2 \text{ mol}^{-2} \text{ sec}^{-1}$  (d)  $0.256 \text{ mol litre}^{-1} \text{ sec}^{-1}$
19. 211 torr, 13.57 min                      20. Zero order

## Daily Practice Problems 3

2. (i)  $a = R_0K, b = \frac{R_0K^2}{2}, c = \frac{R_0K^3}{6}$
2. (i)  $t_{1/2} = 66.66 \text{ min}, k = 0.01039 \text{ min}^{-1}$                       (ii)  $k = 0.06386 \text{ min}^{-1}; t = 36.06 \text{ min}$   
(iii)  $0.03465 \text{ min}^{-1}$                       (iv) (i) 0.740 s (ii) 2.005 s
4. 0.09                      5. (a) 3                      (b) No change
6.  $K = 2.5 \times 10^{-4} \text{ sec}^{-1}$ ,                      7. (a) 46.2 minute (b) 107.3 minute
8. (a)  $2.232 \times 10^{-2} \text{ min}^{-1}$  (b) 62.12 minute                      9. (i) 12.5 %, (ii) 6.25 %, (iii) 1.56%
10. 15.86 %                      11. Time at this point is  $t_{1/2}$  because  $[\text{A}] = [\text{B}]$ : Also  $\frac{d[\text{A}]}{dt} + \frac{d[\text{B}]}{dt} = 0$
12. 5.25 %, 128.33 hr                      14. 200 minute                      15.  $3.59 \times 10^2, 1.1 \times 10^3 \text{ sec}$
16.  $8.6 \times 10^{-4} \text{ sec}; 13.43 \text{ minute}$                       17. 0.023 mol/L                      18.  $K = \frac{2.303}{t} \log_{10} \frac{2P_0}{3P_0 - P}$
19. 26 sec                      20. 85.64                      21.  $1.58 \times 10^{-2}, 233 \text{ atm}$
22. 130.41                      23.  $P'_{(\text{CH}_3)_2\text{N}_2} = 127.55 \text{ mm}, P'_{\text{C}_2\text{H}_6} = 72.45 \text{ mm}$
24. (i)  $6.93 \times 10^{-2} \text{ M/min.}$  (ii)  $3.465 \times 10^{-2} \text{ M/min}$  (iii)  $1.7325 \times 10^{-2} \text{ M/min.}$  (iv)  $8.67 \times 10^{-3}$
25. (i) 250 seconds (ii)  $0.01386 \text{ M sec}^{-1}$
26. (i) 2079 sec (ii) 2772 sec, (iii) 1386 sec.                      (iv) 3465 sec.

## Daily Practice Problems 4

1.  $k = 2.0 \times 10^{-2} \text{ min}^{-1}$                       3. I,  $3.2 \times 10^{-2} \text{ min}^{-1}$                       5. 108.23 ml
8.  $k = 3.27 \times 10^{-3} \text{ min}^{-1}$                       9.  $k = 3.12 \times 10^{-3} \text{ min}^{-1}$                       10.  $r = k [\text{sugar}]^1 [\text{H}^+]^0$
11.  $6.2 \times 10^{-4} \text{ sec}^{-1}$

## CHEMICAL KINETICS

### Daily Practice Problems 5

1. 0.537
2.  $K_b = 1.7 \times 10^{-5} \text{ sec}^{-1}$   $K_c = 1.35 \times 10^{-4}$  (order = 1 for each path)
3. methyl cyclopentene = 23%, cyclohexane = 77%
4. 1990 sec.
5. 7.5937
6. 1.88
7.  $E_a = 209.6 \text{ kJ}$
8. Large value of E
9.  $k = 3.19 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$
10.  $k = 5.10 \times 10^{-5} \text{ s}^{-1}$ ;  $E = 92.011 \text{ kJ/mol}$ ;  $A = 6.73 \times 10^{11} \text{ s}^{-1}$
11.  $k = 10^{-2} \text{ s}^{-1}$ ;  $E = 87.297 \text{ kJ/mol}$ ;  $A = 2.2 \times 10^{14} \text{ s}^{-1}$
12.  $k = 5 \times 10^{-4} \text{ s}^{-1}$ ;  $E = 94.78 \text{ kJ/mol}$ ;  $A = 10^{15} \text{ s}^{-1}$
13.  $t = 19 \text{ sec}$ ,  $E_a = 67.6 \text{ kJ mol}^{-1}$
14.  $E_a^f = 50.80 \text{ kJ/mol}$ ;  $E_a^b = 27.61 \text{ kJ/mol}$
15. 63.18 kJ/mol
16.  $6.4 \times 10^9$
17. 3000 seconds
18. 0.002
19. 24.7 kJ/mol
20.  $T = 310 \text{ K}$
21. Ans. 311.2
22. 4.768
23.  $\approx 12 \text{ kcal}$
25.  $k = A$ , but it is not reasonable since  $E_a$  can not be zero
26. 2033.8
27.  $86.1^\circ \text{C}$
28.  $124.46 \text{ mol}^{-1}$
29.  $2.1645 \times 10^4$
30. 349.04 K

### Daily Practice Problems 6

1. 144
2. 214, 83
3. (i) AD (ii) BCD
4. (a) i- $\beta$  ii- $\alpha$ , (b) i- $\alpha$ , ii- $\alpha$
5. 5
6. B
7. C
8. D
9. A, D
10. C
11. B
12.  $3.7 \times 10^{10}$
13. Bi
14. A
15. C, D
16. A, D
17. A, B, C
18.  $4n+2, 4n, 4n+3, 4n+1, 4n+1$
19. (i)  $^{12}_6\text{C}$  (ii)  $^1_1\text{H}$  (iii)  $\gamma$  (iv)  $^{92}_{36}\text{Kr}$  (v)  $^1_0\text{n}$
- (vi)  $^{76}_{33}\text{As}$  (vii)  $^{16}_0\text{n}$  (viii)  $^4_2\text{He}$
20. (i)  $5\alpha, 5\beta$  (ii)  $3\alpha, 6\beta$  (iii)  $11\alpha, 14\beta$  (iv)  $\alpha, 2\beta$  (v)  $2\alpha$
- (vi)  $3\alpha, \beta$  (vii)  $4\alpha, 2\beta$  (viii)  $7\alpha, 4\beta$  (ix)  $7\alpha, 14\beta$  (x)  $5\alpha, 4\beta$

### Daily Practice Problems 7

1. C
2. C
3. B
4. D
5. D
6. A
7. A
8. B
9. C
10. D
11. C
12. D
13. C
14. A
15. D
16. D
17. B
18. C
19. A
20. B
21. D
22. A
23. D
24. D
25. A
26. D
27. B
28. A
29. B
30. C
31. B
32. A
33. B
34. D
35. B
36. D
37. D
38. A
39. D
40. B
41. A
42. C
43. B
44. C
45. C