Chemical Kinetics

Chapter–4

basic concepts

1. **Chemical Kinetics:** It is the branch of physical chemistry which deals with the study of the rate of chemical reaction and the mechanism by which the reaction occurs.
2. **Rate of Reaction:** It may be defined as the change in concentration of a reactant or product in unit time.
   For a general reaction, interval of $R \longrightarrow P$, the rate of reaction may be expressed as

$$\text{Rate of reaction} = \frac{\text{Decrease in concentration of } R}{\text{Time taken}}$$

$$= \frac{\text{Increase in concentration of } P}{\text{Time taken}}$$

$$\text{Rate of reaction} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

   The negative sign in the rate expression indicates the decrease in the concentration of the reactant and gives a positive value of the rate.
   Units of rate are mol L^{-1} s^{-1} or atm s^{-1} (in gaseous reactions).
   The above expression of rate gives us the average rate of reaction.
3. **Instantaneous Rate of Reaction:** It is the rate of reaction at a particular moment of time and measured as a very small concentration change over a very small interval of time.
   Mathematically, Instantaneous rate = (Average rate) $\Delta t \to 0$
   For a general reaction, $R \longrightarrow P$

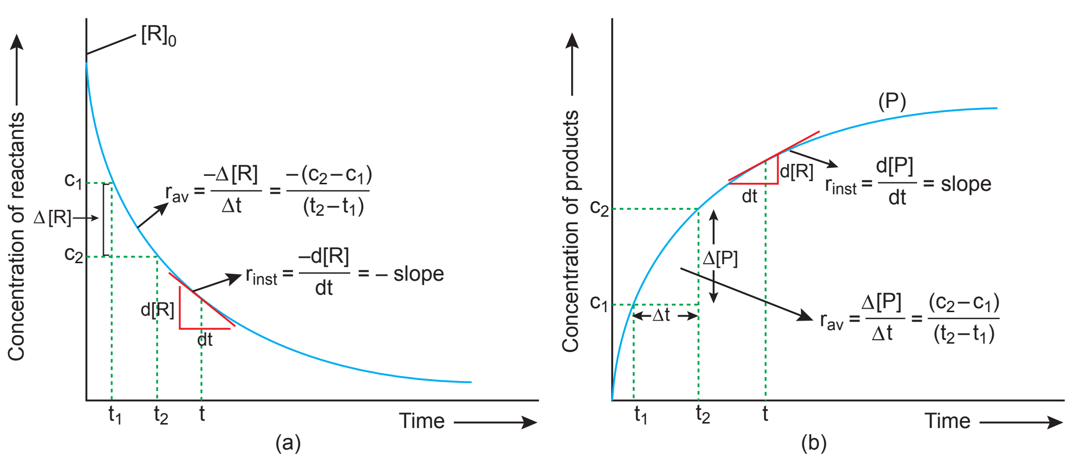


Fig. 4.1: Instantaneous and average rate of reaction

$$\text{Instantaneous rate} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Instantaneous rate can be determined graphically by drawing a tangent at time t on either side of the curve for concentration of A or B vs time and calculating its slope.

Thus,
$$r_{inst} = \frac{-d[R]}{dt} = -\text{ slope (for } R)$$
$$r_{inst} = \frac{+d[P]}{dt} = \text{slope (for } P)$$

4. **General Expression for Rate of Reaction:** For a general reaction,
$$aA + bB \longrightarrow cC + dD$$
$$r_{av} = \frac{-1}{a}\frac{\Delta[A]}{\Delta t} = \frac{-1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$
$$r_{inst} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

5. **Factors Affecting the Rate of a Chemical Reaction:**

   Rate of a reaction is influenced by following factors:

   (*a*) **Nature of reactants:** It has been observed that ionic substances react more rapidly than the substances with covalent bond. This is because ions are immediately available in aqueous solution on dissociation hence, react rapidly but covalent molecules consume part of energy in breaking of bonds.

   (*b*) **Concentration of reactants:** Rate of a reaction is directly proportional to the concentration of reactants.

   (*c*) **Temperature:** Rate of a reaction increases with the increase in temperature.

   (*d*) **Presence of catalyst:** In presence of catalyst, the rate of reaction generally increases and the equilibrium state is attained quickly in reversible reactions.

   (*e*) **Surface area of the reactants:** The smaller the particle size, greater the surface area and faster is the reaction.

   (*f*) **Radiations:** There are many reactions which either do not take place at all or are quite slow in the dark but take place at a considerable speed when exposed to sunlight or ultraviolet radiations, such reactions are called **photochemical reactions**. Examples are photosynthesis of carbohydrates, photography, etc.

