

CHEMICAL KINETICS

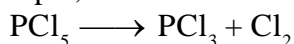
1. Rate of Reaction :

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.,

$$\begin{aligned}\text{Rate of reaction} &= \frac{\text{Decrease in the concentration of a reactant}}{\text{Time interval}} \\ \text{or} &= \frac{\text{Increase in the concentration of a product}}{\text{Time interval}}\end{aligned}$$

For example, consider the reaction ,

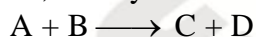


Suppose in a time interval Δt , decrease in concentration of PCl_5 is $\Delta [\text{PCl}_5]$ and increase in the concentration of PCl_3 and Cl_2 are $\Delta [\text{PCl}_3]$ and $\Delta [\text{Cl}_2]$ respectively, where square brackets indicate molar concentrations (moles/litre) of the substances involved. 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 (PCl_5) is decreasing while plus sign along with the other two terms is used to show that the concentration of the products (PCl_3) and (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⁻¹ sec⁻¹ (mol L⁻¹ s⁻¹) or moles litre⁻¹ min⁻¹ (mol L⁻¹ min⁻¹).

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⁻¹ or atm s⁻¹ 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 :

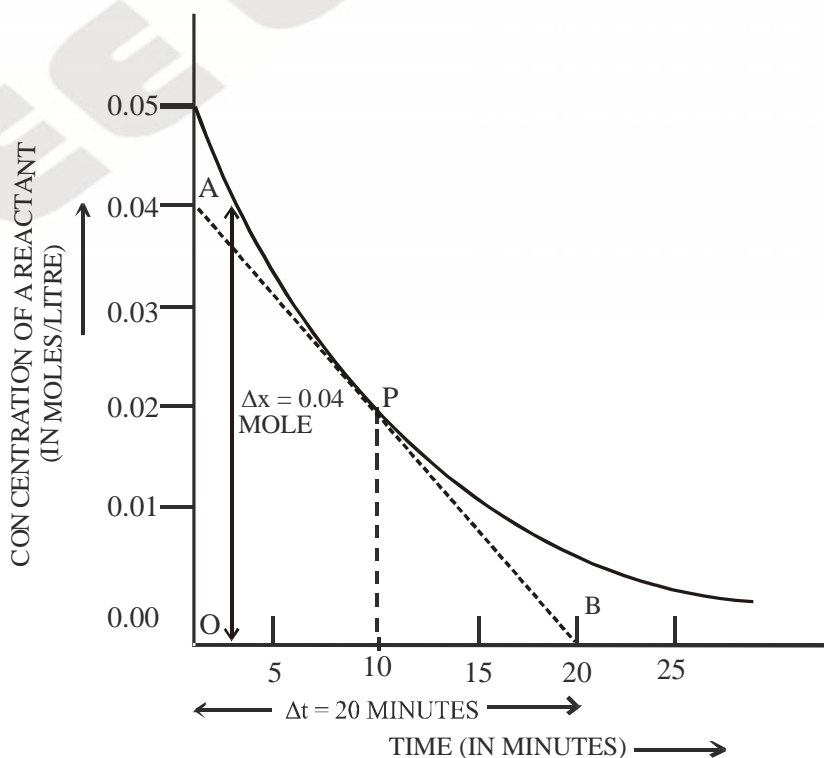
The rate of reaction at any instant of time is the rate of change of concentration (i.e. change of concentration per unit time) of any one of the reactants or products at that particular instant of time.

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 cm^3 or 5 cm^3) at different intervals of time, cool it down immediately to nearly 0°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.



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.

....., 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.

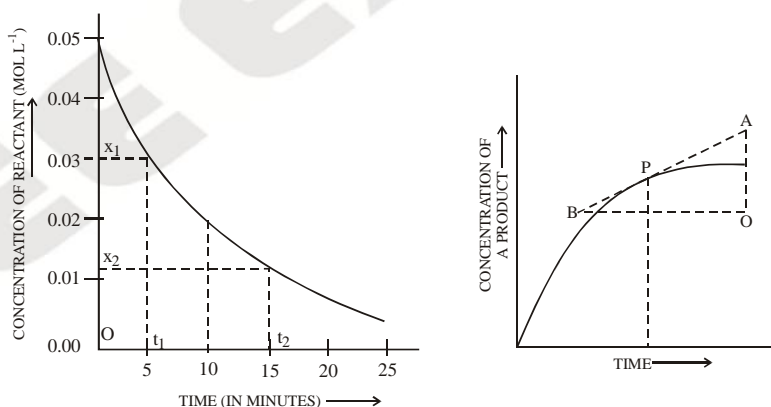


Illustration 1 :

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?

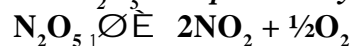
Solution :

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

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

Illustration 2 :

..... 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

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

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

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

[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.

- Calculate the rate constant for a 0.04 M solution, if the instantaneous rate is $1.4 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$.
- Also calculate the rate of reaction when the concentration of N_2O_5 is 1.20 M.
- 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,

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

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

- (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:

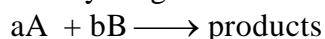
- Concentration of the reactants :** Greater the concentrations of the reactants, faster is the reaction. Conversely, as the concentrations of the reactants decrease, the rate of reactions also decreases.
- Temperature :** The rate of reaction increases with increase of temperature. In most of the cases, 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.

- (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 :

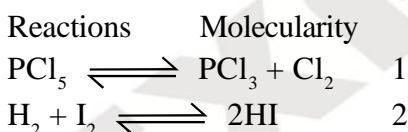
Single step reaction is called *elementary* reaction while a reaction occurring in two or more steps is called *complicated* or *consecutive* reaction. Each step of a complicated reaction is an elementary reaction.

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 .



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

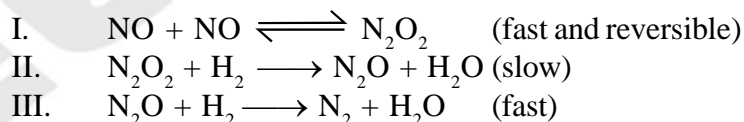
Examples:



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

For example :

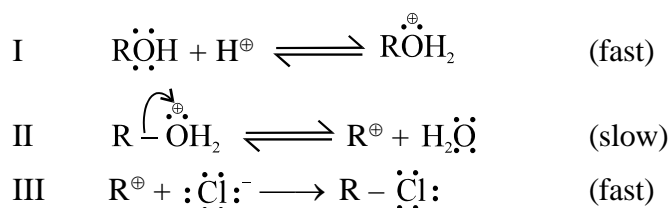
The reaction : $2\text{NO} + 2\text{H}_2 \rightleftharpoons \text{N}_2 + 2\text{H}_2\text{O}$, takes place in the sequence of following three steps .



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

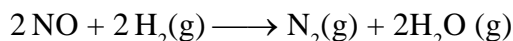
However, there is another view also , according to which molecularity of a complicated reaction is taken to be equal to the number of molecules, atoms or ions of reactant(s) and/or intermediates coming into contact and colliding simultaneously in the slowest step i.e. the rate-determining step (RDS) 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 H_2 constant
- (ii) rate gets just doubled when conc. of H_2 is doubled keeping that of NO constant, and
- (iii) rate increases 8 - fold when concentrations of both NO and 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.

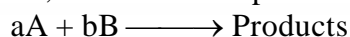
Order of reaction is defined as the sum of the powers of the concentration terms appearing in experimentally observed rate law.

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.,

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

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

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

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

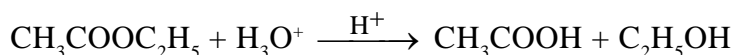
$$\text{Order w.r.t. A} = 0$$

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

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 mole L^{-1} . So there is no appreciable change in the concentration of water and the same remains practically constant.

$k[\text{H}_2\text{O}]$ 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**”.

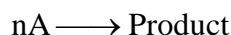
Distinction between Molecularity and Order

- (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



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

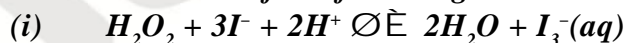
$$\frac{[\text{conc.}]}{\text{sec}} = k[\text{conc.}]^n$$

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

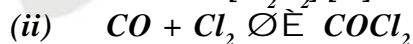
$$= [\text{mole/litre}]^{1-n} \text{sec}^{-1}$$

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 :

- (i) $\text{Rate} = k[\text{H}_2\text{O}_2] [\text{I}^-]$
 Order w.r.t. $\text{H}_2\text{O}_2 = 1$; Order w.r.t. $\text{I}^- = 1$
 Overall order = 2
 Units of $k = (\text{mol L}^{-1})^{1-2} \text{s}^{-1} = \text{mol}^{-1} \text{L s}^{-1}$
- (ii) $\text{Rate} = k[\text{CO}]^2 [\text{Cl}_2]^{1/2}$
 Order w.r.t. to $\text{CO} = 2$; Order w.r.t. $\text{Cl}_2 = 1/2$
 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 ₂]	
1.	0.010	0.010	1.2×10^{-4}
2.	0.010	0.020	2.4×10^{-4}
3.	0.020	0.020	9.6×10^{-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 ⁻¹)	initial conc. of (B) (mol L ⁻¹)	initial rate (mol L ⁻¹ s ⁻¹)
1.	0.10	0.20	3×10^2
2.	0.30	0.40	3.6×10^3
3.	0.30	0.80	1.44×10^4
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.

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 :

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

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

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

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

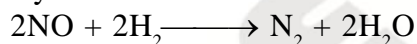
$$\begin{aligned} \text{Expt. (4): Rate} &= k[0.10][0.40]^2 \\ &= 7.5 \times 10^4 \times 0.10 \times 0.40 \times 0.40 \\ &= 1.2 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

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

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

3. Rate Law and Mechanism :

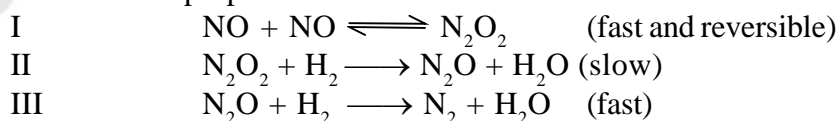
As already mentioned in the reaction:



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 N_2 cannot be faster than the rate of formation of N_2O . So, the rate of overall reaction or rate of formation of 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 (N_2O_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

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

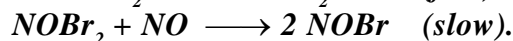
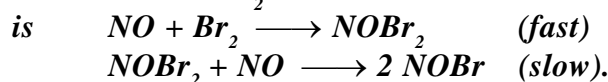
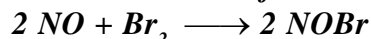
Where $k_{\text{obs}} = k \cdot k_c$ = observed rate constant of the reaction

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

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 NOBr_2 is an intermediate its concentration can be calculated from step 1 as follows :

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

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

Substituting this value in above equation

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

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

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

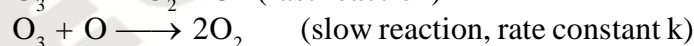
Illustration 8 :

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?

Solution : $\text{O}_3 \rightleftharpoons \text{O}_2 + \text{O}$ (fast reaction)



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

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

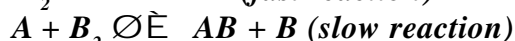
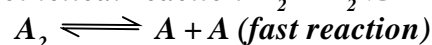
putting the value in (1)

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

$$k = k \times K_c.$$

Illustration 9 :

In hypothetical reaction $\text{A}_2 + \text{B}_2 \rightleftharpoons 2\text{AB}$ follows the mechanism as given below:



Give the rate law and order of reaction.

Solution :

Slowest step is rate determining.

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

Here $[A]$ should be eliminated.

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

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

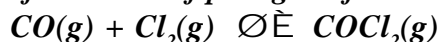
$$\text{From (1). Rate} = k K_c^{1/2} [A_2]^{1/2} [B_2]$$

$$= K[A_2]^{1/2}[B_2] \quad ; \quad [K = k \cdot K_c]$$

$$\text{Order} = 1 + 1/2 = 3/2$$

Illustration 10 :

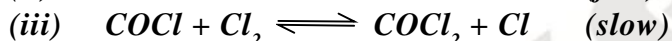
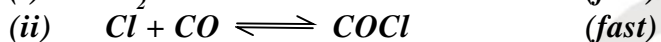
For the formation of phosgene from $CO(g)$ and chlorine,



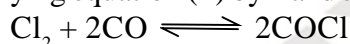
The experimentally determined rate equation is,

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

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 $\propto (a - x)$

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

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

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

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

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

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

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

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

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

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

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

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

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 :

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

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

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

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

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

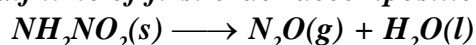
$$\text{Similarly } t_{0.5} = -\frac{2.303}{k_1} \log(1-0.5) = \frac{2.303}{k} \log 2 \quad \dots(3)$$

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

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 NH_2NO_2 is allowed to decompose, calculate

- time taken for NH_2NO_2 to decompose 99% and**
- volume of dry N_2O 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 NH_2NO_2 would be converted to N_2O .

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

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

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

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

$$t = 40.9 \approx 41 \text{ months}$$

$$0.00872 = \frac{2.303}{t} \log_{10} \frac{100}{70}$$

$$t_{1/2} = \frac{0.693}{0.00872} = 79.4 \text{ months}$$

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

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

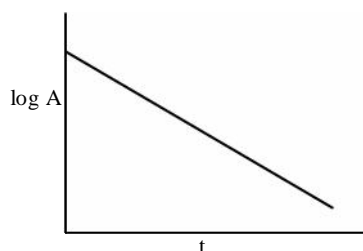
$$\text{or } \log [A] = -\frac{k}{2.303} t + \log [A]_0 \quad \dots (7)$$

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

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

From this, the value of k can be calculated.



- (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.

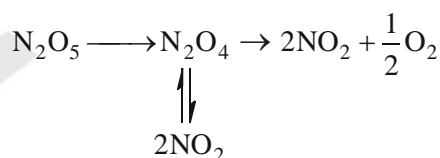
The time taken for half of the reaction to be completed i.e., the time in which the concentration of a reactant is reduced to half of its original value is called Half-life period of the reaction.

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 sec^{-1} , min^{-1} or 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, N_2O_4 and 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 N_2O_5 decomposed (x) i.e.,

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

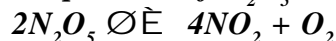
i.e., Substituting these values in the first order equation viz.

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

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:

Time in minutes	10	15	20	25	∞
Volume of O_2 evolved (in ml)	6.30	8.95	11.40	13.50	34.75

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

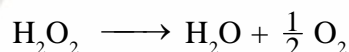
Substituting these values in the first order equation

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

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 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,

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

$$\text{i.e., } a \propto V_0$$

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

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

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

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

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

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

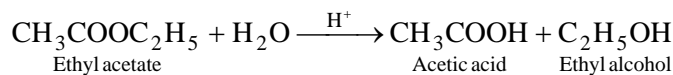
$$(iii) \quad k_1 = \frac{2.303}{30} \log \frac{46.1}{12.3} = 4.404 \times 10^{-2}$$

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.

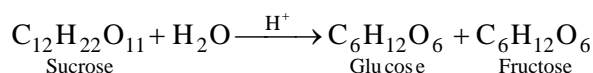
5. Pseudo Unimolecular Reactions :

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

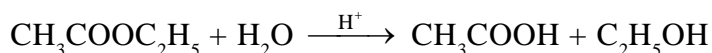
For the first reaction, Rate of reaction $\propto [\text{CH}_3\text{COOC}_2\text{H}_5]$ only
and for the second reaction, Rate of reaction $\propto [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$ only.

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 :

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 CH_3COOH 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 CH_3COOH produced (ii)

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

Amount of CH_3COOH produced } \propto ($V_t - V_0$)
at any instant of time (iii)

But amount of CH_3COOH 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_∞) } of CH_3COOH produced (v)

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

Max. amount of CH_3COOH produced $\propto (V_\infty - V_0)$

But Max. amount of CH_3COOH 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

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

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

Illustration 17 :

In an experiment to study hydrolysis of an ester 0.5 M HCl at 300 K was used. 5 cm³ 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 $\frac{1}{2}$
<i>v</i> (cm ³ 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

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

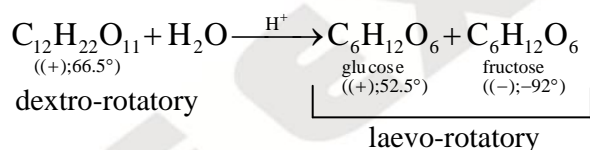
$$(i) \quad k_1 = \frac{2.303}{600} \log \frac{14.0}{(25.5 - 12.0)} = \frac{2.303}{600} \log \frac{14.0}{13.5} = 6.061 \times 10^{-5} \text{ s}^{-1}$$

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

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

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

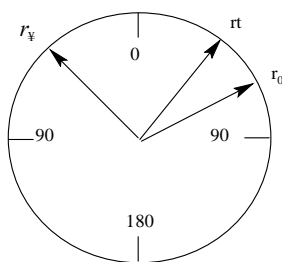
Angle of rotation at any time $t = r_t$

Angle of rotation at ∞ time = r_∞

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 ∞ time



$$= (r_0 - r_\infty) \propto \text{initial conc. of sucrose (a)}$$

$$\text{or } a \propto (r_0 - r_t)$$

$$\text{Thus, } (a - x) \propto (r_0 - r_\infty) - (r_0 - r_t)$$

$$\propto (r_t - r_\infty)$$

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

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.

Time (minutes)	0	10	20	30	60	11½
Rotation (degrees)	+32	25.5	20.0	15.5	5.0	-10.50

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

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

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

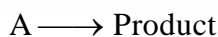
$$(ii) \quad k_1 = \frac{2.303}{20} \log \frac{32 - (-10.5)}{20.0 - (-10.5)} = \frac{2.303}{20} \log \frac{42.5}{30.0} = 0.0166 \text{ min}^{-1}$$

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

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

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

6. Half life of n^{th} Order Reaction :



t = 0	a	0
t = t	a - x	x

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

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

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

Let $a - x = z$

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

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

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

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

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

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

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

7. Catalyst :

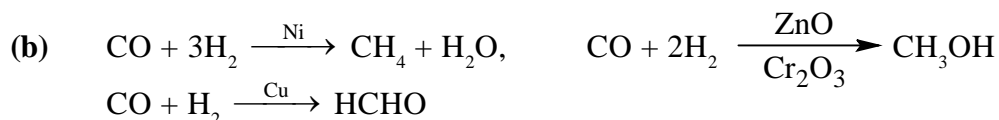
Berzelius used the term catalyst for the first time for the substances which accelerate the rate of chemical reaction. Now the term catalyst has been used for the foreign substances which influence the rate of a reaction and the phenomenon is known as catalysis. Usually two terms are used for catalysis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

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. MnO_2 used as catalyst in granular form for the decomposition of 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 H_2 and 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 H_2O_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.



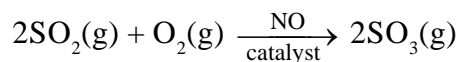
It may therefore be concluded that in some cases nature of products formed depends upon the presence and nature of catalyst used.

- (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.

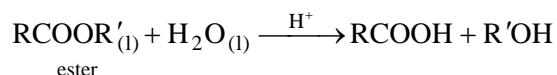
8. Types of Catalysis :

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 H_2SO_4 .

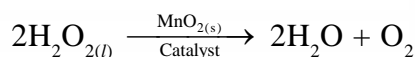


(b) **Solution phase catalysis :** The reactions in which catalyst and reactants are in solution phase or liquid phase of miscible nature.

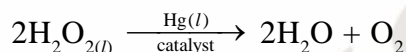


2. **Heterogeneous catalysis :** The reactions in which catalyst and reactants form phase ≥ 2 .

(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.

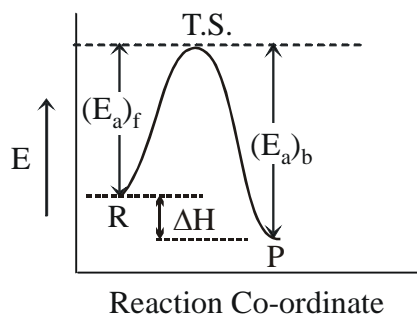
9. Arrhenius Theory :

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

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

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.



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

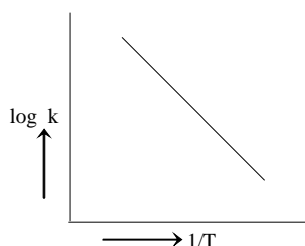
Thus, knowing the slope, the E_a can be easily calculated. The intercept of the line will give the value of $\log A$.

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°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 TK 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°C rise in temperature.

Illustration 19 :

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

Solution :

The Arrhenius equation is

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

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

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

Substituting the given values in the Arrhenius equation,.

$$\log_{10} 3 = \frac{E_a}{8.314 \times 2.303} \left[\frac{323 - 293}{323 \times 293} \right]$$

$$\begin{aligned} E_a &= \frac{2.303 \times 8.314 \times 323 \times 293 \times 0.477}{30} \\ &= 28811.8 \text{ J mol}^{-1} \\ &= 28.8118 \text{ kJ mol}^{-1} \end{aligned}$$

Illustration 20 :

....._a (activation energy) are $4 \times 10^{13} \text{ sec}^{-1}$ and 98.6 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°C if the energy of activation of a catalysed reaction is 162 kJ and for the uncatalysed reaction the value is 350 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.

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

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

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

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

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

$$= 9.7246$$

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

Illustration 23 :

The energy of activation for a reaction is 100 kJ mol^{-1} . Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20°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, $k_2 = Ae^{-25/RT}$

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

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

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

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

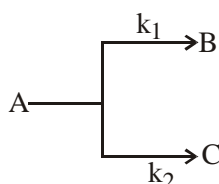
As the things being equal in presence or absence of a catalyst,

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

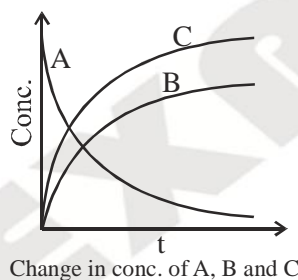
i.e.,
$$\frac{r_2}{r_1} = \frac{k_2}{k_1} = 2.34 \times 10^{13}$$

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

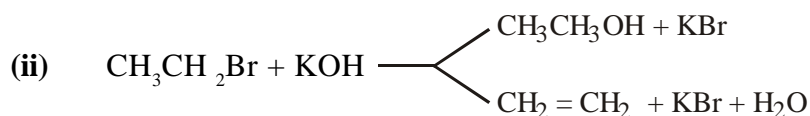
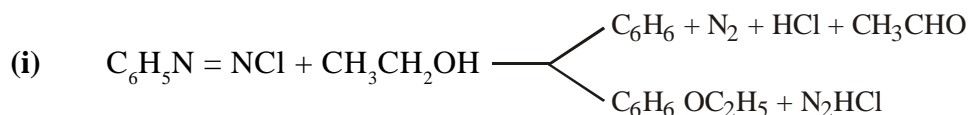
$$\text{rate of formation of } y, \quad \frac{dy_B}{dt} = k_1(a - x);$$

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

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

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

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⁻¹ 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) [\because both processes occur simultaneously]

When equilibrium is reached, the net rate is zero

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

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

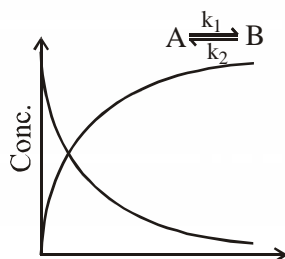
Substituting value of b in eqn. (i)

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

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.



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

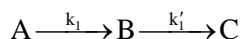
$$\text{or} \quad \log \frac{x_e - x_0}{x_e - x} = (k_1 + k_2)t$$

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

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

$$[B]e^{k'_1 t} = k_1[A]_0 \left[\frac{e^{-(k_1 - k'_1)t}}{-(k_1 - k'_1)} + \frac{1}{k_1 - k'_1} \right]$$

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

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

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.

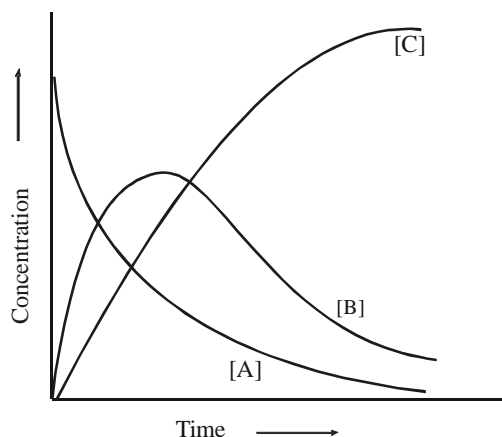


Fig. 1: Typical variations of concentration of A, B and C during the progress of the reaction $A \rightarrow B \rightarrow C$. The actual variations on the values of k_1 and k' .

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

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

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

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

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

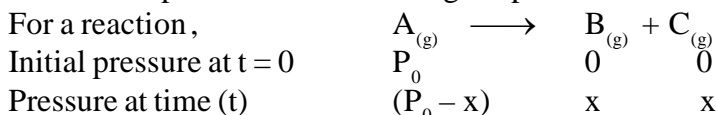
substituting equation (9) in equation (6), we get

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

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) = $P_0 - x + x + x$

$$\begin{aligned} \text{or } P_t &= P_0 + x, & x &= P_t - P_0 \\ a - x &= P_0 - (P_t - P_0) = 2P_0 - P_t \end{aligned}$$

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

Illustration 24 :

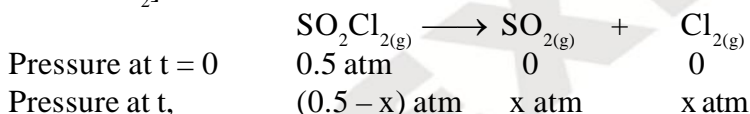
The following rate data was obtained for the first order thermal decomposition of $SO_2Cl_{2(g)}$ at a constant volume.

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. [\because 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° 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°	0	0
Pressure at $t = t$	$P^\circ - 2a$	$3a$	a
Pressure at $t = 2t$	$P^\circ - 2x$	$3x$	x
Given	$P^\circ - 2a + 3a + a = P$		
\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,
 $a \propto 0.062$
 $(a - x) \propto 0.044$

$$\therefore K = \frac{2.303}{t} \log_{10} \frac{0.062}{0.044}$$

$$K = 6.23 \times 10^{-3} \text{ sec}^{-1}.$$

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

$$\therefore 6.23 \times 10^{-3} = \frac{2.303}{100} \log_{10} \frac{0.062}{P}$$

$$\therefore P = 0.033 \text{ atm.}$$

RADIOACTIVITY

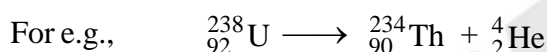
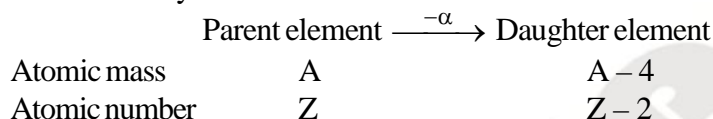
Radioactivity may be defined as a process in which nuclei of certain elements spontaneously disintegrate (transformation into another element by the ejection of α - or β - particle) at a rate characteristic for each particular active isotope (Becquerel, 1896). All the heavy elements from bismuth (atomic 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, $\text{KUO}_2(\text{SO}_4)_2$ 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

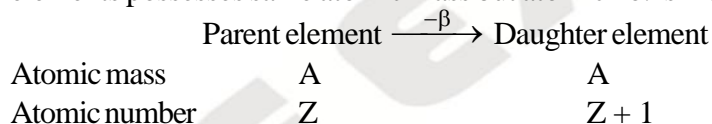
The atomic nuclei of radioactive elements can disintegrate any moment. During disintegration, atoms of new elements having different physical and chemical properties are formed, called daughter elements.

Disintegration occurs by the following processes :

(i) α -particle emission : When an α -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) β -particle emission - When β -particle is emitted from parent element thus formed daughter elements possesses same atomic mass but atomic no. is increased by 1 unit.

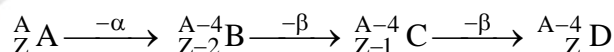


* Elements having same mass number called isobars. (A - same, Z- different)

\therefore daughter element formed by the β -particle emission is an isobar of parent element.



If in a radioactive transformation α & β 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., SO_4^{2-} , PO_4^{3-}

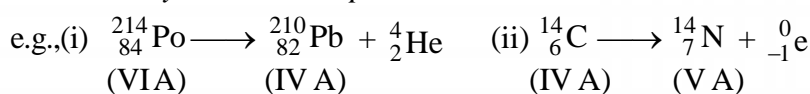
* Compounds having same number of atoms as well as same number of electrons are called isosters.

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 α , β , or γ -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:

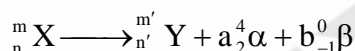
1. **Group displacement law :** The result of α - and β - particle changes can be summed up in the form of group displacement law. "In an α -particle change the resulting element has an atomic weight less by four units and atomic number less by two units and it falls in a group of the periodic table two columns to the left of the original element, and in a β -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 α -and β -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

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

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

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

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

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

λ = Decay constant

However, unlike first order rate constant (K), the decay constant (λ) 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 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

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

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

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

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 :

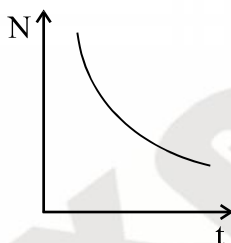
- (a) The phenomenon of spontaneous disintegration of nuclei of unstable atoms is defined as radioactivity.
- (b) Generally it is exhibited by atoms with $A > 192$ and $Z > 82$
- (c) It was discovered by Henry Becquerel
- (d) Lead isotope is the stable end product of any natural radioactive series
- (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.,

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

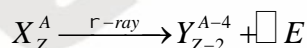
- (b) If N_0 is the number of radioactive nuclei at time $t = 0$, then the number of radioactive nuclei at a later time t is given by, $N = N_0 e^{-\lambda t}$



- (c) The nuclei of unstable atoms decay spontaneously emitting α , β particles and γ 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.

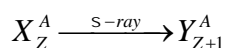
4. Soddy-Fajan's Laws :

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



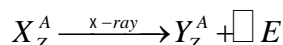
Daughter nucleus will occupy two positions before that of parent nucleus, in periodic table.

- (b) During β -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 γ -decay, the mass number and atomic number of the nucleus remain unchanged



4.

- (a) Emission of α -particle means loss of two protons and two neutrons
- (b) Emission of β -particle means loss of an electron.
- (c) Emission of a γ -ray means no change in charge and mass, but only energy changes

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 , λ = decay constant,

N_A = Avogadro number,

m = mass of material,

W = atomic weight of material,

T = half life of material

6. Decay Constant (λ) :

- (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.

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

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.

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

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

- (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 (τ) :

- (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 τ .
(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 (τ) :

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

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

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

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

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

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

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

$$(h) \quad \ddagger = \frac{\ddagger_r \ddagger_s}{\ddagger_r + \ddagger_s} \text{ (When two particles decay simultaneously)}$$

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

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

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

10. Useful Hints :

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

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

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

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

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

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

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

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

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

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

$$(xi) \quad N-t \text{ graph is a straight line with -ve slope, for slow decay process.}$$

11. Characteristics of α , β , and γ rays

S.No	Property	α -Particles	β -Particles	γ -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 α and β 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. α -emission

(a) Characteristics of α -decay :

- (i) The spectrum of α -particles is a discrete line spectrum.
- (ii) Spectrum of α -particles has fine structure i.e. every spectral line consists of a number of fine lines.
- (iii) The α -emitting nuclei have discrete energy levels i.e energy levels in nuclei are analogous to discrete energy levels in atoms..
- (iv) α -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

(b) Range of α -particles :

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

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

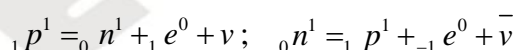
$$(II) \quad \log R = \log 0.318 + \frac{3}{2} \log E$$

(c) Size of the nucleus decreases by α emission**13. Characteristics of β -decay :**

- (i) The energy spectrum of β -particles is continuous i.e. β -particles of all energies upto a certain maximum are emitted
 - (ii) The number of such β -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 β -particles which is known as the end point energy (E_0)
 - (iv) In β -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 β -particles emitted by the same radioactive material may be same or different.
 - (vi) The number of β -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 γ -decay

- (i) The spectrum of γ -rays is a discrete line spectrum.
- (ii) Whenever α or β -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 γ -rays.
- (iii) Knowledge about nuclear energy levels is obtained by γ -spectrum.
- (iv) γ -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 γ -rays in materials

- (i) When γ -rays penetrate matter, then their intensity (a) decreases exponentially with depth (x) inside the matter. The intensity of γ -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 γ -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 (\sim) of that material.
- (iv) Coefficient of absorption
 - (I) $\sim = -\frac{dI/I}{dx}$
 - (II) \sim depends on the wavelength of γ -rays ($\sim \lambda^3$) and the nature of absorbing material

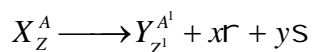
16. Radioactive Series :

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.

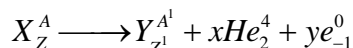
($4n + 1$) is artificial series & $4n$, ($4n + 2$), ($4n + 3$) are natural series.

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

17. To Calculate no of α -particles and β -Particles emitted

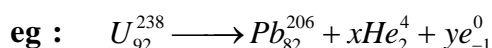


x: no of α -particles emitted y: no of β -particles emitted



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

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



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

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

Units of radioactivity :

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

1 millicurie (mCi) = 3.7×10^7 disintegrations per sec.

1 microcurie (μ Ci) = 3.7×10^4 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 = 3.7×10^4 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 α , β , γ , 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

EXERCISE - I

- 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 $X + 2Y \longrightarrow$ 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 $A(g) \longrightarrow$ 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°C

$$\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \frac{1}{2} \text{O}_2$$
 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 :

$$3\text{I}^- (\text{aq}) + \text{H}_3\text{AsO}_4 (\text{aq}) + 2\text{H}^+ (\text{aq}) \longrightarrow \text{I}_3^- (\text{aq}) + \text{H}_3\text{AsO}_3 (\text{aq}) + \text{H}_2\text{O} (\text{l})$$
 (a) If $-\Delta[\text{I}^-] / \Delta t = 4.8 \times 10^{-4} \text{ M/s}$, what is the value of $\Delta[\text{I}_3^-] / \Delta t$ 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, $\text{rate} = K[A][B]^{2/3}[C]^0$, 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 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 :

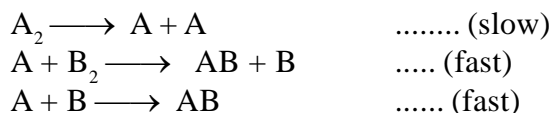
$$\text{CH}_3\text{Br}(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{CH}_3\text{OH}(\text{aq}) + \text{Br}^-(\text{aq})$$
 The reaction is first order in each reactant.
 (a) Write the rate law.
 (b) How does reaction rate change if the OH^- concentration is decreased by factor of 5 ?
 (c) What is the change in rate if the concentrations of both reactants are doubled ?
16. The oxidation of Br^- by 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 Br^- , first order in BrO_3^- , and second order in H^+ .
 (a) Write the rate law
 (b) What is the overall reaction order ?
 (c) How does the reaction rate change if the H^+ concentration is tripled ?
 (d) What is the change in rate if the concentrations of both Br^- and 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 Cl_2 concentration alone, only doubles the rate. What is the order of the reaction with respect to NO and 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 $[\text{C}] = 0.8 \text{ M}$.

20. If the pressure of gaseous reactant is changed by 3 times the rate of reaction changes by 5.2 times. Determine
- (i) order of reaction (ii) unit of rate constant
- (iii) effect on rate of reaction if volume of container is reduced to $\frac{1}{16}$ th of the original

EXERCISE - II

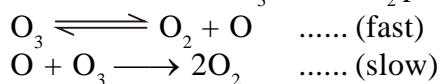
- The rate law for the single-step reaction, $2A + B \longrightarrow 2C$, is given by :
 (A) Rate = $K[A] \cdot [B]$ (B) Rate = $K[A]^2 \cdot [B]$
 (C) Rate = $K[2A] \cdot [B]$ (D) Rate = $K[A]^2 \cdot [B]^0$
- The correct expression the rate of reaction of elementary reaction, $A + B \longrightarrow C$ is
 (A) $\frac{d[C]}{dt} = K[A]$ (B) $\frac{d[C]}{dt} = K[B]$ (C) $-\frac{d[A]}{dt} = K[A][B]$ (D) $-\frac{d[A]}{dt} = K[A]$
- Select the intermediate in the following reaction mechanism :
 $O_3(g) \rightleftharpoons O_2(g) + O(g), O_3 + O \longrightarrow 2O_2$
 (A) $O_3(g)$ (B) $O(g)$ (C) $O_2(g)$ (D) None
- The elementary step of the reaction, $2Na + Cl_2 \longrightarrow 2NaCl$ is found to follow III order kinetics, its molecularity is :
 (A) 1 (B) 2 (C) 3 (D) 4
- For the reaction $2NO_2 + F_2 \longrightarrow 2NO_2F$, following mechanism has been provided :
 $NO_2 + F_2 \xrightarrow{\text{slow}} NO_2F + F$
 $NO_2 + F \xrightarrow{\text{fast}} NO_2F$
 Thus rate expression of the above reaction can be written as :
 (A) $r = k [NO_2]^2 [F_2]$ (B) $r = k [NO_2][F_2]$
 (C) $r = k [NO_2]$ (D) $r = k [F_2]$
- The reaction $2NO + Br_2 \longrightarrow 2NOBr$, Obey's the following mechanism:
 $NO + Br_2 \xrightleftharpoons{\text{fast}} NOBr_2$; $NOBr_2 + NO \xrightarrow{\text{slow}} 2NOBr$
 The rate expression of the above reaction can be written as:
 (A) $r = k [NO]^2 [Br_2]$ (B) $r = k [NO] [Br_2]$
 (C) $r = k [NO] [Br_2]^2$ (D) $r = k [NOBr_2]$
- The reaction $2A \longrightarrow B + C$ follows zero order kinetics. The differential rate equation for the reaction is:
 (A) $\frac{dx}{dt} = K[A]^0$ (B) $\frac{dx}{dt} = K[A]^2$ (C) $\frac{dx}{dt} = K[B][C]$ (D) $\frac{dx}{dt} = K[A]$
- For the elementary step, $(CH_3)_3CBr(aq) \longrightarrow (CH_3)_3C^+(aq) + Br^-(aq)$ the molecularity is:
 (A) Zero (B) 1 (C) 2 (D) cannot ascertained
- Following mechanism has been proposed for a reaction ,
 $2A + B \longrightarrow D + E$
 $A + B \longrightarrow C + D$ (slow)
 $A + C \longrightarrow E$ (fast)
 The rate law expression for the reaction is:
 (A) $r = K[A]^2[B]$ (B) $r = K[A][B]$ (C) $r = K[A]^2$ (D) $r = K[A][C]$
- A reaction, $A_2 + B_2 \longrightarrow 2AB$ occurs by the following mechanism ;



Its order would be:

- (A) 3/2 (B) 1 (C) zero (D) 2

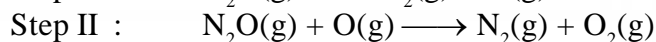
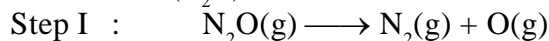
11. The chemical reaction, $2O_3 \longrightarrow 3O_2$ proceeds as follows :



The rate law expression should be:

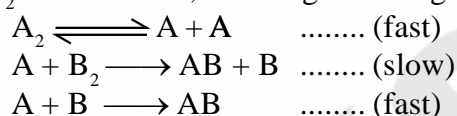
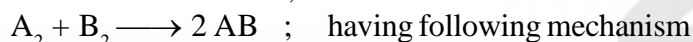
- (A) $r = K [O_3]^2$ (B) $r = K [O_3]^2 [O_2]^{-1}$ (C) $r = K [O_3][O_2]$ (D) Unpredictable

12. The following two step mechanism has been proposed for the gas-phase decomposition of nitrous oxide (N_2O):

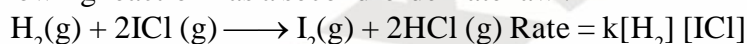


- (a) Write the chemical equation for overall reaction.
 (b) Identify any reaction intermediates.
 (c) What is the molecularity of each of the elementary reactions ?
 (d) What is the molecularity of the overall reaction ?