6. **Rate Law:** It is an experimentally determined expression which relates the rate of reaction with concentration of reactants.

   For a hypothetical reaction,
$$A + B \longrightarrow \text{Products}$$
$$\text{Rate} \propto [A]^m [B]^n$$
   or
$$\text{Rate} = k[A]^m [B]^n$$
   where k is a constant called specific rate of reaction or rate constant.

   If $[A] = [B] = 1 \text{ mol L}^{-1}$ then
$$\text{Rate} = k$$
   Thus, rate constant may be defined as the rate of reaction when the concentration of each reactant in the reaction is unity.

7. **Order of Reaction:** It may be defined as the sum of powers of the concentration of the reactants in the rate law expression.

   Order of a reaction can be 0, 1, 2, 3 and even a fraction.

   For a hypothetical reaction,
$$aA + bB + cC \longrightarrow \text{Products}$$
   Let rate $= k[A]^m [B]^n [C]^p$

   where, m = order of reaction with respect to A

   n = order of reaction with respect to B

   p = order of reaction with respect to C

   Overall order of reaction $= m + n + p$

Units of rate constant:

For an nth order reaction, $A \longrightarrow$ Product

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

or

$$k = \frac{\text{Rate}}{[\text{A}]^n} = \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n}$$

$$= (\text{concentration})^{1-n}\ \text{time}^{-1}$$

On considering S.I. unit of concentration as mol L^{-1} and time as seconds, the unit of $k = (\text{mol L}^{-1})^{1-n}\ \text{s}^{-1}$

(*a*) Examples of zero order reactions

(*i*) Some enzyme catalysed reactions and reactions which occur on metal surfaces.

(*ii*) Decomposition of gaseous ammonia on a hot platinum surface.

$$2NH_3(g) \xrightarrow[\text{Pt Catalyst}]{1130K} N_2(g) + 3H_2(g)$$

(*iii*) $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$

(*iv*) $2HI(g) \xrightarrow{\text{gold}} H_2(g) + I_2(g)$

Unit of $k = \text{mol L}^{-1}\text{s}^{-1}$

(*b*) Examples of 1st order reactions

(*i*) All radioactive disintegrations are of the first order.

(*ii*) Decomposition of sulphuryl chloride.

$$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$$

Unit of $k = \text{s}^{-1}$. Therefore, change in unit concentration does not alter the value of k.

(*c*) Examples of 2nd order reactions

(*i*) $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

(*ii*) $NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$

Unit of k = litre mol^{-1} second^{-1}

(*d*) Examples of 3rd order reactions

(*i*) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

(*ii*) $2NO(g) + Br_2(g) \longrightarrow 2NOBr(g)$

Unit of k = litre^2 mol^{-2} second^{-1}

8. (*a*) **Elementary reaction:** A reaction which take place in one step is called an **elementary reaction**. When a sequence of elementary reactions gives the products, the reaction is called **complex reaction**.

(*b*) **Molecularity:** The number of reacting species (molecules, atoms, ions) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.

Reactions are classified as unimolecular, bimolecular and trimolecular for molecularity 1, 2 and 3 respectively.

Examples:

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$ (Unimolecular reaction)

$2HI(g) \longrightarrow H_2(g) + I_2(g)$ (Bimolecular reaction)

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ (Trimolecular reaction)

The probability of more than three molecules colliding simultaneously is rare. Therefore, molecularity of a reaction does not extend beyond three. Molecularity can be defined only for an elementary reaction and has no meaning for a complex reaction.

(*c*) **Intermediates:** The species which are produced in one step and consumed in another are called intermediates.

(*d*) **Mechanism of reaction:** A series of elementary reactions proposed to account for the overall reaction is called mechanism of reaction. The overall rate of the reaction is controlled by the slowest step in a reaction and is called the **rate determining step**.

Consider the reaction, $2H_2O_2 \xrightarrow[\text{Alkaline medium}]{I^-} 2H_2O + O_2$

The rate equation for this reaction is found to be

$$\text{Rate} = -\frac{1}{2}\frac{d}{dt}[H_2O_2] = k[H_2O_2]\,[I^-]$$

Evidences suggest that this reaction takes place in two steps as follows:

Step I. $H_2O_2 + I^- \xrightarrow{\text{Slow}} H_2O + IO^-$ (Intermediate)

Step II. $H_2O_2 + IO^- \xrightarrow{\text{Fast}} H_2O + I^- + O_2$

The first step, being slow, is the rate determining step. Thus, the rate of formation of intermediate, IO^- will determine the rate of reaction.