13. What is the order of reaction ,

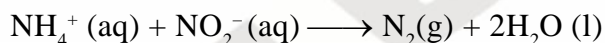


14. The following reaction has a second-order rate law :



Devise a possible reaction mechanism.

15. Initial rate data at 25°C are listed in the table for the reaction



Experiment No.	Initial $[NH_4^+]$	Initial $[NO_2^-]$	Initial rate of consumption of NH_4^+ (M/s)
1.	0.24	0.10	7.2×10^{-6}
2.	0.12	0.10	3.6×10^{-6}
3.	0.12	0.15	5.4×10^{-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 , $A + B + C \longrightarrow \text{product}$

given :

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

using that, determine

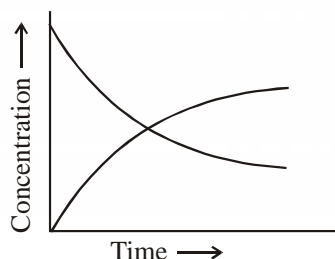
- rate law
 - order of reaction with respect to A₂ and B₂ and overall order of reaction
 - value and unit of rate constant
 - effect on rate of reaction on doubling the volume of container.
18. The data given below are for the reaction of NO and Cl₂ to form NOCl at 295 K.
- | [Cl ₂] | [NO] | Initial rate (mol litre ⁻¹ sec ⁻¹) |
|--------------------|------|---|
| 0.05 | 0.05 | 1×10^{-3} |
| 0.15 | 0.05 | 3×10^{-3} |
| 0.05 | 0.15 | 9×10^{-3} |
- What is the order w.r.t. NO and Cl₂ in the reaction
 - Write the rate expression
 - Calculate the rate constant
 - Determine the reaction rate when conc. of Cl₂ and NO are 0.2 M and 0.4 M respectively.
19. The decomposition of NH₃ on tungsten surface follows zero order kinetics. The half life is 5 minutes for an initial pressure of 70 torr of NH₃. 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.

EXERCISE - III

- 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.
- 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?
 - 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?
 - For a certain reaction it takes 20 minutes for the initial concentrations of 34.8 mol L⁻¹ to become 17.4 mol L⁻¹ and another 20 minutes to become 8.7 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 H_2O_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°C . What % of SO_2Cl_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°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 .
15. For the decomposition of N_2O_5 , the rate constant is $6.2 \times 10^{-4} \text{ sec}^{-1}$ at 45°C . It begins with

one mole of N_2O_5 in a litre flask, how long would it take for 20% N_2O_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°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°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 Cl_2O_7 at 400 K in gaseous phase to Cl_2 and 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°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 :
- Initial rate
 - Rate after 600 seconds
 - Rate after 75 % of the reaction is completed
 - 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 :
- $t_{1/2}$ of the reaction
 - rate of reaction when concentration is 5 M.
26. Rate constant of a first order reaction is 10^{-3} sec . Calculate time in seconds when concentration is changing from :
- 2 M to 0.25 M
 - 16 M to 1 M
 - 6.4 M to 1.6 M
 - 4 M to 0.125 M

EXERCISE - IV

1. The following data represent for the decomposition of NH_4NO_2 in aqueous solution

Time in minute	10	15	20	25	∞
Volume of 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 H_2O_2 from the following data

Time in minute	10	15	20	25	∞
Vol. of O_2 given by H_2O_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 N_2 evolved at definite intervals of time. Calculate O. R. and rate constant

Time in minute	0	2.0	5.5	7.0	∞
Volume of N_2 in mL	0	10	25	35	163

4. The decomposition of N_2O_5 in chloroform was followed by measuring the volume of 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 O_2 gas obtainable was 100cm^3 . In 500 minutes, 90cm^3 of O_2 were evolved. Calculate the first order rate constant of the reaction.

5. The specific rate constant of the decomposition of N_2O_5 is 0.008 min^{-1} . The volume of O_2 collected after 20 minute is 16 mL. Find the volume that would be collected at the end of reaction. NO_2 formed is dissolved in CCl_4 .

6. Derive order of reaction, for the decomposition of H_2O_2 from the following data.

Time in minute	0.	10	20	30
Volume of KMnO_4 needed for H_2O_2	25	16	10.5	7.09

7. The kinetics of hydrolysis of methyl acetate in excess dilute HCl at 25°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	∞
Titre value (in mL)	19.24	24.20	26.60	32.23	42.03

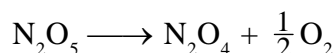
8. The acid catalysed hydrolysis of an organic compound A at 30°C has half life of 100 minute when carried out in a buffer solution of $\text{pH} = 5$ and 10 minute when carried out at $\text{pH} = 4$. Both the times the half life are independent of the initial concentration of A. If the rate of reaction 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	∞
Rotation in degree	+46.75	+41.0	+30.75	+12.75	-18.75

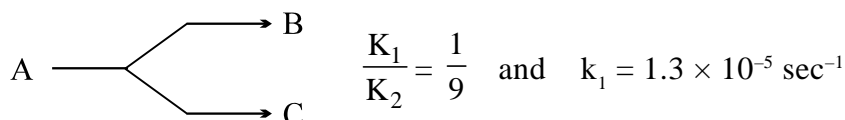
Calculate rate constant.

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 N_2O_5 in CCl_4 at 45°C produces 5.02 mL of O_2 in 1198 sec and 9.58 mL O_2 after a long time. Calculate rate constant assuming I order for the reaction.



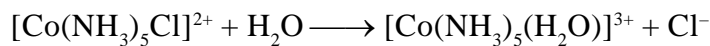
EXERCISE - V

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°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°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°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 ΔH° for this reaction is -200 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 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



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°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°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°C .

13. The time required for 20 % completion of a first order reaction at 27°C is 1.5 times that required for its 30 % completion at 37°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°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.

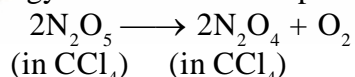
16. Calculate the ratio of the catalysed and uncatalysed rate constant at 20°C if the energy of activation of a catalysed reaction is 20 kJ mol^{-1} and for the uncatalysed reaction is 75 kJ mol^{-1} .

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 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°C rise in temperature at 25°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°C



are 100 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 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°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°C .

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 kJ mol^{-1} . The activation energy is lowered by 19 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 kJ mol^{-1} . Calculate the ratio between the rate constant of these reactions at 27°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 ?

EXERCISE - VI

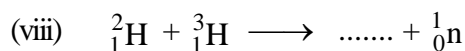
- Q.1 Calculate the number of neutrons in the remaining atom after emission of an alpha particle from ${}_{92}^{238}\text{U}$ atom.
- Q.2 Radioactive disintegration of ${}_{88}^{226}\text{Ra}$ takes place in the following manner into RaC.

$$\text{Ra} \xrightarrow{-\alpha} \text{Rn} \xrightarrow{-\alpha} \text{RaA} \xrightarrow{-\alpha} \text{RaB} \xrightarrow{-\beta} \text{RaC}$$
Determine mass number and atomic number of RaC.
- Q.3 A radioactive element A disintegrates in the following manner

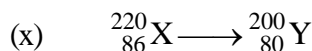
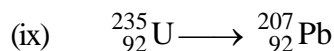
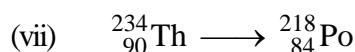
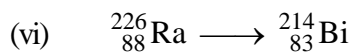
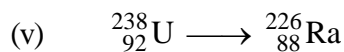
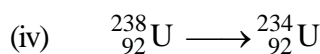
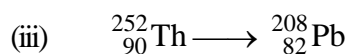
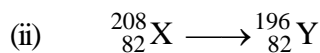
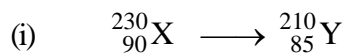
$$\text{A} \xrightarrow{-\alpha} \text{B} \xrightarrow{-\beta} \text{C} \xrightarrow{-\beta} \text{D}$$
 - (i) Which one of the elements A, B, C, D are isotopes ?
 - (ii) Which one of the elements A, B, C, D are isobars ?
- Q.4 Write the particles emitted from each nucleides in the following reactions :
 (a) ${}_{90}^{231}\text{Th} \xrightarrow{\text{(i)}} {}_{91}^{231}\text{Pa} \xrightarrow{\text{(ii)}} {}_{89}^{227}\text{Ac}$ (b) ${}_{85}^{217}\text{At} \xrightarrow{\text{(i)}} {}_{83}^{213}\text{Bi} \xrightarrow{\text{(ii)}} {}_{81}^{209}\text{Tl}$
- Q.5 An atom has atomic mass 232 and atomic number 90. During the course of disintegration, it emits 2β -particles and few α -particles. The resultant atom has atomic mass 212 and atomic number 82. How many α -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 ${}_{92}^{235}\text{U}$ decays in a number of steps to an isotope of ${}_{82}^{207}\text{Pb}$. 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 α - and 6- β 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 α -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 = 3.7×10^{10} dis/minute
 (D) Actinium series starts with 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 = 3.7×10^{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) ${}^9_4\text{Be} + {}^4_2\text{He} \longrightarrow \dots + {}^1_0\text{n}$ (ii) ${}^6_3\text{Li} + \dots \longrightarrow {}^7_3\text{Li} + {}^1_1\text{H}$
- (iii) ${}^9_4\text{Be} + \dots \longrightarrow {}^8_4\text{Be} + {}^1_0\text{n}$
- (iv) ${}^{235}_{92}\text{U} + {}^1_0\text{n} \longrightarrow {}^{141}_{56}\text{Ba} + \dots + 3 {}^1_0\text{n}$
- (v) ${}^{31}_{15}\text{P} + {}^1_1\text{H} \longrightarrow {}^{31}_{16}\text{S} + \dots$ (vi) ${}^{75}_{33}\text{As} + {}^2_1\text{H} \longrightarrow \dots + {}^1_1\text{H}$
- (vii) ${}^{63}_{29}\text{Cu} + {}^4_2\text{He} \longrightarrow {}^{37}_{17}\text{Cl} + 14 {}^1_1\text{H} + \dots$

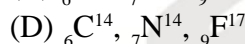
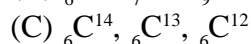
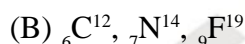
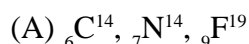


Q.20 Calculate α and β particles emitted during the process.

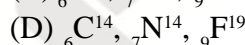
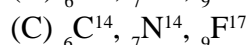
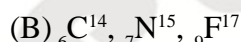
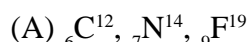


EXERCISE - VII

1. The triad of nuclei that represents isotopes is:



2. The triad of nuclei that represents isotones is:



3. The rate of radioactive disintegration..... with time:

(A) Increases

(B) Decreases

(C) Is constant

(D) May increase

4. 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

5. Decrease in atomic no. is observed during:

(A) Alpha emission

(B) Electron capture

(C) Positron emission

(D) all

6. Successive emission of an α -particle and two β -particles by an atom of an element results in the formation of its:

(A) Isodiapher

(B) Isomorph

(C) Isotope

(D) Isotherm

7. If N_0 is the initial number of nuclei, number of nuclei remaining undecayed at the end of n th half life is:

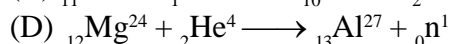
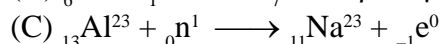
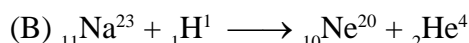
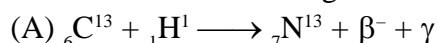
$$\text{(A)} \quad 2^{-n} N_0$$

$$\text{(B)} \quad 2^n N_0$$

$$\text{(C)} \quad n^{-2} N_0$$

$$\text{(D)} \quad n^2 N_0$$

8. Which one of the following nuclear reaction is correct:



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:

$$\text{(A)} \quad 10^{-14} \text{ g}$$

$$\text{(B)} \quad 10^{-6} \text{ g}$$

$$\text{(C)} \quad 10^{-15} \text{ g}$$

$$\text{(D)} \quad 10^{-3} \text{ g}$$

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 $t_{1/2} = 14$ 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 α -and β -particles emitted during the transformation of ${}^{232}_{90}\text{Th}$ to ${}^{208}_{82}\text{Pb}$ 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) $1/8$ g (D) $1/16$ 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 = 4.5×10^9 year). The age of the rock would be:
(A) 4.5×10^9 year (B) 9×10^9 year (C) 13.5×10^9 year (D) 2.25×10^9 year
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) 1.128×10^9 yr (B) 2.128×10^9 yr (C) 3.128×10^9 yr (D) None
25. The number of α - and β - particles emitted in the nuclear reaction ${}^{228}_{90}\text{Th} \longrightarrow {}^{212}_{83}\text{Bi}$ are:
(A) 4α and 1β (B) 3α and 7β (C) 8α and 1β (D) 4α and 7β
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 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 $1/64$ th 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 4.5×10^9 year. If 80 g of this was taken, the time taken for it to decay to 40 g will be:
(A) 2.25×10^9 year (B) 4.50×10^9 year (C) 6.75×10^9 year (D) 8.75×10^9 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 α -decay is 4.5×10^9 year. The time taken in year for the decay of $15/16$ part of this isotope is:
(A) 9.0×10^9 (B) 1.8×10^{10} (C) 4.5×10^9 (D) 2.7×10^{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) 4.8×10^{10} (B) 3.7×10^{10} (C) 9.2×10^6 (D) 3.7×10^8
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 4×10^6 nuclei at the start, then after how

- many year they will be left 0.5×10^6 .
 (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) 100×500 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 ${}_Z A^m \longrightarrow {}_{Z-4} B^{m-8} + 2 {}_2 \text{He}^4$. 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 β -particle emitted during the change ${}_a X^c \longrightarrow {}_d Y^b$ 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

<i>[A] mol/litre</i>	<i>[B] mol litre⁻¹</i>	<i>Initial rate mol litre⁻¹ time⁻¹</i>
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

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

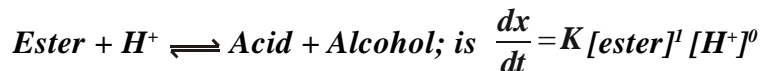
- (ii) Pressure after 100 sec may be calculated as

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

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

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 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 H^+ ion is doubled velocity will be unaffected.

Problem 4 :

The reaction $2A + B + C \rightarrow D + 2E$; 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, $\frac{dx}{dt} = K[A]^1[B]^2[C]^0$
 (ii) When concentration of A, B and C are doubled then rate will be

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

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

Problem 5 :

At 27°C it was observed, during a reaction of hydrogenation that the pressure of 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

$$\therefore PV = nRT$$

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

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

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

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

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

Problem 6 :

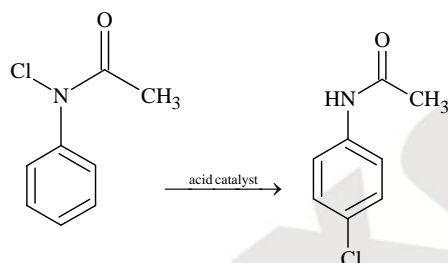
In presence of an acid N-chloro acetanilide changes slowly into p-chloro acetanilide. Former substance liberated iodine from KI and not the later and hence progress of reaction can be measured by titrating iodine liberated with $\text{Na}_2\text{S}_2\text{O}_3$ solution, the results obtained were as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

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

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

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

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

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

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

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 a value of 1.26×10^{13} 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

$\dots -E/RT$ we get

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

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

$$E = 58.5 \text{ kcal}$$

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

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 ,

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

Initial pressure of NO (atm)	Initial pressure of H_2 (atm)	Rate (atm min ⁻¹)
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_2 (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

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

$$m = 2$$

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

$$n = 1$$

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

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 α -active radio isotope are disintegrating in a sealed container. In one hour the helium gas collected at STP is 11.2 cm^3 . Calculate the half-life of the radio-isotope.

Solution :

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

Since, helium atom corresponds to α -particle. Thus, Rate of disintegration = 3.01×10^{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 ${}_Z^AX^A$ (half life 10 days) decays to give ${}_{Z-2}Y^{A-4}$. If 1.00 gm atom of ${}_Z^AX^A$ is kept in a sealed tube, how much helium will accumulate in 20 days ? Express the result in 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

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

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

Concentration decayed to α -particles = $1 - \frac{1}{4} = \frac{3}{4}$ gm atom. An α -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 $^{-1}$ 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

$$\frac{67.7}{70.7} \times 100 = 95.75\%$$

$$\text{i.e., } 0.1 \times \frac{95.75}{100} = 0.09575 \text{ mg}$$

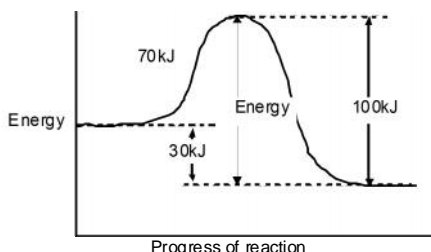
OBJECTIVE

Problem 1 :

If a reaction $A + B \rightleftharpoons C$ is exothermic to the extent of 30 kJ/mol and the forward reaction has an activation energy 70 kJ/mol, the activation energy for the reverse reaction is

- (A) 30 kJ/mol (B) 40 kJ/mol (C) 70 kJ/mol (D) 100 kJ/mol

Solution : (D)



By seeing the curve, activation energy for backward reaction = 100 kJ

Problem 2 :

The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°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

$$\frac{[A^0]}{2^{n_1}} = \frac{[B_0]}{2^{n_2}} \Rightarrow \frac{4}{2^{n_1}} = \frac{1}{2^{n_2}}, [A_0] = 4[B_0]$$

$$\therefore \frac{2^{n_1}}{2^{n_2}} = 4 \Rightarrow 2^{n_1-n_2} = (2)^2 \therefore n_1 - n_2 = 2$$

$$\therefore n_2 = (n_1 - 2) \quad \dots(1)$$

$$\text{Also } t = n_1 \cdot t_{1/2(A)} = n_2 \times t_{1/2(B)}$$

(Let concentration of both become equal after time t)

$$\frac{n_1 \cdot t_{1/2(A)}}{n_2 \cdot t_{1/2(B)}} = 1 \text{ P } \frac{n_1 \cdot 5}{n_2 \cdot 15} = 1 \text{ P } \frac{n_1}{n_2} = 3 \quad \dots(2)$$

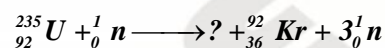
For equation (1) and (2)

$$n_1 = 3, n_2 = 1$$

$$t = 3 \times 5 = 15 \text{ minute}$$

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 4×10^{-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)

$$\text{Rate} \propto \sqrt{\text{concentration}}, \text{Rate} = k\sqrt{\text{concentration}}$$

$$k = \frac{\text{Rate}}{(\text{concentration})^{1/2}} = \frac{4 \times 10^{-6}}{(4 \times 10^{-4})^{1/2}} = \frac{4 \times 10^{-6}}{2 \times 10^{-2}} = 2 \times 10^{-4} \text{ mole}^{1/2} \text{ L}^{-1/2} \text{ S}^{-1}$$

Problem 7 :

A catalyst lowers the activation energy of a reaction from 20 kJ mole^{-1} to 10 kJ mole^{-1} . The temperature at which the uncatalysed reaction will have the same rate as that of the catalysed at 27°C is

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

Solution : (B)

$$\frac{E'_a}{T_1} = \frac{E_a}{T_2} = \frac{10}{300} = \frac{20}{T_2} \quad \therefore T_2 = 600 \text{ K} = 327^\circ\text{C}$$

Problem 8 :

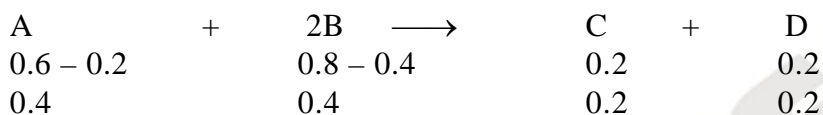
The reaction, $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A and B are $P_A = 0.60$ and $P_B = 0.80 \text{ atm}$. When $P_C = 0.2 \text{ atm}$ the rate of reaction relative to the initial rate is

- (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)

$$K = \frac{0.6932}{120} \quad \dots(1)$$

$$K = \frac{2.303}{t} \log \frac{a}{0.10a} = \frac{2.303}{t} \log 10 \quad \dots(2)$$

Equating (1) and (2) $\frac{0.6932}{120} = \frac{2.303}{t}$

$$t = 399 \text{ minutes}$$

Problem 10 :

If concentration are measured in mole/litre and time in minutes, the unit for the rate constant of a 3rd 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) min^{-1}

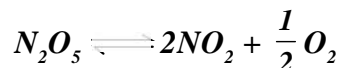
Solution : (B)

$$K = [\text{conc.}]^{1-n} \text{min}^{-1}$$

$$\text{For 3}^{\text{rd}} \text{ order reaction} = [\text{mole/litre}]^{1-3} \text{min}^{-1} = \text{lit}^2 \cdot \text{mole}^{-2} \text{min}^{-1}$$

Problem 11 :

What is the activation energy for the decomposition of N_2O_5 as



If the values of the rate constants are 3.45×10^{-5} and 6.9×10^{-3} at $27^\circ C$ and $67^\circ C$ respectively.

- (A) $102 \times 10^2 \text{ kJ}$ (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] mol L ⁻¹	[B ₂] mol L ⁻¹	Rate mol L ⁻¹ min ⁻¹
0.5	1.0	2.5×10^{-3}
1.0	1.0	5.0×10^{-3}
0.5	2.0	1×10^{-2}

Hence the order of reaction w.r.t. A and B₂ 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)

$$\frac{2.5 \times 10^{-3}}{1 \times 10^{-2}} = \left(\frac{1.0}{2.0} \right)^\beta$$

$$\frac{1}{4} = \left(\frac{1}{2} \right)^\beta$$

$$\beta = 2$$

Problem 14 :

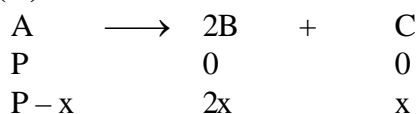
For the first order reaction $A_{(g)} \rightarrow 2B_{(g)} + C_{(g)}$, the initial pressure is $P_A = 90 \text{ mm Hg}$, the pressure after 10 minutes is found to be 180 mm Hg. The rate constant of the reaction is :

(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

$$180 = P - x + 2x + x$$

$$180 = 90 + 2x$$

$$2x = 90, x = 45$$

$$K = \frac{2.303}{t} \log \frac{P}{P-x} = \frac{2.303}{10} \log \frac{90}{90-45} = \frac{2.303}{10} \log 2 = \frac{0.6932}{10}$$

$$= 0.6932 = \frac{0.6932}{60} = 1.1555 \times 10^{-3} \text{ sec}^{-1}$$

ASSIGNMENTS

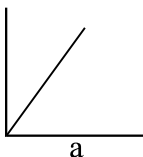
OBJECTIVE QUESTIONS

Level – I

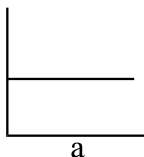
- Q.1** The rate of the simple reaction $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$, when the volume of the reaction vessel is doubled—
 (A) will grow eight times of its initial rate (B) rate reduce to one-eights of its initial rate
 (C) will grow four times of its initial rate (D) reduce to one-fourth of its initial rate
- Q.2** The rate expression for the reaction $\text{A}(\text{g}) + \text{B}(\text{g}) \rightarrow \text{C}(\text{g})$ is $\text{rate} = \text{K} \text{C}_\text{A}^2 \text{C}_\text{B}^{1/2}$. What changes in the initial concentration of A and B will cause the rate of reaction increase by a factor of eight
 (A) $\text{C}_\text{A} \times 2$; $\text{C}_\text{B} \times 2$ (B) $\text{C}_\text{A} \times 2$; $\text{C}_\text{B} \times 4$ (C) $\text{C}_\text{A} \times 1$; $\text{C}_\text{B} \times 4$ (D) $\text{C}_\text{A} \times 4$; $\text{C}_\text{B} \times 1$
- Q.3** Given that k is the rate constant for some order of any reaction at temperature T, then the value of $T \xrightarrow{\lim} \infty \log k$, (where A is the Arrhenius constant) is –
 (A) $A/2.303$ (B) A (C) $2.303A$ (D) $\log A$
- Q.4** According to the Arrhenius equation a straight line is to be obtained by plotting the logarithm of the rate constant of a chemical reaction ($\log k$) against –
 (A) T (B) $\log T$ (C) $1/T$ (D) $\log 1/T$
- Q.5** Select the rate law that corresponds to the data shown for the following reaction :
 $\text{A} + \text{B} \longrightarrow \text{C}$

Expt. No.	$[\text{A}]_0$	$[\text{B}]_0$	initial rate
1.	0.012	0.035	0.10
2.	0.024	0.070	0.80
3.	0.024	0.035	0.10
4.	1.012	0.070	0.80

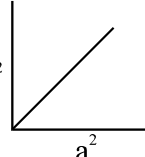
- (A) $\text{rate} = k[\text{B}]^3$ (B) $\text{rate} = k[\text{B}]^4$ (C) $\text{rate} = k[\text{A}][\text{B}]^3$ (D) $\text{rate} = k[\text{A}]^2[\text{B}]^2$
- Q.6** If in the fermentation of sugar in an enzymatic solution that is 0.12 M, the concentration of the sugar is reduced to 0.06 M in 10h to 0.03 M in 20 h, what is the order of the reaction :
 (A) 1 (B) 2 (C) 3 (D) 0
- Q.7** Which of the following curves represents a 1st order reaction :
- (A)



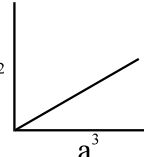
(B)



(C)



(D)


- Q.8** Rate constant of a reaction with a virus is $3.3 \times 10^{-4} \text{s}^{-1}$. Time required for the virus to become 75% to activate is :
 (A) 35 min (B) 70 min (C) 105 min (D) 175 min

- Q.9** Inversion of a sugar follows first order rate equation which can be followed by noting the change in rotation of the plane of polarization of light in the polarimeter. Of r_∞ , r_t and r_0 are the rotation at $t \rightarrow \infty$, $t = t$ and $t = 0$, then first order reaction can be written as –
- (A) $k = \frac{1}{t} \ln \frac{r_t - r_\infty}{r_0 - r_\infty}$ (B) $k = \frac{1}{t} \ln \frac{r_0 - r_\infty}{r_t - r_\infty}$ (C) $k = \frac{1}{t} \ln \frac{r_0}{r_t}$ (D) $k = \frac{1}{t} \ln \frac{r_\infty - r_t}{r_\infty - r_0}$
- Q.10** The half life period of a first order reaction, $A \rightarrow \text{Product}$ is 10 minutes. In what period of time is the concentration of A is reduced to 10% of the original concentration :
- (A) 26 min (B) 33 min (C) 71 min (D) 90 min
- Q.11** For the reaction $B + 2D \rightarrow 3T$, $-\frac{dC_B}{dt} = kC_B C_D^2$. The expression for, $-\frac{dC_D}{dt}$ will be :
- (A) $2k C_B C_D^2$ (B) $\frac{1}{2} k C_B C_D^2$ (C) $4k C_B C_D^2$ (D) $\frac{1}{4} k C_B C_D^2$
- Q.12** For a given reaction of first order, it takes 20 minutes for the concentration to drop from 1.0 M to 0.6 M. The time required for the concentration to drop from 0.6 M to 0.36 M will be :
- (A) more than 20 minutes (B) less than 20 minutes
(C) equal to 20 minutes (D) infinity
- Q.13** Time required to decompose half of the substance for nth order reaction is inversely proportional to :
- (A) a^{n+1} (B) a^{n-1} (C) a^{n-2} (D) a^n
- Q.14** $A \rightarrow B$, $\Delta H = -10 \text{ kJ mol}^{-1}$, $E_a = 50 \text{ kJ mol}^{-1}$, then E_a of $B \rightarrow A$ will be :
- (A) 40 kJ mol^{-1} (B) 50 kJ mol^{-1} (C) -50 kJ mol^{-1} (D) 60 kJ mol^{-1}
- Q.15** If for any reaction, the rate constant is equal to the rate of the reaction at all concentration. The order is :
- (A) 0 (B) 2 (C) 1 (D) 3
- Q.16** For a given reaction the concentration of the reactant plotted against time gave a straight line with negative slope. The order of the reaction is :
- (A) 3 (B) 2 (C) 1 (D) 0
- Q.17** What is the order of a chemical reaction $A + 2B \xrightarrow{k} C$. If the rate of formation of C increases by a factor of 2.82 on doubling the concentration of A and increases by a factor of 9 on tripling the concentration of B.
- (A) $7/2$ (B) $7/4$ (C) $5/2$ (D) $5/4$
- Q.18** When a β -particle is emitted by the atom of a radioactive element, the new species formed possesses:
- (A) same atomic mass and atomic number less by one unit
(B) same atomic mass and atomic number less by two units
(C) same atomic mass and atomic number higher by one unit
(D) same atomic mass and atomic number higher by two units
- Q.19** The number of α - and β -particle emitted in the nuclear reaction ${}_{90}^{228}\text{Th} \rightarrow {}_{83}^{212}\text{Bi}$ are :
- (A) $8\alpha, 1\beta$ (B) $4\alpha, 7\beta$ (C) $3\alpha, 7\beta$ (D) $4\alpha, 1\beta$

- Q.20** A radioactive element A on disintegration gives two elements B and C., If B is helium and C is the element of atomic number 90 and atomic mass 234, the element A is :
- (A) ${}_{92}^{238}\text{U}$ (B) ${}_{88}^{234}\text{Ra}$ (C) ${}_{90}^{234}\text{Sc}$ (D) ${}_{91}^{234}\text{Pa}$
- Q.21** The number of α -particles emitted per second by 1 g of ${}^{226}\text{Ra}$ is 3.7×10^{10} . The decay constant is
(A) $1.39 \times 10^{-11} \text{ sec}^{-1}$ (B) $13.9 \times 10^{-11} \text{ sec}^{-1}$ (C) $139 \times 10^{-10} \text{ sec}^{-1}$ (D) $13.9 \times 10^{-10} \text{ sec}^{-1}$
- Q.22** One curie of activity is equivalent to :
(A) 3.7×10^{17} disintegrations per sec (B) 3.7×10^{10} disintegrations per sec
(C) 3.7×10^{14} disintegrations per sec (D) 3.7×10^3 disintegrations per sec
- Q.23** Radioactivity of a radioactive element remains 1/10 of the original radioactivity after 2.303 seconds. The half life period is :
(A) 2.303 (B) 0.2303 (C) 0.693 (D) 0.0693
- Q.24** The half life periods of four isotopes are given below :
(i) 7.6 years (ii) 4000 years, (iii) 6000 years (iv) 3.2×10^5 years
Which of the above isotopes is most stable ?
(A) iv (B) iii (C) ii (D) i
- Q.25** Which of the following transformations is not correct ?
(A) ${}_{33}^{75}\text{As} + {}_2^4\text{He} \longrightarrow {}_{35}^{78}\text{Br} + {}_0^1\text{n}$ (B) ${}_3^7\text{Li} + {}_1^1\text{H} \longrightarrow {}_4^7\text{Be} + {}_0^1\text{n}$
(C) ${}_{21}^{45}\text{Sc} + {}_0^1\text{n} \longrightarrow {}_{20}^{45}\text{Ca} + {}_0^1\text{n}$ (D) ${}_{83}^{209}\text{Bi} + {}_1^2\text{H} \longrightarrow {}_{84}^{210}\text{Po} + {}_0^1\text{n}$
- Q.26** A sample of rock from moon contains equal number of atoms of uranium and lead ($t_{1/2}$ for U = 4.5×10^9 years). The age of the rock would be :
(A) 9.0×10^9 years (B) 4.5×10^9 years (C) 13.5×10^9 years (D) 2.25×10^9 years

Level – II

- Q.1** The rate of reaction becomes 2 times for every 10°C rise in temperature. How the rate of reaction will increase when temperature is increased from 30°C to 80°C :
 (A) 16 (B) 32 (C) 64 (D) 128

- Q.2** For the consecutive unimolecular-type first order reaction $A \xrightarrow{k_1} R \xrightarrow{k_2} S$, the concentration of component R, C_R at any time t is given by :

$$C_R = C_{AO} K_1 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)} \right]$$

if $C_A = C_{AO}$, $C_R = C_{RO} = 0$ at $t = 0$

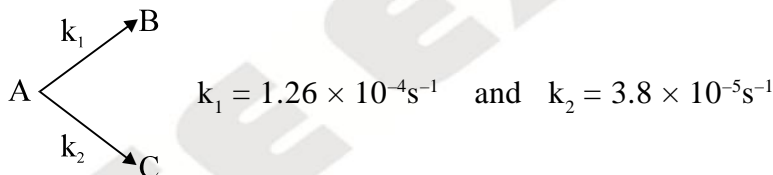
the time at which the maximum concentration of R occurs is :

(A) $t_{\max} = \frac{k_2 - k_1}{\ln(k_2/k_1)}$ (B) $t_{\max} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$ (C) $t_{\max} = \frac{e^{k_2/k_1}}{k_2 - k_1}$ (D) $t_{\max} = \frac{e^{k_2 - k_1}}{k_2 - k_1}$

- Q.3** A consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ is characterised by –
 (A) maxima in the concentration of A (B) maxima in the concentration of B
 (C) maxima in the concentration of C (D) high exothermicity

- Q.4** For the chemical reaction $A + B + C \xrightarrow{k} D$, it was found that the rate of the reaction doubled when the concentration of B was doubled, that the rate of reaction doubled when the concentration of both A and B were doubled, and quadrupled when the concentration of both B and C were doubled. The order of the reaction is :
 (A) 2 (B) 3 (C) 4 (D) 6

- Q.5** A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as :



The percentage distributions of B and C are :

- (A) 80% B and 20% C (B) 76.83% B and 23.17 % C
 (C) 90% B and 10% C (D) 60% B and 40% C
- Q.6** For a gas reaction at T(K) the rate is given by – $\frac{dp_A}{dt} = k' p_A^2$ atm/hr. If the rate equation is

expressed as : $-r_A = -\frac{1}{V} \frac{dN_A}{dt} = k C_A^2$, mol/(litre-hr), the rate constant k is given by –

- (A) $k = k'$ (B) $k = k' RT$ (C) $k = k'/RT$ (D) $k = k'(RT)^2$
 where R = ideal gas law constant, cal/g mol K.

- Q.7** The activation energies of two reactions are E_{a1} and E_{a2} with $E_{a1} > E_{a2}$. If the temperature of the reacting system is increased from T_1 to T_2 predict which of the following alternative is correct

(A) $\frac{K'_1}{K_1} = \frac{K'_2}{K_2}$ (B) $\frac{K'_1}{K_1} > \frac{K'_2}{K_2}$ (C) $\frac{K'_1}{K_1} < \frac{K'_2}{K_2}$ (D) $\frac{K'_1}{K_1} < 2 \frac{K'_2}{K_2}$

- Q.8** The reaction $\nu_1 A + \nu_2 B \rightarrow \text{products}$ is first order with respect to A and zero-order with respect to B. If the reaction is started with $[A]_0$ and $[B]_0$, the integrated rate expression of this reaction would be –

(A) $\ln \frac{[A]_0}{[A]_0 - x} = k_1 t$ (B) $\ln \frac{[A]_0}{[A]_0 - \nu_1 x} = \nu_1 k_1 t$
 (C) $\ln \frac{[A]_0}{[A]_0 - \nu_1 x} = k_1 t$ (D) $\ln \frac{[A]_0}{[A]_0 - \nu_1 x} = -\nu_1 k_1 t$

- Q.9** When the mechanism of reaction is not known, one often attempts to fit the data with an n^{th} order rate equation of the form

$$-r_A = -\frac{dC_A}{dt} = kC_A^n$$

for $n \neq 1$, the integration of this equation yields –

(A) $C_A^{1+n} - C_{A_0}^{1+n} = (1+n)kt$ (B) $C_A^{1-n} - C_{A_0}^{1-n} = (1-n)kt$
 (C) $C_A^{1-n} - C_{A_0}^{1-n} = (n-1)kt$ (D) $C_A^{1-n} - C_{A_0}^{1-n} = kt/(n-1)$

- Q.10** For the chemical reaction $A \rightarrow \text{products}$, the rate of disappearance of A is given by :

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A / (1 + k_2 C_A)$$

At low C_A the reaction is of the first-order with rate constant :

(A) k_1/k_2 (B) k_1 (C) $k_1 k_2$ (D) $k_1/(k_1 + k_2)$

- Q.11** A first order homogeneous reaction of the type $X \rightarrow Y \rightarrow Z$ (consecutive reaction) is carried out in a CSTR. Which of the following curves respectively show the variation of the concentration of X, Y and Z with time –

(A) I, II, II (B) III, II, I (C) III, I, II (D) II, III, I

- Q.12** For the consecutive unimolecular-type first order reaction $A \xrightarrow{k_1} R \xrightarrow{k_2} S$, the concentration of component A, C_A at any time t is given by –

(A) $C_A = C_{A_0} e^{(k_1+k_2)t}$ (B) $C_A = C_{A_0} e^{-(k_1+k_2)t}$ (C) $C_A = C_{A_0} e^{-k_1 t}$ (D) $C_A = C_{A_0} e^{k_1 t}$

- Q.13** The energy of activation for a reaction is 100 kJ/mol. Presence of a catalyst lowers the energy of activation by 75%. The ratio of $k_{\text{cat}}/k_{\text{uncat}}$ ($T = 298 \text{ K}$) –

(A) 23.4×10^{15} (B) 2.34×10^{13} (C) 1.324×10^5 (D) 3.25×10^6

- Q.14** For a certain reaction of order n , the time for half change, $t_{1/2}$, is given by $t_{1/2} = \frac{[2 - \sqrt{2}]}{k} \times C_0^{1/2}$

where k is the rate constant and C_0 is the initial concentration what is n :

(A) 1 (B) 2 (C) 0 (D) 0.5

- Q.15** In the Lindemann theory of unimolecular reactions, it is shown that the apparent rate constant

for such a reaction is $k_{\text{app}} = \frac{k_1 C}{1 + \alpha C}$ where C is the concentration of the reactant, k_1 and α are constants. Calculate the value of C for which k_{app} has 90% of its limiting value at C tending to infinitely large values, given $\alpha = 9 \times 10^5$.