9. **Pseudo First Order Reaction:** A reaction which is not truly of first order but under certain conditions becomes reaction of the first order is called a pseudo first order reaction. For example, the inversion of cane sugar is a bimolecular reaction but it is a first order reaction as concentration of H_2O is quite large and does not change appreciably.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$\text{Rate} = k\,[C_{12}H_{22}O_{11}]$$

10. **Zero Order Reactions:** In such reactions, the rate remains constant throughout the course of reaction, *i.e.*, the rate does not change with the change in concentration of reactants.

$$\text{Rate} = k\,[\text{Reactant}]^0 \quad \text{or} \quad \text{Rate} = k$$

Zero order reactions generally occur in a heterogeneous system, wherein the reactant is absorbed on the surface of a solid catalyst (here it is converted into product). The fraction of the surface of the catalyst covered by the reactant is proportional to its concentration at low values and the rate of reaction is of the first order. However, after certain concentration limit of the reactant, the surface of the catalyst is fully covered. As the concentration of the reactant further increases, no change in it takes place. Thus, rate becomes independent of concentration and the order of reaction becomes zero.

Integrated rate law for zero order reaction:

Consider a general zero order reaction

$$R \longrightarrow P$$

As it is a reaction of zero order

$$\therefore \quad \frac{-d[R]}{dt} = k[R]^0 = k \quad \Rightarrow \quad -d[R] = kdt$$

$$-\int dt[R] = k\int dt$$

$$-[R] = kt + C \qquad \ldots(i)$$

where C is constant of integration.

When $t = 0$, $[R] = [R]_0$

$$C = -[R]_0$$

Substituting the value of C in equation (*i*), we get

$$-[R] = kt - [R]_0$$

$$kt = [R]_0 - [R]$$

$$t = \frac{1}{k}\{[R]_0 - [R]\} \qquad \ldots(ii)$$

or

$$k = \frac{1}{t}\{[R]_0 - [R]\}$$

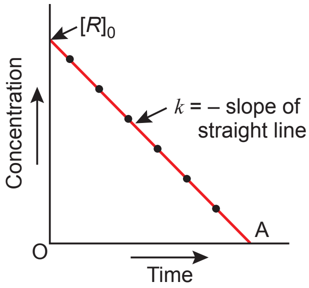


Fig. 4.2: Variation of concentration with time for a zero order reaction

Half-life of a reaction: It is the time in which the concentration of a reactant is reduced to half of its original value.

Half-life period of a zero order reaction:

When $[R] = \frac{[R]_0}{2}, t = t_{1/2}$

Substituting these values in equation (*ii*), we get

$$\therefore \qquad t_{1/2} = \frac{1}{k}\left\{[R]_0 - \frac{[R]_0}{2}\right\}$$

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

$$t_{1/2} \propto [R]_0$$

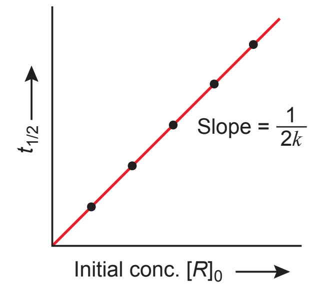


Fig. 4.3: Plot of $t_{1/2}$ versus initial concentration $[R]_0$ for a zero order reaction

11. **First Order Reactions:** In this class of reactions, the rate of reaction is directly proportional to the first power of the concentration of reacting substance.

$$\text{Rate} = k[\text{Reactant}]^1$$

Integrated rate law for 1st order reaction:

Consider the general first order reaction

$$R \longrightarrow P$$

As the reaction follows first order kinetics,

$$\therefore \qquad \frac{-d[R]}{dt} \propto [R]$$

$$\frac{-d[R]}{dt} = k[R] \qquad \Rightarrow \qquad \frac{-d[R]}{[R]} = k[dt]$$

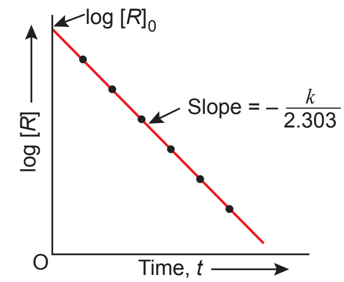


Fig. 4.4: Plot of log $[R]$ versus t

Integrating both sides, we get

$$-\ln [R] = kt + C \qquad ...(i)$$

where C is constant of integration

When $t = 0$, $[R] = [R]_0$

$$-\ln [R]_0 = 0 + C$$

Substituting the value of C in (*i*), we get

$$-\ln [R] = kt - \ln [R]_0$$

$$\ln [R] = -kt + \ln [R]_0$$

$$kt = \ln\frac{[R]_0}{[R]} = 2.303 \log\frac{[R]_0}{[R]}$$

$$\log\frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

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

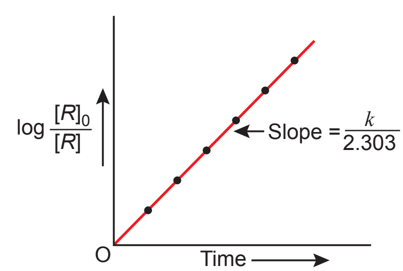


Fig. 4.5: Plot of log $[R]_0/[R]$ versus time (t)