(A) $10^{-6} \text{ mol/litre}$ (B) $10^{-4} \text{ mol/litre}$ (C) $10^{-5} \text{ mol/litre}$ (D) $5 \times 10^{-5} \text{ mol/litre}$

Q.16 Given that for a reaction of order n the integrated form of the rate equation is

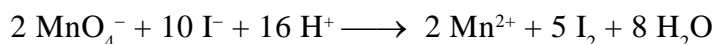
$k = \frac{1}{t(n-1)} \left[\frac{1}{C^{n-1}} - \frac{1}{C_0^{n-1}} \right]$ where C_0 and C are the values of the reactant concentration at the start and after time t . What is the relationship between $t_{3/4}$ and $t_{1/2}$ where $t_{3/4}$ is the time required for C to become $\frac{1}{4} C_0$:

- (A) $t_{3/4} = t_{1/2} [2^{n-1} + 1]$ (B) $t_{3/4} = t_{1/2} [2^{n-1} - 1]$
 (C) $t_{3/4} = t_{1/2} [2^{n+1} - 1]$ (D) $t_{3/4} = t_{1/2} [2^{n+1} + 1]$

Q.17 Rate constant of a reaction is 0.0693 min^{-1} . Starting with 10 mol, rate of the reaction after 10 min is :

- (A) $0.693 \text{ mol min}^{-1}$ (B) $0.0693 \times 2 \text{ mol min}^{-1}$
 (C) $0.0693 \times 5 \text{ mol min}^{-1}$ (D) $0.0693 \times (5)^2 \text{ mol min}^{-1}$

Q.18 The instantaneous rate of disappearance of the MnO_4^- ion in the following reaction is $4.56 \times 10^{-3} \text{ Ms}^{-1}$



The rate of appearance of I_2 is :

- (A) $1.14 \times 10^{-3} \text{ Ms}^{-1}$ (B) $5.7 \times 10^{-3} \text{ Ms}^{-1}$
 (C) $4.56 \times 10^{-4} \text{ Ms}^{-1}$ (D) $1.14 \times 10^{-2} \text{ Ms}^{-1}$

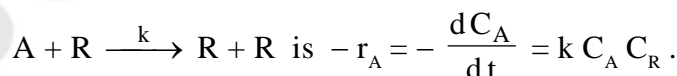
Q.19 Which of the following statements is not correct ?

- (A) Law of mass action and rate law expressions are same for single step reactions
 (B) Molecularity of the slowest elementary step of a complex reaction gives molecularity of reaction
 (C) Both order and molecularity have normally a maximum value of 3
 (D) Molecularity of a complex reaction $\text{A} + 2\text{B} \longrightarrow \text{C}$ is 3.

Q.20 Which of the following are correct ?

- (A) total collision rate \propto mean speed \propto absolute temperature
 (B) total collision rate $\propto \frac{1}{\text{mean speed}} \propto \frac{1}{\text{absolute temperature}}$
 (C) total collision rate \propto mean speed \propto (absolute temperature) $^{1/2}$
 (D) total collision rate \propto (mean speed) $^2 \propto$ (absolute temperature) 3

Q.21 The rate equation for an autocatalytic reaction ,



The rate of disappearance of reactant A is maximum where :

- (A) $C_{\text{A}} = 2 C_{\text{R}}$ (B) $C_{\text{A}} = C_{\text{R}}$ (C) $C_{\text{A}} = C_{\text{R}}/2$ (D) $C_{\text{A}} = (C_{\text{R}})^{1/2}$

Q.22 The decomposition of a gaseous substance A to yield gaseous products ,

$\text{A}(\text{g}) \longrightarrow 2 \text{B}(\text{g}) + \text{C}(\text{g})$ follows first order kinetics . If the total pressure at the start of an experiment & 9 minutes after the start are 169 mm and 221 mm , what is the rate constant ?

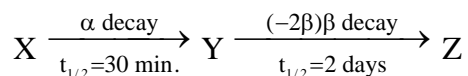
- (A) 0.6804 min^{-1} (B) 0.3024 min^{-1} (C) 0.4536 min^{-1} (D) 0.3780 min^{-1}

Q.23 The decay constant of ^{226}Ra is $1.37 \times 10^{-11} \text{ sec}^{-1}$. A sample of ^{226}Ra having an activity of 1.5 milli curie will contain atoms.

- (A) 4.05×10^{18} (B) 3.7×10^{17} (C) 2.05×10^{15} (D) 4.7×10^{10}

- Q.24** Which among the following is wrong about isodiaphers ?
 (A) they have the same difference of neutrons and protons or same isotopic number
 (B) nuclide and its decay product after α -emission are isodiaphers
 (C) ${}_Z A^m \longrightarrow {}_{Z-2} B^{m-4} + {}_2 \text{He}^4$ 'A' and 'B' are isodiaphers
 (D) all correct

- Q.25** A radioactive element decays as



which of the following statements about this decay process is incorrect ?

- (A) after two hours, less than 10% of the initial X is left
 (B) maximum amount of Y present at any time before 30 min is less than 50% of the initial amount of X.
 (C) atomic number of X and Z are same
 (D) the mass number of Y is greater than X
- Q.26** Among the following nuclides, the highest tendency to decay by (β^+) emission is –
 (A) Cu^{59} (B) ${}^{63}\text{Cu}$ (C) ${}^{67}\text{Cu}$ (D) ${}^{68}\text{Cu}$

Level – III

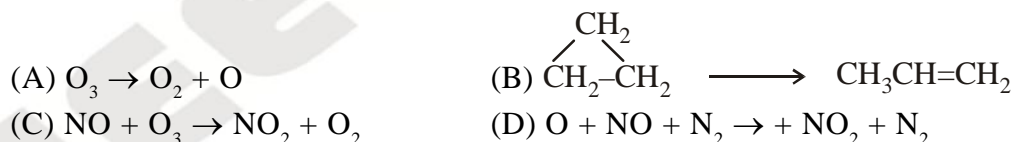
- Q.1** Which of the following statement are correct ?
- (A) The order of a reaction is the sum of the components of all the concentration terms in the rate equation.
- (B) The order of a reaction with respect to one reactant is the ratio of the change of logarithm of the rate of the reaction to the change in the logarithm of the concentration of the particular reactant, keeping the concentration all other reactants constant
- (C) Orders of reactions can be whole numbers or fractional numbers.
- (D) The order of a reaction can only be determined from the stoichiometric equation for the reaction.

- Q.2** Which of the following statements are correct ?
- (A) The rate of the reaction involving the conversion of ortho-hydrogen to parahydrogen is $-\frac{d[H_2]}{dt} = k[H_2]^{3/2}$
- (B) The rate of the reaction involving the thermal decomposition of acetaldehyde is $k[CH_3CHO]^{3/2}$
- (C) In the formation of phosgene gas from CO and Cl_2 , the rate of the reaction is $k[CO][Cl_2]^{1/2}$
- (D) In the decomposition of H_2O_2 , the rate of the reaction is $k[H_2O_2]$.

- Q.3** Which of the following isomerization reactions is of the first order ?
- (A) cyclopropane \rightarrow propane
- (B) cis-but-2-ene \rightarrow trans-but-2-ene
- (C) vinyl allyl ether \rightarrow pent-4-enal
- (D) $CH_3NC \rightarrow CH_3CN$

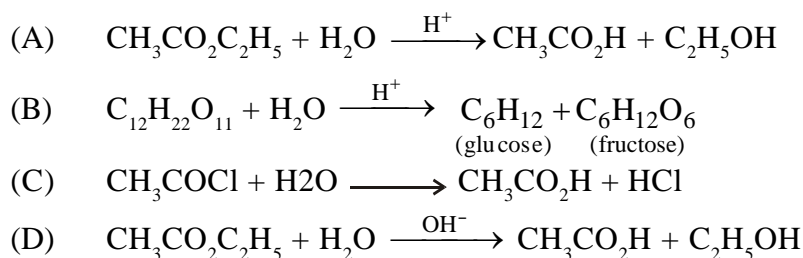
- Q.4** Which of the following reactions is of the first order ?
- (A) The decomposition of ammonium nitrate in an aqueous solution
- (B) The inversion of cane-sugar in the presence of an acid
- (C) The acidic hydrolysis of ethyl acetate
- (D) All radioactive decays.

- Q.5** Which of the following are examples of unimolecular reactions?



- Q.6** The calculation of the pre-exponential factor is based on the
- (A) idea that, for a reaction to take place, the reactant species must come together
- (B) Calculation of the molecularity of the reaction
- (C) idea that the reactant species must come together, leading to the formation of the transition state which then transforms into the products
- (D) calculation of the order of the reaction

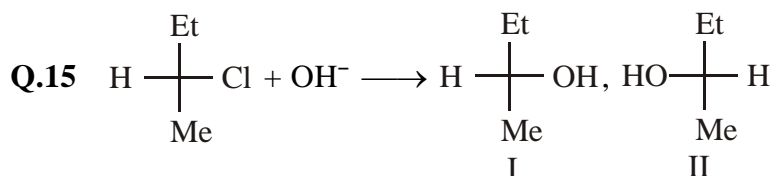
- Q.7** Which of the following are examples of pseudo-unimolecular reactions?



- Q.8** In which of the following ways does an activated complex differ from an ordinary molecule ?
 (A) It is quite unstable and has no independent existence.
 (B) ΔH°_f is probably positive
 (C) The system has a greater vibrational character.
 (D) The system has no vibrational character.
- Q.9** The basic theory behind Arrhenius's equation is that
 (A) the number of effective collisions is proportional to the number of molecules above a certain threshold energy
 (B) as the temperature increases, so does the number of molecules with energies exceeding the threshold energy.
 (C) the rate constant is function of temperature.
 (D) the activation energy and pre-exponential factor are always temperature-independent
- Q.10** In arrhenius's equation, $k = A \exp \left(-\frac{E_a}{RT} \right)$. A may be termed as the rate constant at
 (A) very low temperature (B) very high temperature
 (C) zero activation energy (D) the boiling temperature of the reaction mixture
- Q.11** Which of the following statements are correct about half-life period.
 (A) It is proportional to initial concentration for zeroth order.
 (B) average life = 1.44 half-life for first order reaction
 (C) time of 75% reaction is thrice of half-life period in second order reaction
 (D) 99.9% reaction takes place in 100 minutes for the case when rate constant is 0.0693 min^{-1}
- Q.12** $\text{Zn} + 2\text{H}^+ \longrightarrow \text{Zn}^{2+} + \text{H}_2$
 Half-life period is independent of concentration of zinc at constant pH. For the constant concentration of Zn, rate becomes 100 times when pH is decreased from 3 to 2. Hence
 (A) $\frac{dx}{dt} = k[\text{Zn}]^0[\text{H}^+]^2$ (B) $\left(\frac{dx}{dt} \right) = k [\text{Zn}] [\text{H}^+]^2$
 (C) rate is not affected if concentration of zinc is made four times and that of H^+ ions is halved.
 (D) rate becomes four times if concentration of H^+ ion is doubled at constant Zn concentration,.
- Q.13.** In which of the following case, E_a of the backward reaction is greater than that of the forward reaction?
 (A) $\text{A} + 10 \text{ kcal} \longrightarrow \text{B}$, $E_a = 50 \text{ kcal}$ (B) $\text{A} + 20 \text{ kcal} \longrightarrow \text{B}$, $E_a = 40 \text{ kcal}$
 (C) $\text{A} + 40 \text{ kcal} \longrightarrow \text{B}$, $E_a = 10 \text{ kcal}$ (D) $\text{A} - 40 \text{ kcal} \longrightarrow \text{B}$, $E_a = 20 \text{ kcal}$
- Q.14** $\text{A} \longrightarrow \text{B} + \text{C}$
 (g) (g) (g)

$$\frac{-d[\text{A}]}{dt} = k[\text{A}]$$

 At the starting pressure is 100 mm and after 10 min, pressure is 120 mm. hence rate constant (min^{-1}) is:
 (A) $\frac{2.303}{10} \log \frac{120}{100}$ (B) $\frac{2.303}{10} \log \frac{100}{20}$ (C) $\frac{2.303}{10} \log \frac{100}{80}$ (D) $\frac{2.303}{10} \log \frac{100}{120}$



Which of the following statements are correct?

- (A) it is unimolecular nucleophilic substitution reaction S_N1 if I or II is formed.
- (B) it is bimolecular nucleophilic substitution reaction S_N2 if I or II is formed.
- (C) it is S_N1 if I and its enantiomer are formed so that mixture is racemic.
- (D) it is S_N2 if II is formed.

Q.16 The reaction, $A(g) + 2B(g) \longrightarrow C(g) + D(g)$

Initial pressure of A and B are respectively $p_A = 0.60 \text{ atm}$, $p_B = 0.80 \text{ atm}$. When $p_C = 0.20 \text{ atm}$, the rate of the reaction relative to the initial rate, is

- (A) $\frac{1}{48}$ (B) $\frac{1}{24}$ (C) $\frac{1}{6}$ (D) $\frac{1}{4}$

Q.17 Rate constant k varies with temperature by eqn:

$$\log k (\text{min}^{-1}) = 5 - \frac{2000 \text{ K}}{T}. \text{ We can conclude}$$

- (A) pre-exponential factor A is 5
(B) E_a is 2000 kcal
(C) pre-exponential factor A is 10^5
(D) E_a is 9.212 kcal.

Q.18 The rate law for the dimerisation of NO_2 is

$$\frac{-d[\text{NO}_2]}{dt} = k [\text{NO}_2]^2$$

Which of the following changes will change the value of the specific rate constant, K :

- (A) Doubling the total pressure on the system
(B) doubling the temperature
(C) both
(D) none

Q.19 For a reaction for which the activation energies of the forward and reverse directions are equal in value:

- (A) the stoichiometry is the mechanism
(B) $\Delta H = 0$
(C) $\Delta S = 0$
(D) the order is zero.

Q.20 A reaction is catalysed by H^+ ion. In presence of H_A , rate constant is $2 \times 10^{-3} \text{ min}^{-1}$ and in presence of H_B rate constant is $1 \times 10^{-3} \text{ min}^{-1}$ H_A and H_B both being strong acids, we may conclude.

- (A) Equilibrium constant is 2
(B) H_A is stronger than HB
(C) relative strength of HA and HB is 2
(D) HA is weaker than HB and relative strength is 0.5

Level – IV

Instruction: From Question (1 to 6) match the items under Column (A) with items under Column (B). Select the correct answer from the sets (A), (B), (C) and (D).

1. Match the following

Column A

(i) Half life of first order reaction

(ii) Arrhenius equation

(iii) Molar concentration

(iv) Half life period of zero order reaction

(A) i-b, ii-a, iii-d, iv-c

(C) i-c, ii-b, iii-a, iv-d

Column B

(a) Active mass

(b) $Ae^{-E_a/RT}$

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

(d) $\frac{a}{2k}$

(B) i-a, ii-c, iii-b, iv-d

(D) i-c, ii-b, iii-d, iv-a

2. Match the following

Column A

(i) Rate of reaction

(ii) $\frac{\Delta[A]}{\Delta t}$

(iii) Unit of rate of reaction

(A) i-c, ii-a, iii-b

(A) i-a, ii-c, iii-b

Column B

(a) $\text{Mol L}^{-1} \text{time}^{-1}$

(b) $\frac{dx}{dt}$

(c) Average rate of reaction

(B) i-a, ii-b, iii-c

(D) i-b, ii-c, iii-a

3. Match the following

Column A

(i) Zero order reaction

(ii) First order reaction

(iii) Second order reaction

(iv) Instantaneous rate

(v) Temperature coefficient

(vi) Rate equation for third order reaction

(vii) Acidic hydrolysis of ester

(A) i-e, ii-f, iii-g, iv-c, v-a, vi-d, vii-b

(C) i-e, ii-g, iii-f, iv-d, v-a, vi-c, vii-b

Column B

(a) $\frac{k_{t+10}}{k_t}$

(b) $\frac{dx}{dt}$

(c) $-\frac{dx}{dt} = k[A]^2[B]$

(d) $\text{H}_2 + \text{Cl}_2 \xrightarrow{h\nu} 2\text{HCl}$

(e) $\text{CH}_3\text{COOCH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{CH}_3\text{OH}$

(f) $2\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$

(g) Pseudo-unimolecular reaction

(B) i-d, ii-f, iii-e, iv-b, v-a, vi-c, vii-g

(D) i-b, ii-c, iii-a, iv-d, v-f, vi-g, vii-e

4. Match the following

**Column I
order****Column II
Rate reaction**

(i) Zero

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

(ii) One

(b) $k_0 = \frac{x}{t}$

(iii) Two

(c) $k_3 = \frac{x(2a-x)}{t.2a^2(a-x)^2}$

(iv) Three

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

(A) i-b, ii-d, iii-a, iv-c

(B) i-d, ii-b, iii-c, iv-a

(C) i-c, ii-a, iii-b, iv-d

(D) i-a, ii-b, iii-c, iv-d

5. Match the following

**Column I
Order****Column II
Value of $t_{0.5}$** **Column III
Unit of K**

(i) Zero

(a) $t_{0.5} = \frac{0.693}{k_1}$

(A) $1.\text{mole}^{-1}\text{time}^{-1}$

(ii) One

(b) $t_{0.5} = \frac{A}{2k_0}$

(B) time^{-1}

(iii) Two

(c) $t_{0.5} = \frac{3}{2k_3a^2}$

(C) $l^2.\text{mole}^2\text{time}^{-1}$

(iv) Three

(d) $t_{0.5} = \frac{1}{k_{2a}}$

(D) $\text{mol l}^{-1} \text{time}^{-1}$

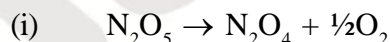
(A) i-b,D, ii-a,B, iii-d,A iv-c-C

(B) i-a,A, ii-c,B, iii-b,C iv-d-D

(C) i-c,C, ii-b,A, iii-a,B iv-d-D

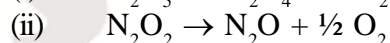
(A) i-d,B, ii-c,C, iii-b,D iv-a-A

6. Match the following

column I**Column II****Column II**

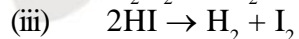
(a) Order = 3,

(A) molecularity = 2



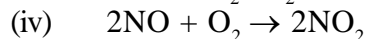
(b) Order = 2,

(B) molecularity = 3



(c) Order = 1,

(C) molecularity = 1



(d) Order = 1,

(D) molecularity = 1

(A) i-a,C, ii-b,D, iii-c,A, iv-d,B

(B) i-d,A, ii-c,B, iii-b,C, iv-a,D

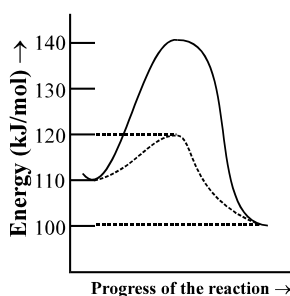
(C) i-c,C, ii-d,D, iii-a,B, iv-b,A

*(D) i-d,C, ii-c,D, iii-b,A, iv-a,B

SUBJECTIVE QUESTIONS

Level – I

- Q.1** 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 kJ mol^{-1} respectively. At what temperature, the reaction will have specific rate constant $1.1 \times 10^{-3} \text{ sec}^{-1}$?
- Q.2** The rate constant is given by Arrhenius equation, $k = Ae^{-E_a/RT}$ calculate the ratio of the catalysed and uncatalysed rate constants at 25°C if the energy of activation of a catalysed reaction is 162 kJ and for the uncatalysed reaction the value is 350 kJ .
- Q.3** 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.
- Q.4** The energy of activation for a reaction is 100 kJ mol^{-1} . Presence of a catalyst lowers the energy of activation by 75% . What will be effect on rate of reaction at 20°C , other things being equal.
- Q.5** The gas phase decomposition, $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$ follows the first order rate law. At a given temperature the rate constant of the reaction is $7.5 \times 10^{-3} \text{ s}^{-1}$. The initial pressure of N_2O_5 is 0.1 atm .
 (i) Calculate time of decomposition of N_2O_5 so that the total pressure becomes 0.15 atm .
 (ii) What will be the total pressure after 150 seconds ?
- Q.6** At a certain temperature the half change period for the catalytic decomposition of ammonia were found as follows : Calculate the order of reaction .
- Q.7** In hydrogenation reaction at 25°C , it is observed that hydrogen gas pressure falls from 2 atm to 1.2 atm in 50 min . Calculate the rate of reaction in molarity per sec. $R = 0.0821 \text{ litre atm degree}^{-1} \text{ mol}^{-1}$.
- Q.8** A drop of solution (volume 0.05 ml) contains $3 \times 10^{-6} \text{ mol H}^+$ ions. If the rate of disappearance of the H^+ ions is $1 \times 10^7 \text{ mol litre}^{-1} \text{ sec}^{-1}$, how long would it take for H^+ ions in the drop to disappear ?
- Q.9** Consider Fig. for a reaction, $\text{A}_2 + \text{B}_2 \rightleftharpoons 2\text{AB}$



- (a) Calculate ΔH of the reaction.
- (b) Calculate the energy of activation for forward and backward reaction.
- (c) The dotted line curve is the path in the presence of a catalyst. What is the energy of activation for the forward and backward reaction in the presence of the catalyst ?
 What is the lowering in activation energy in the presence of the catalyst ?
- (d) Will the catalyst change the extent of the reaction ?
- Q.10** 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 the rate constants 'k' in terms of p_0 , p and t . Assume the reaction to be first order.

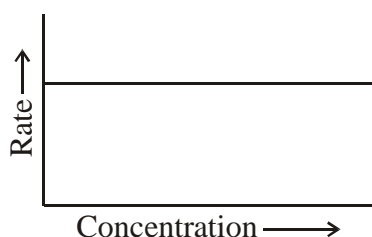
- Q.11** In the fission of ${}_{92}\text{U}^{235}$, 6% of the fission product is ${}_{42}\text{Mo}^{99}$. This material is radioactive and decays as follows :
- $${}_{42}\text{Mo}^{99} \longrightarrow \text{X} + {}_{43}\text{Tc}^{99}$$
- $${}_{43}\text{Tc}^{99} \longrightarrow \text{X} + \text{Y}$$
- What are X & Y.
- Q.12** A radioactive element (A) of atomic weight 238 and atomic no. 92 loses 7α and 14β -particles. What will be approximate atomic weight of last element B ? How would it be related with original element ?
- Q.13** An atomic battery wrist watch uses ${}_{61}\text{Pm}^{147}$ as a source of β -particles ($t_{1/2} = 2.62$ year) for energy required for its operation. How long would it take for the rates of β -emission in the battery to reduced by 5% of its original value ?
- Q.14** A sample contains 10^{-2} kg each of two substance A and B with half lives of 4 and 8 second respectively. The atomic weight of A and B are in the ratio of 1 : 2. Find the amount of A and B after an interval of 16 second. Also report the ratio of initial rates of decay of these two.
- Q.15** The lowest level C^{14} activity for experimental detection is 0.03 dis/min/g of C^{14} . What is the maximum age of an object that can be determined by C^{14} method ? The activity of C^{14} in atmosphere is 15 dis/min/g of C^{14} .
($t_{1/2}$ of $\text{C}^{14} = 5730$ year)
- Q.16** Complete the following nuclear reactions :
- | | |
|---|---|
| (a) ${}_4\text{Be}^9 + {}_2\text{He}^4 \longrightarrow {}_6\text{C}^{12} + \dots\dots\dots$ | (b) ${}_1\text{T}^3 + {}_1\text{D}^2 \longrightarrow {}_2\text{He}^4 + \dots\dots\dots$ |
| (c) ${}_7\text{N}^{14} + {}_2\text{He}^4 \longrightarrow {}_8\text{O}^{17} + \dots\dots\dots$ | (d) ${}_{92}\text{U}^{235} + {}_0\text{n}^1 \longrightarrow {}_{56}\text{Ba}^{137} + {}_{36}\text{Kr}^{93} + \dots\dots\dots$ |
| (e) ${}_{29}\text{Cu}^{53} \longrightarrow {}_{28}\text{Ni}^{53} + \dots\dots\dots$ | (f) $2 {}_1\text{H}^3 \longrightarrow {}_2\text{He}^4 + \dots\dots\dots$ |
- Q.17** Write equation for the following transformations :
- | | |
|--|---|
| (a) ${}_7\text{N}^{14} (\text{n}, \text{p})$ | (b) ${}_{19}\text{K}^{39} (\text{p}, \alpha)$ |
|--|---|
- Q.18** Calculate the no. of neutrons in the product obtained in the following transformation :
- $${}_{92}\text{X}^{238} \longrightarrow \text{A} + {}_2\text{He}^4$$
- Q.19** To which radioactive series the following appears during disintegrations :
- $${}_{89}\text{Ac}^{228} ; {}_{89}\text{Ac}^{227}$$
- Q.20** Atoms ${}_7\text{A}$, ${}_8\text{B}$ and ${}_9\text{C}^{17}$ are such that ${}_8\text{B}$ is an isobar of ${}_7\text{A}$ and atom ${}_9\text{C}^{17}$ is isotone to ${}_8\text{B}$. Calculate the mass no. for A and B.

- Q.11** The isotopes ^{238}U and ^{235}U occurs in nature in the ratio of 140 : 1. Assuming that at the time of earth formation, they were present in equal ratio, make an estimation of the age of earth. The half life period of ^{238}U and ^{235}U are 4.5×10^9 and 7.13×10^8 years respectively.
- Q.12** A solution contains 1 millicurie of L-phenyl alanine C^{14} (uniformly labbled) in 2.0 mL solution. The activity of labelled sample is given as 150 milli curie/milli mole. Calculate :
(a) the concentration of sample in the solution in mole/litre
(b) the activity of the solution in terms of counting per minute/mL at a counting efficiency of 80%
- Q.13** A mixture of Pu^{239} and Pu^{240} has a specific activity of 6×10^9 dps per g sample. The half lives of the isotopes are 2.44×10^4 year and 6.58×10^3 years respectively. Calculate the composition of mixture.
- Q.14** The half life of ^{212}Pb is 10.6 hours. It undergoes decay to its daughter (unstable) element ^{212}Bi of half life 60.5 minute. Calculate the time at which the daughter element will have maximum activity ?
- Q.15** All naturally occurring rubidium ores contain ^{87}Sr resulted from the beta decay of ^{87}Rb , i.e., $^{87}_{37}\text{Rb} \longrightarrow ^{87}_{38}\text{Sr} + {}_{-1}^0\text{e}$.
In naturally occurring rubidium, 278 of every 1000 rubidium atoms are ^{87}Rb . A mineral containing 0.85% Rb was analysed and found to contain 0.0089% Sr. Assuming that all of the strontium originated by radioactive decay of ^{87}Rb , estimate the age of mineral. Half life of ^{87}Rb is 4.7×10^{10} year
- Q.16** $^{235}_{92}\text{U}$ has a half life of 7.1×10^8 year and its daughter element $^{231}_{90}\text{Th}$ has half life of 24.6 hr. What is the mass of $^{231}_{90}\text{Th}$ in equilibrium with 1g $^{235}_{92}\text{U}$?
- Q.17** The mean lives of a radioactive substance are 1620 year and 405 year for α -emission and β -emission respectively. Find out the time during which three fourth of a sample will decay if it is decaying both by α -emission and β -emission simultaneously.

Level-III

CBSE QUESTION

- Q.1** How the concentration of reactant influenced the rate of reaction [1982, 83]
- Q.2** The reaction $\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ is first order with respect to N_2O_5 . Its rate constant is $6.2 \times 10^{-6} \text{ s}^{-1}$. If in the beginning $[\text{N}_2\text{O}_5]$ is 15 mol L^{-1} , calculate the rate of reaction in the beginning. [1990]
- Q.3** Define rate of reaction. [1992]
- Q.4** Identify the reaction order if the unit of the rate constant is sec^{-1} . [1992]
- Q.5** The reaction $\text{A} + 2\text{B} \longrightarrow \text{C}$ obeys the rate equation, $\text{Rate} = \text{K}[\text{A}]^{1/2} [\text{B}]^{3/2}$. What is the order of the reaction. [1992]
- Q.6** According to Arrhenius hypothesis rate of reaction increases with increase in temperature. Give reason. [1992]
- Q.7** State Einstein's law of photochemical equivalence. [1992]
- Q.8** For a first order reaction, it takes 5 minutes for the initial concentration of 0.6 mol L^{-1} to become 0.4 mol L^{-1} . How long in all, it take for initial concentration to become 0.3 mol L^{-1} . [1993]
- Q.9** State two factors which affect the rate of a chemical reaction. [1993]
- Q.10** What is the usefulness of initial rate method. [1993]
- Q.11** The rate constant of a reaction with respect to reactant A is 6 min^{-1} . If we start with $[\text{A}] = 0.8 \text{ mol L}^{-1}$, when would $[\text{A}]$ reach the value of 0.08 mol L^{-1} . [1991, 1994]
- Q.12** The rate constant of the reaction is $2 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$. What is the order of reaction [1996]
- Q.13** Following graph is a plot of the rate of a reaction vs concentration of the reactant. What is the order of the reaction [1996]



- Q.14** The slope of the line in a graph of $\log k$ (k = rate constant) versus $1/T$ for a reaction is -5841 K . Calculate the energy of activation for this reaction. [$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$] [1997]
- Q.15** What do you mean by order of reaction? How is it different from molecularity ? [1998]
- Q.16** The decomposition of N_2O_5 in CCl_4 solution follows the first order rate law. The concentrations of N_2O_5 measured at different time intervals are given below:
- | | | | | | | | |
|--|-----|-----|-----|-----|-----|------|------|
| Time in second (t) | 0 | 80 | 160 | 410 | 600 | 1130 | 1720 |
| $[\text{N}_2\text{O}_5] \text{ mol/L}$ | 5.5 | 5.0 | 4.8 | 4.0 | 3.4 | 2.4 | 1.6 |
- Calculate its rate constant at $t = 410$ and $t = 1130 \text{ s}$. What do these result show ? [1998]

- Q.17** A first order reaction is 20% complete in 10 minutes. Calculate the time taken by the reaction for 75 % completion. [1998]
- Q.18** Find the two third life, $t_{2/3}$, of a first order reaction in which $k = 5.4 \times 10^{-14} \text{ s}^{-1}$. [1999]
- Q.19** The catalytic decomposition of H_2O was studied by titrating it at different time intervals with KMnO_4 solution. Calculate the rate constant from the following data assuming the reactions to be the first order. [1999]
- Q.20** The decomposition of phosphine, $4\text{PH}_3(\text{g}) \rightarrow \text{P}_4 + 6\text{H}_2(\text{g})$ has rate law $\text{rate} = k [\text{PH}_3]$. The rate constant is $6.0 \times 10^{-4} \text{ s}^{-1}$ at 300K and activation energy is $3.05 \times 10^5 \text{ J mol}^{-1}$. What is the value of rate constant at 310 K ? [$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$] [1999]
- Q.21** The rate of a particular reaction doubles when temperature changes from 27°C to 37°C. Calculate the energy of activation for such a reaction [$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$] [1992, 1999]
- Q.22** Distinguish between reaction rate and reaction rate constant (specific reaction rate) of a reaction. [1986, 1987, Comptt.89, 1998, 2000 Comptt.]
- Q.23** Give one example of photochemical reaction. [2000]
- Q.24** For the reaction $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$, how are the rate of reaction $\frac{-d[\text{H}_2]}{dt}$ and $\frac{d[\text{NH}_3]}{dt}$ interrelated ? [2000]
- Q.25** The rate of reaction is given by: $\text{Rate} = k [\text{N}_2\text{O}_5]$. In this equation what does k stand for ? [2000]
- Q.26** Why is the instantaneous rate of a reaction does not change when a part of the reacting solution is taken out ? [2000]
- Q.27** Under what conditions does the rate of a reaction equal its rate constant? [2000]
- Q.28** A first order reaction is 20% complete in 10 minutes. Calculate the time for 75% completion of the reaction. [2000]
- Q.29** In general it is observed that the rate of a chemical reaction doubles with every 10° rise in temperature. If this generalization holds for a reaction in the temperature range 295 K to 305 K, what would be the value of activation energy for this reaction? ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$) [2000]
- Q.30** Show that the time required for the completion of $3/4^{\text{th}}$ reaction of first order is twice the time required for completion of $1/2$ of the reaction. [2000]
- Q.31** What is the effect of catalyst on activation energy ? Explain.

OR

- What aspect of the reaction is influenced by the presence of catalyst which increases the rate or possibility of the reaction ? [2001]
- Q.32** A reactant with initial concentration 'a' mol lit^{-1} follows zero order kinetic with a rate constant $k \text{ mol lit}^{-1} \text{ sec}^{-1}$. In how much time will the reaction go to completion ? [2001]
- Q.33** A reaction is 50% completed in 2 hour and 75% complete in 4 hours what is the order of the reaction.? [1996, 2001]

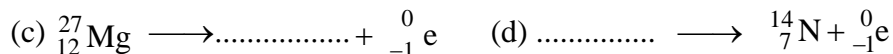
- Q.34** The reaction $\text{SO}_2\text{Cl}_2 \longrightarrow \text{SO}_2 + \text{Cl}_2$ is a first order reaction with $k = 2.2 \times 10^{-5} \text{ s}^{-1}$ at 320°C . Calculate the percentage of SO_2Cl_2 that is decomposed on heating this gas for 30 min. [2001]
- Q.35** Calculate the time required for the completion of 90% of a reaction of first order kinetics .
[$t_{1/2}$ reaction = 44.1 minutes] [2001]
- Q.36** The decomposition of compound is found to follow a first order rate law. If it takes 15 minutes for 20 per cent of original material to react. calculate :
(i) the specific rate constant
(ii) the time at which 10 per cent of the original material remains unreacted
(iii) the time it takes for the next 20 per cent of the reactant left to react after the first 15 minutes. [2002]
- Q.37** The rate constant of reaction is $1.5 \times 10^7 \text{ sec}^{-1}$ at 50°C and $4.5 \times 10^7 \text{ sec}^{-1}$ at 100°C . Calculate the value of activation energy, E_a for the reaction [$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$] [2003]
- Q.38** What are photochemical reactions ? Explain the mechanism of the photochemical reaction between hydrogen and chlorine gas. [2003]

[Radio Activity]

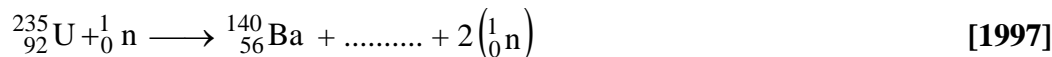
- Q.1** Complete the following reactions:
 ${}^{55}_{25}\text{Mn} (n, \gamma) \dots\dots;$ [1980]
- Q.2** Give the main differences between nuclear fission and fusion. [1991]
- Q.3** What is the main use of ${}^{14}_6\text{C} \longrightarrow {}^{14}_7\text{N} + {}^0_{-1}\text{e}$ nuclear disintegration? [1991]
- Q.4** How many α -particles and β -particles are emitted when ${}^{238}_{92}\text{U}$ changed to ${}^{230}_{90}\text{Th}$? [1992]
- Q.5** Write the principle of neutron activation analysis. [1992]
- Q.6** Name the major centres for research and development work in atomic energy in India. [1992, 1993]
- Q.7** Starting with 1.0 gm of a radioactive sample, 0.25 g of it is left after 5 days. Calculate the amount which was left after one day. [1993]
- Q.8** Calculate the energy released in the fusion reaction per atom of helium formed:
 ${}^2_1\text{H} + {}^3_1\text{H} \longrightarrow {}^4_2\text{He} + {}^1_0\text{n}$
Given the following masses:
 ${}^2_1\text{H} = 2.014$; ${}^3_1\text{H} = 3.016$; ${}^4_2\text{He} = 4.0303$; ${}^1_0\text{n} = 1.009$ [1994]
- Q.9** A radioactive substance is half disintegrated in 40 minutes. What is the time required for the decay of 75% of the element? [1994]
- Q.10** Complete the reaction ${}^7_3\text{Li} (\alpha, \dots\dots) \longrightarrow {}^8_3\text{Li}$ [1995]
- Q.11** Complete the following reaction : ${}^{14}_7\text{N} (n, \dots\dots) {}^{14}_6\text{C}$ [1995]
- Q.12** Fill in the blank: Alpha rays are fast moving..... nuclei. [1996]

Q.13 Fill in the blank: The radioactive series consisting of man made elements is filled..... [1996]

Q.14 Balance the following nuclear equations: [1997]



Q.15 Complete the following nuclear reaction



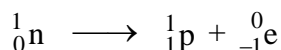
Q.16 Complete the following reactions:



Q.17 Complete the following : ${}^{23}_{11}\text{Na} + \dots\dots\dots \longrightarrow {}^{23}_{12}\text{Mg} + {}^1_0\text{n}.$ [1993, 1998]

Q.18 Why are fusion reactions in nuclear chemistry referred to as thermonuclear reactions? [1999]

Q.19 Calculate the energy change in J/mol for the nuclear reaction



[Given $m = 1.00728$ amu, $m_n = 1.00867$ amu and velocity of light in air, $c = 3 \times 10^8 \text{ ms}^{-1}$]

Q.20 Write nuclear reactions for the following transformation : [1999]



Q.21 (i) State the factors on which rate of radioactive decay depends.

(ii) Thorium isotope, ${}^{232}_{90}\text{Th}$, is an alpha particle emitter with a half-life of 1.41×10^{10} year.

Given a 0.25 g of sample of this thorium, how many α -particles will it emit per second.

($N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)

[1999]

Q.22 Explain the principle of radiocarbon dating. [1996, 1999]

Q.23 (i) What is the nuclear fission reaction?

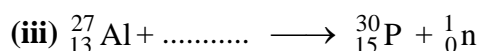
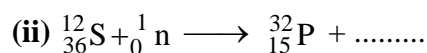
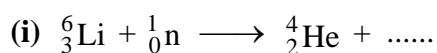
(ii) Describe the basic principle of a nuclear reactor.

[2000]

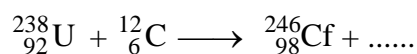
Q.24 (a) In what context is the term critical mass used?

(b) Starting with 1.0 g of a radioactive sample, 0.25 g of it is still left after 5 days. Calculate the amount which was left after one day. [2001]

Q.25 Complete the following nuclear reactions and name the type of nuclear transformation involved in each case [2002]



Q.26 Complete the nuclear equation [2003]



Q.27 Complete the nuclear equation



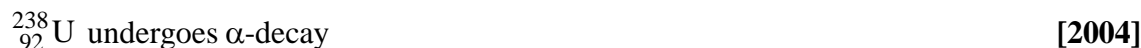
Q.28 Define the group displacement laws with example. [2004]

Q.29 Discuss the use of radioactive isotopes [2004]

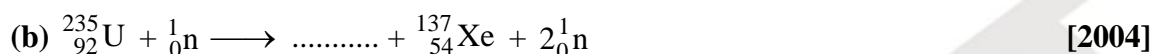
- (i) in studying reaction mechanism (ii) in the treatment of diseases
(iii) in agriculture.

Q.30 Give one example of each of (i) β^+ emission (ii) K-capture. [2004]

Q.31 Write the nuclear reactions for the following radioactive decay.