where $[R]_0$ is initial concentration and $[R]$ is the final concentration.

Half-life period for a first order reaction

When $\qquad t = t_{1/2}, \quad [R] = \frac{[R]_0}{2}$

$$t_{1/2} = \frac{2.303}{k}\log\frac{[R]_0}{[R]_0/2} = \frac{2.303}{k}\log 2$$

$$t_{1/2} = \frac{2.303}{k} \times 0.3010 \qquad \text{or} \qquad t_{1/2} = \frac{0.693}{k}$$

Since no concentration term is involved, therefore, $t_{1/2}$ for a first order reaction is independent of initial concentration.

12. Integrated Rate Equation for a Gaseous System: Consider a typical first order gas phase reaction.

$$A(g) \longrightarrow B(g) + C(g)$$

Let P_i be the initial pressure of A and P_t the total pressure at time 't' and P_A, P_B and P_C be the partial pressures of A, B and C respectively at time t.

$$\text{Total pressure, } P_t = P_A + P_B + P_C \text{ (pressure units)}$$

If x atm be the decrease in pressure of A at time t and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.

	$A(g) \longrightarrow$	$B(g)$	+	$C(g)$
At $t = 0$	P_i atm	0 atm		0 atm
At time $= t$	$(P_i - x)$ atm	x atm		x atm

$$P_t = (P_i - x) + x + x = P_i + x \quad or \quad x = P_t - P_i$$

$$P_A = P_i - x = P_i - (P_t - P_i) = 2P_i - P_t$$

$$k = \frac{2.303}{t}\log\frac{P_i}{P_A} = \frac{2.303}{t}\log\frac{P_i}{(2P_i - P_t)}$$

13. Determination of Order of Reaction:

There are many methods available for the determination of order of reaction.

(*a*) Graphical method (*b*) Initial rate method (*c*) Integrated rate law method

(*a*) Graphical method: This method is applicable to those reactions wherein only one reactant is involved.

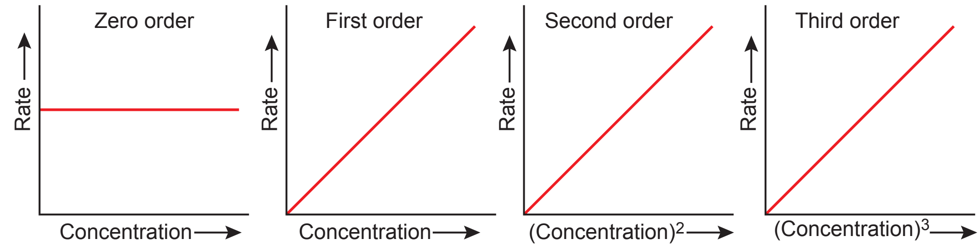


Fig. 4.6

(*b*) Initial rate method: This method is used to determine the order of reaction in such cases where more than one reactant is involved. It involves determination of order of reaction with respect to each reactant separately. For this, order of a particular reactant is determined. A series of experiment are carried out in which the concentration of that particular reactant is changed whereas the concentration of other reactants are kept constant. In each experiment, the rate is determined from the plot of concentration vs time. Similarly, concentration of another reactant is varied keeping the concentration of rest of the reactant constant and initial rate is determined. The data obtained are then compared to see how the initial rate depends on the initial concentration of each reactant. Thus, on the basis of the results the form of rate law is determined.

(*c*) Integrated rate law method: There are integrated rate law equations which are very convenient to understand the variation in concentration with time, for different order of reactions. After studying the concentrations at various intervals of time, the data are put in all the integrated rate law equations one by one. The expression which gives a constant value of the rate constant decides the order of the reaction.

Zero order equation; $k = \dfrac{[R]_0 - [R]}{t}$,

First order equation; $k = \dfrac{2.303}{t}\log\dfrac{[R]_0}{[R]}$

14. Temperature Dependence of Rate of a Reaction:

(*a*) Temperature coefficient: It is defined as the ratio of rate constants of the reaction at two temperatures differing by 10°.

$$\text{Temperature coefficient} = \frac{\text{Rate constant at } (T + 10)°}{\text{Rate constant at } T°}$$

For most of the reactions, temperature coefficient lies between 2 and 3.