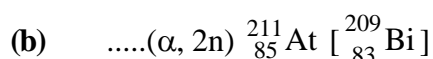


Q.32 Complete the equations for the following nuclear process:



Q.33 Discuss the principle of neutron activation analysis. [2004]

Q.34 Complete the following reactions:



Level-IV

JEE PROBLEMS

- Q.1** The rate of reaction between A and B increases by a factor of 100, when the concentration of A is increased 10 folds. The order of reaction with respect to A is : [1987]
(A) 10 (B) 2 (C) 1 (D) 20
- Q.2** For the reaction, $A + B \longrightarrow C$, the following data were obtained. In the first experiment, when the initial concentrations of both A and B are 0.1 M, the observed initial rate of formation of C is $1 \times 10^{-4} \text{ mol lit}^{-1} \text{ min}^{-1}$. In the second experiment when the initial concentration of A and B are 0.1 M and 0.3 M, the initial rate is $9.0 \times 10^{-4} \text{ mol litre}^{-1} \text{ minute}^{-1}$. In the third experiment when the initial conc. of both A & B are 0.3 M, initial rate is $2.7 \times 10^{-3} \text{ mol litre}^{-1} \text{ minute}^{-1}$. [1987]
(a) Write rate law for this reaction.
(b) Calculate the value of specific rate constant for this reaction.
- Q.3** A first order gaseous reactions has $K = 1.5 \times 10^{-6} \text{ sec}^{-1}$ at 200°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 ? [1987]
- Q.4** For a first order reaction, the rate of the reaction doubles as the concentration of the reactants double. [True/False] [1987]
- Q.5** Catalyst makes a reaction more exothermic .[True/False] [1987]
- Q.6** The rate of chemical change is directly proportional to _____. [1987]
- Q.7** The hydrolysis of ethyl ethanoate in _____ medium is a _____ order reaction. [1987]
- Q.8** The rate law for the reaction, $\text{RCl} + \text{NaOH(aq)} \longrightarrow \text{ROH} + \text{NaCl}$ is given by, $\text{Rate} = k[\text{RCl}]$. The rate of reaction will be – [1988]
(A) unaffected by increasing temperature of the reaction
(B) doubled on doubling the concentration of NaOH
(C) halved on reducing the concentration of NaOH to one half
(D) halved on reducing the concentration of RCl to one half
- Q.9** 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 ? [1988]
- Q.10** A 1st order reaction is 50 % complete in 30 minute at 27°C and in 10 minute at 47°C . Calculate the : [1988]
(a) Rate constant for reaction at 27°C and 47°C .
(b) Energy of activation for the reaction.
(c) Energy of activation for the reverse reaction if heat of reaction is -50 kJ mol^{-1} .
- Q.11** In the first order reaction, the concentration of reactant decreases from 1.0 M to 0.25 M in 20 minutes. The value of specific rate is – [1988]
(A) 69.32 (B) 6.932 (C) 0.6932 (D) 0.06932
- Q.12** 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 : [1989]
(a) the rate constant. (b) pressure of Cl_2O_7 after 100 sec.

- Q.13** The decolorization of KMnO_4 by oxalic acid is catalysed by [1989]
- Q.14** The half life of a first order reaction is 10 minutes. The time required for the concentration of the reactant to change from 0.08 M to 0.01 M is : [1990]
(A) 20 minutes (B) 30 minutes (C) 40 minutes (D) 50 minutes
- Q.15** The rate of an exothermic reaction increases with increase in temperature. [T/F] [1990]
- Q.16** In the Arrhenius equation for a certain reaction, the values of A and E_a (energy of activation) are $4 \times 10^{13} \text{ sec}^{-1}$ and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half life period be 10 minute ? [1990]
- Q.17** Catalytic decomposition of nitrous oxide by gold at 900°C at an initial pressure of 200 mm was 50 % in 53 minute and 73 % in 100 minute. [1990]
(a) What is the order of reaction ?
(b) Calculate velocity constant.
(c) How much will it decompose in 100 minute at the same temperature but at an initial pressure of 600 mm ?
- Q.18** The decomposition of N_2O_5 according to equation $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ is a first order reaction. After 30 minute from start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of reaction. [1991]
- Q.19** The experimental data for the reaction, $2\text{A} + \text{B}_2 \longrightarrow 2\text{AB}$ are as follows. Write probable rate expression. [1991]

[A]	[B ₂]	Rate
mol litre ⁻¹	mol litre ⁻¹	mol litre ⁻¹ sec ⁻¹
0.50	0.50	1.6×10^{-4}
0.50	1.0	3.2×10^{-4}
1.00	1.0	3.2×10^{-4}

- Q.20** Two reaction (I) $\text{A} \longrightarrow \text{Products}$ (II) $\text{B} \longrightarrow \text{Products}$ follows first order kinetics. The rate of the reaction (I) is doubled when temperature is raised from 300 K to 310 K. The half life for this reaction at 310 K is 30 minute. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (II) is half that of reaction (I). Calculate the rate constant of reaction (II) at 300 K. [1992]
- Q.21** What will be the initial rate of a reaction if its rate constant is 10^{-3} min^{-1} and the concentration of reactant is 0.2 mol dm^{-3} ? How much of reactant will be converted into products in 200 minute ? [1992]
- Q.22** The rate of a gaseous reaction is given by the expression $k \cdot [\text{A}] \cdot [\text{B}]$. If the volume of the reaction vessel is suddenly reduced to one fourth of the initial volume, the reaction rate relative to original rate will be— [1992]
(A) $\frac{1}{16}$ (B) $\frac{1}{8}$ (C) 8 (D) 16
- Q.23** The reaction $\text{L} \longrightarrow \text{M}$ is started with 10 g of L. After 30 and 90 minutes, 5 g and 1.25 g of L are left respectively. The order of reaction is : [1993]
(A) 0 (B) 2 (C) 1 (D) 3

Q.24 A first order reaction $A \rightarrow B$ requires activation energy of 70 kJ mol^{-1} . When a 20% solution of A was kept at 25°C for 20 minute, 25% decomposition took place. What will be the per cent decomposition in the same time in a 30% solution maintained at 40°C ? Assume that activation energy remains constant in this range of temperature? [1993]

Q.25 The data given below are for the reaction of NO and Cl_2 to form NOCl at 295 K. [1993]

$[\text{Cl}_2]$	$[\text{NO}]$	Initial rate ($\text{mol litre}^{-1} \text{ sec}^{-1}$)
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

- (a) What is the order w.r.t NO and Cl_2 in the reaction?
 (b) Write the rate expression.
 (c) Calculate the rate constant.
 (d) Determine the reaction rate when conc. of Cl_2 and NO are 0.2 M and 0.4 M respectively.

Q.26 A substance reacts according to I order kinetics and rate constant for the reaction is $1 \times 10^{-2} \text{ sec}^{-1}$. If its initial concentration is 1 M, [1993]

- (a) What is initial rate? (b) What is rate after 1 minute?

Q.27 The gas phase decomposition of dimethyl ether follows first order kinetics,



The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minute. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minute? Assume ideal gas behaviour. [1993]

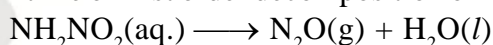
Q.28 The first order reaction has a half life period of 69.3 s. At 0.10 mol l^{-1} reactant concentration, the reaction rate will be : [1994]

- (A) $1.0 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$ (B) $1.0 \times 10^{-3} \text{ mol l}^{-1} \text{ s}^{-1}$
 (C) $1.0 \times 10^{-1} \text{ mol l}^{-1} \text{ s}^{-1}$ (D) $6.39 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$

Q.29 For the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is 0.001 kg h^{-1} . The rate of conversion of H_2 under the same condition is _____ kg h^{-1} . [1994]

- (A) 0.0017 kg h^{-1} (B) 0.002 kg h^{-1} (C) 0.003 kg h^{-1} (D) 0.005 kg h^{-1}

Q.30 The half time of first order decomposition of nitramide is 2.1 hour at 15°C . [1994]

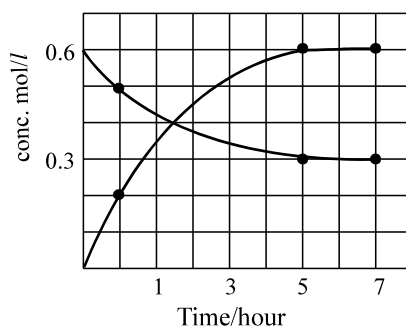


If 6.2 g of NH_2NO_2 is allowed to decompose, calculate

- (i) time taken for NH_2NO_2 to decompose 99%.
 (ii) volume of dry N_2O produced at this point measured at STP.

Q.31 The progress of reaction $A \rightleftharpoons nB$ with time is presented in the figure. Determine: [1994]

- (i) the value of n
 (ii) the equilibrium constant, K and
 (iii) the initial rate of conversion of A.



Q.32 From the following data from the reaction between A and B.

[1994]

[A] mol litre ⁻¹	[B] mol litre ⁻¹	Initial rate mol litre ⁻¹ sec ⁻¹	
		300 K	320 K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	-
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	-

Calculate :

- the order of reaction with respect to A and with respect to B.
- the rate constant at 300 K.
- the energy of activation.
- the pre-exponential factor.

Q.33 At 380 °C, the half life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol⁻¹. Calculate the time required for 75 % decomposition at 450°C.

[1995]

Q.34 The following data are for the reaction $\text{A} + \text{B} \longrightarrow \text{products}$:

[1995]

Conc. of A (M)	conc. of B (M)	Initial Rate (mol L ⁻¹ s ⁻¹)
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.1	1.0×10^{-2}
0.5	0.5	1.0×10^{-2}

- What is the order with respect to A and B for the reaction ?
- Calculate the rate constant.
- Determine the reaction rate when the concentrations of A and B are 0.2 M and 0.35 M respectively.

Q.35 The rate constant of a first order reaction is $4 \times 10^{-3} \text{ s}^{-1}$. At a reactant concentration of 0.02 mol ℓ^{-1} , the rate of reaction would be :

[1995]

- (A) $8 \times 10^{-5} \text{ mol } \ell^{-1} \text{ s}^{-1}$ (B) $4 \times 10^{-3} \text{ mol } \ell^{-1} \text{ s}^{-1}$
 (C) $2 \times 10^{-1} \text{ mol } \ell^{-1} \text{ s}^{-1}$ (D) $4 \times 10^{-1} \text{ mol } \ell^{-1} \text{ s}^{-1}$

Q.36 The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25 °C are $3.0 \times 10^{-4} \text{ s}^{-1}$, 104.4 kJ mol⁻¹ and $6.0 \times 10^{14} \text{ s}^{-1}$ respectively. The value of the rate constant as $T \longrightarrow \infty$ is :

[1996]

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

Q.37 The rate constant (k) for the reaction $2\text{A} + \text{B} \longrightarrow \text{Products}$, was found to be $2.58 \times 10^{-5} \ell \text{ mol}^{-1} \text{ s}^{-1}$ after 15 sec, $2.60 \times 10^{-5} \ell \text{ mol}^{-1} \text{ s}^{-1}$ after 30 sec and $2.55 \times 10^{-5} \ell \text{ mol}^{-1} \text{ s}^{-1}$ after 50 sec. Hence the order of the reaction is :

[1996]

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

- Q.38** The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25 % completion at 308 K. If the pre-exponential factor for the reaction is $3.56 \times 10^9 \text{ s}^{-1}$, calculate its rate constant at 318 K and also the energy of activation. [1997]
- Q.39** The rate constant for the first order decomposition of a certain reaction is given by the equation,
- $$\ln K(\text{sec}^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T}$$
- Calculate : [1997]
- (a) the energy of activation. (b) the rate constant at 500 K.
(c) At what temperature will its half life period be 256 minute ?
- Q.40** In the Arrhenius equation, $k = A \exp(-E/RT)$, A may be termed as the rate constant at : [1997]
- (A) $T = 0$ (B) $T = 298 \text{ K}$ (C) $T \rightarrow \infty$ (D) none
- Q.41** The rate constant of a first order reaction, $A \rightarrow \text{Products}$, is $60 \times 10^{-4} \text{ s}^{-1}$ its rate at $[A] = 0.01 \text{ mol l}^{-1}$ would be : [1997]
- (A) $60 \times 10^{-6} \text{ mol l}^{-1} \text{ min}^{-1}$ (B) $36 \times 10^{-4} \text{ mol l}^{-1} \text{ min}^{-1}$
(C) $60 \times 10^{-2} \text{ mol l}^{-1} \text{ min}^{-1}$ (D) $36 \times 10^{-1} \text{ mol l}^{-1} \text{ min}^{-1}$
- Q.42** For a first order reaction : [1998]
- (A) the degree of dissociation is equal to $(1 - e^{-kt})$
(B) a plot of reciprocal concentration of the reactant vs time gives a straight line
(C) the time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction
(D) the pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}
- Q.43** The rate constant of a reaction is $1.5 \times 10^7 \text{ sec}^{-1}$ at 50°C and $4.5 \times 10^7 \text{ sec}^{-1}$ at 100°C . Evaluate the Arrhenius parameters. A and E_a . [1998]
- Q.44** For a first order reaction $A \longrightarrow \text{Product}$, the rate of reaction at $[A] = 0.2 \text{ mol l}^{-1}$ is $1.0 \times 10^{-2} \text{ mol l}^{-1} \text{ min}^{-1}$. The half life period for the reaction is : [1999]
- (A) 832 s (B) 440 s (C) 416 s (D) 14 s
- Q.45** The rate constant for an isomerisation reaction, $A \longrightarrow B$ is $4.5 \times 10^{-3} \text{ min}^{-1}$. If the initial concentration of A is 1M, calculate the rate of the reaction after 1 hr. [1999]
- Q.46** The rate constant for the reaction, $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$ is $3.0 \times 10^{-5} \text{ s}^{-1}$. If the rate is $2.40 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$, then conc. of N_2O_5 (in mol L^{-1}) is – [2000]
- (A) 1.4 (B) 1.2 (C) 0.04 (D) 0.8
- Q.47** A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation energy barrier by 20 kJ mol^{-1} . [2000]
- Q.48** (a) In a reaction with initially 0.12 M, the concentration of reactant is reduced to 0.06 M in 10 hour and to 0.03 M in 20 hour. [2001]
- (i) What is order of reaction ? (ii) What is rate constant ?
(b) The rate of a first order reaction is $0.04 \text{ mol litre}^{-1} \text{ s}^{-1}$ at 10 minute and $0.03 \text{ mol litre}^{-1} \text{ s}^{-1}$ at 20 minute after initiation. Find the half life of the reaction.

- Q.49** If 'I' is the intensity of absorbed light and 'C' is the concentration of AB for the photochemical process $AB + h\nu \rightarrow AB^*$, rate of formation of AB^* is directly proportional to [2001]
 (A) C (B) I (C) I^2 (D) C.I.

- Q.50** Some $PH_3(g)$ is introduced into a flask at $600^\circ C$ containing an inert gas. PH_3 proceeds to decompose into $P_4(g)$ and $H_2(g)$ and the reaction goes to completion. The total pressure is given below as a function of time. Find the order of the reaction and calculate the rate constant. [2001]

Time (sec)	0	60	120	∞
P(mm Hg)	262.40	272.90	275.51	276.40

- Q.51** The vapour pressure of two miscible liquids A and B are 300 and 500 mm of Hg respectively. In a flask 10 moles of A is mixed with 12 moles of B. However, as soon as B is added, A starts polymerising into a completely insoluble solid. The polymerisation follows first order kinetics. After 100 minutes, 0.525 mole of a solute is dissolved which arrest the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation, and ideal behaviour for the final solution. [2001]

- Q.52** Consider the chemical reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$. The rate of this reaction can be expressed in terms of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions – [2002]

(A) $\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

(B) $\text{Rate} = -\frac{d[N_2]}{dt} = -3\frac{d[H_2]}{dt} = 2\frac{d[NH_3]}{dt}$

(C) $\text{Rate} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

(D) $\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{d[H_2]}{dt} = \frac{d[NH_3]}{dt}$

- Q.53** In a first order reaction the conc. of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in $2 \times 10^4 \text{ sec}$. The rate constant of reaction in sec^{-1} is – [2003]

(A) 2×10^4 (B) 3.45×10^{-5} (C) 1.386×10^{-4} (D) 2×10^{-4}

- Q.54** The reaction $X \longrightarrow \text{Product}$ follow first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M. Then the rate of reaction when concentration of X is 0.01 M. [2004]

(A) $1.73 \times 10^{-4} \text{ M min}^{-1}$ (B) $3.47 \times 10^{-5} \text{ M min}^{-1}$
 (C) $3.47 \times 10^{-4} \text{ M min}^{-1}$ (D) $1.73 \times 10^{-5} \text{ M min}^{-1}$

- Q.55** For the given reaction, $A + B \longrightarrow \text{Products}$ Following data were given [2004]

Initial conc. (m/L)	Initial conc. (m/L)	Initial rate [$\text{mL}^{-1}\text{s}^{-1}$]
[A]	[B]	
0.1	0.1	0.05
0.2	0.1	0.1
0.1	0.2	0.05

- (a) write the rate equations. (b) calculate the rate constant.

- Q.56** At constant temperature and volume, X decomposes as
 $2X(g) \longrightarrow 3Y(g) + 2Z(g)$; P_x is the partial pressure of X. [2005]

Observation No.	Time (in minute)	P_x (in mm of Hg)
1	0	800
2	100	400
3	200	200

- (i) What is the order of reaction with respect to X?
 (ii) Find the rate constant.
 (iii) Find the time for 75% completion of the reaction
 (iv) Find the total pressure when pressure of X is 700 mm of Hg.
- Q.57** Which one of the following statement for order of reaction is not correct ? [2005]
 (A) Order can be determined experimentally
 (B) Order of reaction is equal to sum of the powers of concentration terms in differential rate law.
 (C) It is not affected with the stoichiometric coefficient of the reactants
 (D) Order cannot be fractional.
- Q.58.** $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)^+]$; $k_1 = 6.8 \times 10^{-3}$
 $[Ag(NH_3)^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+]$; $k_2 = 1.6 \times 10^{-3}$
 then formation constant of $[Ag(NH_3)_2]^+$ is [2006]
 (A) 6.8×10^{-6} (B) 1.08×10^{-5} (C) 1.08×10^{-6} (D) 6.8×10^{-5}

[Radioactivity]

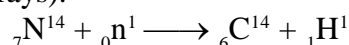
- Q.1** What mass of C^{14} with $t_{1/2} = 5730$ year has activity equal to one curie ? [1986]
Q.2 The disintegration rate of a certain radioactive sample at any instant is 4750 dpm. Five minutes later, the rate becomes 2700 dpm. Calculate half life of sample. [1986]
Q.3 ${}_{90}Th^{234}$ disintegrates to give ${}_{82}Pb^{206}$ as the final product. How many α and β -particles are emitted out during this process ? [1986]
Q.4 A certain radio isotope ${}_Z X^A$ ($t_{1/2} = 10$ days) decays to give ${}_{Z-2} Y^{A-4}$. If one g atom of ${}_Z X^A$ is kept in a sealed vessel, how much He will accumulate in 20 days at STP ? [1987]
Q.5 0.1 g atom of radioactive isotope ${}_Z X^A$ (half life 5 days) is taken. How many number of atoms will decay during eleventh day ? [1988]
Q.6 A freshly prepared radioactive source of half life period 2 hours emits radiations of intensity which is 64 times the permissible safe level. The minimum time after which it would be possible to work with this source is [1988]
 (A) 6 hours (B) 12 hours (C) 24 hours (D) 48 hours
Q.7 Nuclear reaction accompanied with emission of neutron(s) is : [1988]
 (A) ${}_{13}^{27}Al + {}_2^4He \longrightarrow {}_{15}^{30}P$ (B) ${}_{6}^{12}C + {}_1^1H \longrightarrow {}_7^{13}N$
 (D) ${}_{15}^{30}P \longrightarrow {}_{14}^{30}Si + {}_0^1e$ (D) ${}_{96}^{240}Am + {}_2^4He \longrightarrow {}_{97}^{244}Bk + {}_0^1e$
Q.8 10 g atoms of α -active radioactive isotope are disintegrating in a sealed container. In one hour, the He gas collected at STP is 11.2 cm^3 . Calculate half life of radioactive isotope. [1989]

- Q.9** An experiment requires minimum β -activity produced at the rate of 346 β -particles per minute. The half life period of $_{42}\text{Mo}^{99}$ which is a β -emitter is 66.6 hr. Find the minimum amount of $_{42}\text{Mo}^{99}$ required to carry out the experiment in 6.909 hours. [1989]
- Q.10** $_{92}\text{U}^{238}$ by successive radioactive decays changes to $_{82}\text{Pb}^{206}$. A sample of uranium ore was analysed and found to contain 1.0 g U^{238} and 0.1 g Pb^{206} . Assuming that Pb^{206} has accumulated due to decay of uranium, find out the age of ore. $t_{1/2}$ for $\text{U}^{238} = 4.5 \times 10^9$ year. [1990]
- Q.11** $_{84}\text{Po}^{210}$ decays with α -particle to $_{82}\text{Pb}^{206}$ with a half life of 138.4 days. If 1.0 g of $_{84}\text{Po}^{210}$ is placed in a sealed tube, how much helium will accumulate in 69.2 days ? Express the answer in cm^3 at STP. Also report the volume of He formed if 1 g of $\text{Po}^{210}\text{O}_2$ is used. [1991]
- Q.12** In nature a decay chain series starts with $_{90}\text{Th}^{232}$ and finally terminates at $_{82}\text{Pb}^{208}$. A thorium ore sample was found to contain 8×10^{-5} mL of He at STP and 5×10^{-7} g of Th^{232} . Find the age of ore sample assuming that source of He to be only due to decay of Th^{232} . Also assume complete retention of He within the ore. [1992]
 $t_{1/2} \text{Th}^{232} = 1.39 \times 10^{10}$ year.
- Q.13** The nucleic ratio of $_{1}\text{H}^3$ to $_{1}\text{H}^1$ in a sample of water is $8.0 \times 10^{-18} : 1$. Tritium undergoes decay with a half life period of 12.3 year. How many tritium atoms would 10.0 g of such a sample contains 40 year after the original sample is collected ? [1992]
- Q.14** Successive emission of an α -particle and two β -particle by an atom of a radioactive element results in the formation of its : [1993]
 (A) isobar (B) isomer (C) isotone (D) isotope
- Q.15** A small amount of solution containing Na^{24} radio nucleide with activity $A = 2 \times 10^3$ dps was administered into blood of a patient in a hospital. After 5 hour, a sample of the blood drawn out from the patient showed an activity of 16 dpm per c.c. $t_{1/2}$ for $\text{Na}^{24} = 15$ hr. Find – [1994]
 (a) volume of the blood in patient
 (b) Activity of blood sample drawn after a further time of 5 hr.
- Q.16** One of the hazards of nuclear explosion is the generation of Sr^{90} and its subsequent incorporation in bones. This nucleide has a half life of 28.1 year. Suppose one microgram was absorbed by a new-born child, how much Sr^{90} will remain in his bones after 20 years ? [1995]
- Q.17** A sample of U^{238} (half life = 4.5×10^9 yr) ore is found to contain 23.8 g of U^{238} and 20.6 g of Pb^{206} . Calculate the age of the ore. [1996]
- Q.18** Ac^{227} has a half life of 22 year with respect to radioactive decay. The decay follows two parallel paths, one leading the Th^{227} and the other leading to Fr^{223} . The percentage yields of these two daughters nucleides are 2% and 98.0% respectively. What is the rate constant in year^{-1} for each of the separate paths ? [1996]
- Q.19** $_{13}^{27}\text{Al}$ is stable isotope. $_{13}^{29}\text{Al}$ is expected to disintegrate by : [1996]
 (A) α -emission (B) β -emission (C) positron emission (D) proton emission
- Q.20** With what velocity should an α -particle travel towards the nucleus of a copper atom so as to arrive at a distance 10^{-13} meter from the nucleus of the copper atom ? [1997]

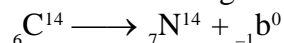
- Q.21** Write a balanced equation for the reaction ${}_{14}^{\text{N}}$ with α -particle. [1997]
- Q.22** The number of neutron accompanying the formation of ${}_{54}^{139}\text{Xe}$ and ${}_{38}^{94}\text{Sr}$ from the absorption of a slow neutron by ${}_{92}^{235}\text{U}$, followed by nuclear fission is – [1999]
(A) 0 (B) 2 (C) 1 (D) 3
- Q.23** Calculate no. of α and β -particles emitted when ${}_{92}\text{U}^{238}$ changes into radioactive ${}_{82}\text{Pb}^{206}$. [2000]
- Q.24** On analysis a sample of uranium ore was found to contain 0.277 g of ${}_{82}\text{Pb}^{206}$ and 1.667 g of ${}_{92}\text{U}^{238}$. The half life period of U^{238} is 4.51×10^9 year. If all the lead were assumed to have come from decay of ${}_{92}\text{U}^{238}$, what is the age of earth. [2000]
- Q.25** ${}^{64}\text{Cu}$ (half life = 12.8 h) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay products and calculate partial half lives for each of the decay processes. [2002]
- Q.26** ${}^{23}\text{Na}$ is the more stable isotope of Na. Find out the process by which ${}^{24}_{11}\text{Na}$ can undergo radioactive decay– [2003]
(A) α emission (B) β^- emission (C) β^+ emission (D) K electron capture
- Q.27** Complete and balance the following reactions [2004]
 ${}_{92}\text{Th}^{234} \longrightarrow \dots\dots\dots + 7 {}_2\text{H}^4 + {}_{-1}\beta^0$
- Q.28** Complete and balance the following reactions [2005]
(i) ${}_{92}\text{Th}^{234} + {}_0^1\text{n}^1 \longrightarrow \dots\dots\dots + {}_{52}\text{Te}^{137} + {}_{40}\text{Zr}^{92}$
(ii) ${}_{34}\text{Se}^{86} \longrightarrow 2 {}_{-1}\text{e}^0 + \dots\dots\dots$

Read the passage given below and answer the questions that follows. [2006]

Several short-lived radioactive species have been used to determine the age of wood or animal fossils. One of the most interesting substances is ${}^{14}_6\text{C}$ (half-life 5760 year) which is used in determining the age of carbon-bearing materials (e.g. wood, animal fossils, etc.) Carbon-14 is produced by the bombardment of nitrogen atoms present in the upper atmosphere with neutrons (from cosmic rays).



thus carbon-14 is oxidised to CO_2 and eventually ingested by plants and animals. The death of plants or animals put an end to the intake of C^{14} from the atmosphere. After the amount of C^{14} in the dead tissues starts decreasing due to its disintegration as per the following reaction:



The C^{14} isotope enters the biosphere when carbon dioxide is taken up in plant photosynthesis. Plants are eaten by animals, which exhale C^{14} as CO_2 . Eventually, C^{14} participates in many aspects of the carbon cycle. The C^{14} lost by radioactive decay is constantly replenished by the production of new isotopes in the atmosphere. In this decay-replenishment process, a dynamic equilibrium is established whereby the ratio of C^{14} to C^{12} remains constant in living matter. But when an individual plant or an animal dies, the C^{14} isotope in its is no longer replenished, so the ratio decreases as C^{14} decays. So, the number of C^{14} nuclei after time t (after the death of living matter) would be less than in a living matter. The decay constant can be calculated using the following formula,

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

The intensity of the cosmic rays have remain the same for 30,000 years. But since some years the changes in this are observed due to excessive burning of fossil fuel and nuclear tests.

- Q.29** Why do we use the carbon dating to calculate the age of the fossil? [2006]
 (A) Rate of exchange of carbon between atmosphere and living is slower than decay of C^{14}
 (B) It is not appropriate to use C^{14} dating to determine age
 (C) Rate of exchange of C^{14} between atmosphere and living organism is so fast that an equilibrium is set up between the intake of C^{14} by organism and its exponential decay.
 (D) none of the above
- Q.30** What should be the age of the fossil for meaningful determination of its age? [2006]
 (A) 6 years (B) 6000 years
 (C) 60,000 years (D) can be used to calculate any case
- Q.31** A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be T_1 and T_2 at the respective places then [2006]
 (A) The age of the fossil will increase at the place where explosion has taken place and $T_1 - T_2$

$$= \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

 (B) The age of the fossil will decrease at the place where explosion has taken place and $T_1 - T_2$

$$= \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

 (C) The age of fossil will be determined to be same
 (D) $\frac{T_1}{T_2} = \frac{C_1}{C_2}$
- Q.32** A positron is emitted from ${}_{11}^{23}\text{Na}$. The ratio of the atomic mass and atomic number of the resulting nuclide is [2007]
 (A) 22/10 (B) 22/11 (C) 23/10 (D) 23/12

ANSWERS

EXERCISE - I

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

EXERCISE - II

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 : $A = -1, B = 1/2, C = 0$, 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

EXERCISE - III

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 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 $[A] = [B]$: Also $\frac{d[A]}{dt} + \frac{d[B]}{dt} = 0$
12. 5.25 %, 128.33 hr 14. 200 minute 15. 3.59×10^2 , $1.1 \times 10^3 \text{ sec}$
16. $8.6 \times 10^{-4} \text{ sec}$; 13.43 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. 1.58×10^{-2} , 233 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) 8.67×10^{-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.

EXERCISE - IV

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. $6.2 \times 10^{-4} \text{ sec}^{-1}$

EXERCISE - V

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. 6.4×10^9 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°C 28. 124.46 mol^{-1} 29. 2.1645×10^4
30. 349.04 K

EXERCISE - VI

1. 144 2. 214, 83 3. (i) AD (ii) BCD
4. (a) i- β ii- α , (b) i- α , ii- α 5. 5
6. B 7. C 8. D 9. A, D
10. C 11. B 12. 3.7×10^{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_1H (iii) γ (iv) $^{92}_{36}\text{Kr}$ (v) ^1_0n

- (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) 2α
 (vi) $3\alpha, \beta$ (vii) $4\alpha, 2\beta$ (viii) $7\alpha, 4\beta$ (ix) $7\alpha, 14\beta$ (x) $5\alpha, 4\beta$

EXERCISE - VII

- | | | | | |
|-------|-------|-------|-------|-------|
| 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 |

OBJECTIVE QUESTION ANSWERS**Level-I**

- | | | | | | |
|-------|-------|-------|-------|-------|-------|
| 1. B | 2. B | 3. D | 4. C | 5. A | 6. A |
| 7. B | 8. B | 9. B | 10. B | 11. A | 12. B |
| 13. B | 14. D | 15. A | 16. C | 17. A | 18. C |
| 19. D | 20. A | 21. A | 22. B | 23. C | 24. A |
| 25. C | 26. B | | | | |

Level-II

- | | | | | | |
|-------|-------|-------|-------|-------|-------|
| 1. B | 2. B | 3. B | 4. A | 5. B | 6. B |
| 7. B | 8. B | 9. C | 10. B | 11. B | 12. C |
| 13. B | 14. D | 15. C | 16. A | 17. C | 18. D |
| 19. D | 20. C | 21. B | 22. B | 23. A | 24. D |
| 25. D | 26. C | | | | |

Level-III

- | | | | | | |
|--------|---------|---------|---------|----------|---------|
| 1. ABC | 2. ABCD | 3. ABCD | 4. ABCD | 5. AB | 6. AC |
| 7. ABC | 8. AC | 9. ABC | 10. BC | 11. ABCD | 12. BCD |
| 13. D | 14. C | 15. CD | 16. C | 17. CD | 18. B |
| 19. B | 20. BC | | | | |

Level-IV

- | | | | | | |
|------|------|------|------|------|------|
| 1. C | 2. D | 3. B | 4. A | 5. A | 6. D |
|------|------|------|------|------|------|

SUBJECTIVE QUESTION ANSWERS

Level-I

1. $T = 310.96 \text{ K}$
2. $\frac{K_{\text{cat}}}{k_{\text{uncat}}} = 8.88 \times 10^{32}$
3. $A = 5.04 \times 10^5 \text{ s}^{-1}$
4. $r_2/r_1 = 2.34 \times 10^{13}$
5. (i) $t = 53.4 \text{ sec}$ (ii) total pressure = 0.201 atm
6. II order
7. $1.09 \times 10^{-5} \text{ mol lit}^{-1}\text{sec}^{-1}$
8. time = $6 \times 10^{-9} \text{ sec}$
9. (a) $\Delta H = -10 \text{ kJ/mol}$ (b) $E_f = 30 \text{ kJ/mol}; E_b = 40 \text{ kJ/mol}$
(c) $E_f = 10 \text{ kJ/mol}; E_b = 20 \text{ kJ/mol}$ (d) NO
10. $K = \frac{2.303}{t} \log_{10} \frac{2P_0}{3P_0 - P}$
11. $_{-1}e^0, {}_{44}Y^{99}$
12. ${}^{210}_{92}\text{B}^{210}$, A and B are isotopes
13. 0.194 year
14. $6.25 \times 10^{-4} \text{ kg}; 2.5 \times 10^{-3} \text{ kg}; 4:1$
15. 51379.28 year
16. (a) ${}_0n^1$ (b) ${}_0n^1$ (c) ${}_1\text{H}^1$ (d) ${}_6\text{n}^1$ (e) ${}_{+1}e^0$ (f) ${}_2\text{n}^1$
17. (a) ${}_7\text{N}^{14} + {}_0n^1 \longrightarrow {}_6\text{C}^{14} + {}_1\text{p}^1$ (b) ${}_{19}\text{K}^{39} + {}_1\text{H}^1 \longrightarrow {}_{18}\text{Ar}^{36} + {}_2\text{He}^4$
18. ${}_{90}\text{Th}^{234}$, 144 neutrons
19. $(4n + 3)$ series
20. 16

Level-II

1. $A = 115.98 \text{ sec}^{-1}$
2. total pressure = 379.73 mm Hg
3. $K = 7.512 \times 10^{-3} \text{ min}^{-1}$
4. 77 % cyclohexene
5. 1.188×10^{17}
6. $A = 2p^0 - \frac{(2p^0 - p)^2}{p^0}$
7. 36.2%
8. 1 : 2.449
10. (a) 90 mm (b) 47 mm (c) 10.677 min
11. $t = 6.04 \times 10^9 \text{ years}$
12. (a) $3.33 \times 10^{-2} \text{ M}$ (b) $88.8 \times 10^7 \text{ cpm/mL}$
13. $\text{Pu}^{239} = 38.95\%$, $\text{Pu}^{240} = 61.05\%$
14. 227.1 min
15. $2.51 \times 10^9 \text{ year}$
16. $3.89 \times 10^{-12} \text{ g}$
17. 449.24 year

Level-III

2. $9.30 \times 10^{-5} \text{ mol L}^{-1} \text{ sec}^{-1}$
4. First order
5. Second order
8. 8.548 min
11. 0.384 min
12. Second order
13. Zero order
14. $111.838 \text{ kJ mol}^{-1}$
16. First order
17. $103.27 \times \log 5 = 72.19 \text{ min.}$
18. $20.35 \times 10^{12} \text{ sec.}$
19. $8.52 \times 10^{-4} \text{ s}^{-1}$
20. $k_2 = 30.98 \times 10^{-3} \text{ sec}^{-1}$
21. 53.599 kJ
28. $t = 62.13 \text{ minutes}$
29. $51.86 \text{ kJ mol}^{-1}$
33. First order
34. 3.8%
35. 146.68 min
36. (i) $1.49 \times 10^{-2} \text{ min}^{-1}$ (ii) 154.56 (iii) 29.94 min
37. $22.01 \text{ kJ mol}^{-1}$

[Radio activity]

1. $^{56}_{25}\text{Mn}$ 7. 0.758 gm 8. 16.758 MeV
 9. $t = 80.0$ 10. ^3_2He 11. ^1_0n
 12. ^4_2He 14. (a) $^0_{-1}\text{e}$ (b) $^{17}_8\text{N}$ (c) $^{27}_{13}\text{Al}$ (d) $^{14}_6\text{C}$ 15. $^{94}_{36}\text{Kr}$
 16. (a) ^1_1H (b) $^{30}_{15}\text{P}$ 17. ^1_1H 19. $12.487 \times 10^{10} \text{ J mol}^{-1}$
 21. (ii) 1011 α particles 24. (b) 0.7586 gm
 25. (i) ^3_1H (n, α type) (ii) ^1_1H (n, p type) (iii) ^1_0n (α , n type) 26. 4^1_0n
 27. $2^0_{+1}\text{e} + \nu$ 32. (a) $^{32}_{15}\text{P}$ (b) $^{97}_{38}\text{Sr}$
 34. (a) ^2_1H (b) $^{209}_{83}\text{Bi}$ (c) $^{254}_{102}\text{No}$ (d) $^{243}_{97}\text{Bk}$

Level-IV

1. B 2. (a) $\text{Rate} = k[\text{A}]^1[\text{B}]^2$ (b) $k = 0.1 \text{ lit}^2 \text{ mol}^{-2} \text{ min}^{-1}$
 3. 5.25% , 128.33 hr 4. T 5. F
 6. concentration of reactants 7. acidic, I 8. D
 9. 398.78 min
 10. (a) $K_1 = 2.31 \times 10^{-2} \text{ min}^{-1}$, $k_2 = 6.93 \times 10^{-2} \text{ min}^{-1}$ (b) $E_a = 43.85 \text{ kJ mol}^{-1}$
 (c) $93.85 \text{ kJ mol}^{-1}$
 11. D 12. (a) $K = 6.23 \times 10^{-3} \text{ sec}^{-1}$ (b) $P = 0.033 \text{ atm}$
 13. Mn^{+2} ions 14. B 15. F
 16. $T = 311.35 \text{ K}$ 17. (a) = I order (b) $k = 1.308 \times 10^{-2} \text{ min}^{-1}$ (c) 73%
 18. $k = 5.206 \times 10^{-3} \text{ min}^{-1}$ 19. $\left[\frac{dx}{dt} = k[\text{B}_2]^1 \right]$ 20. K_{II} at 300 K = 0.0327 min^{-1}
 21. $\text{Rate} = 2 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$; $x = 18.12\%$ 22. D
 23. C 24. % decomposition = 67.21%
 25. (a) order wrt $\text{NO} = 2$, $\text{Cl}_2 = 1$ (b) $r = k[\text{Cl}_2]^1[\text{NO}_2]^2$
 (c) $k = 8 \text{ lit}^2 \text{ mol}^{-2} \text{ sec}^{-1}$ (d) $r = 0.256 \text{ mol lit}^{-1} \text{ sec}^{-1}$
 26. (a) $\text{Rate} = 1 \times 10^{-2} \text{ mol lit}^{-1} \text{ sec}^{-1}$ (b) rate after 1 min = $5.49 \times 10^{-3} \text{ mol lit}^{-1} \text{ sec}^{-1}$
 27. total pressure = 0.75 atm 28. B 29. A
 30. (i) $t_{99\%} = 13.95 \text{ hour}$ (ii) 2.217 litre
 31. (i) $n = 2$ (ii) $K = 1.2 \text{ mol lit}^{-1}$ (iii) initial rate of conversion of A = $0.1 \text{ mol lit}^{-1} \text{ hour}^{-1}$
 32. (i) order w.r.t A = 2; B = 1 (ii) $K = 2.66 \times 10^8 \text{ lit}^2 \text{ mol}^{-2} \text{ sec}^{-1}$
 (iii) $E_a = 55.44 \text{ kJ/mol}$ (iv) $A = 1.140 \times 10^{18}$
 33. $t = 20.39 \text{ min}$