(*b*) Collision frequency (*z*): It is defined as total number of collisions per unit volume per unit time.

(*c*) Effective collisions: Collisions which lead to the formation of product molecules are called effective collisions.

Rate of reaction $= f \times z$, where z is the collision frequency and f is the fraction of collisions, which are effective.

(*d*) Threshold energy: The minimum energy that the reacting molecules must possess in order to undergo effective collisions to form the product is called threshold energy.

(*e*) Activated complex: The arrangement of atoms corresponding the energy maxima (threshold energy) during the course of a reaction is called activated complex or transition state. The activated complex has partial reactant character and partial product character.

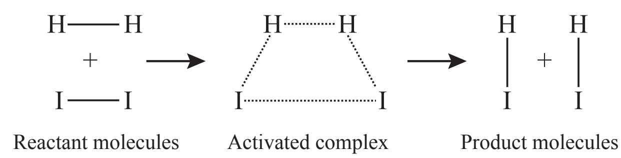


Fig. 4.7: Formation of activated complex from H_2 and I_2 during HI formation

Characteristics of an activated complex

(*i*) The potential energy of the activated complex is maximum.

(*ii*) The activated complex has a transient existence and breaks up at a definite rate to form the products.

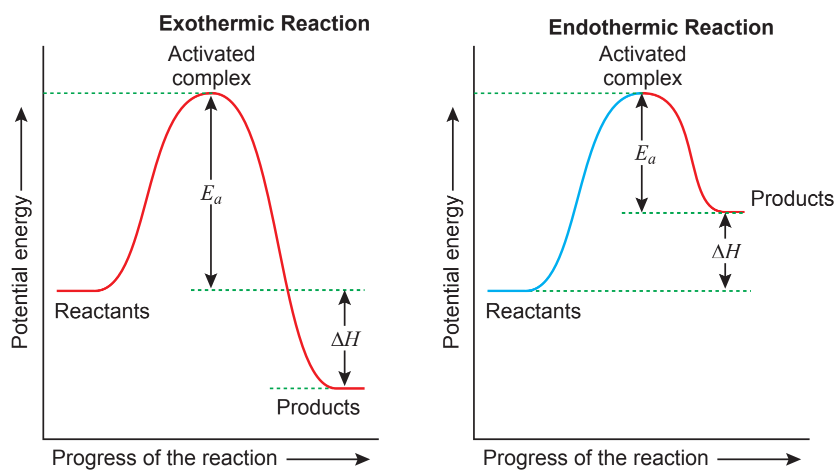


Fig. 4.8: Concept of Activation Energy

(*f*) Activation energy: The energy required to form activated complex is called activation energy. It is the difference between the threshold energy and the average energy possessed by the reacting molecules.

Activation energy (E_a) = Threshold energy – Average energy possessed by reacting molecules

$$\text{Reactants} \xrightarrow{\text{Activation energy}} \text{Activated complex} \xrightarrow{\text{Energy}} \text{Products}$$

For fast reactions, activation energies are low whereas for slow reactions activation energies are high.

(*g*) Arrhenius equation: It relates rate constant with temperature in the following way:

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

where A is constant called frequency factor, E_a is the energy of activation.

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

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$

A plot of $\log k$ vs. $1/T$ is a straight line whose slope is $-\dfrac{E_a}{2.303\,R}$ and intercept is $\log A$.

If k_1 and k_2 are the rate constants at two temperatures T_1 and T_2, then

$$\log k_1 = \log A - \frac{E_a}{2.303\,RT_1} \qquad ...(i)$$

$$\log k_2 = \log A - \frac{E_a}{2.303\,RT_2} \qquad ...(ii)$$

Subtracting (*i*) from (*ii*), we get,

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

or

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

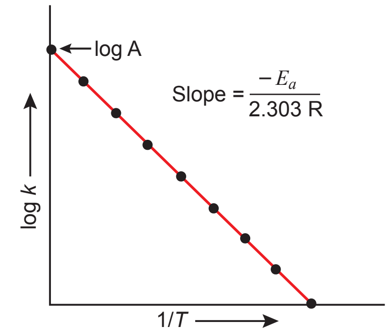


Fig. 4.9: log k vs $1/T$

(*h*) Effect of temperature on rate of reaction:

Increasing the temperature of a reaction mixture increases the fraction of molecules, which collide with energies greater than E_a. It is clear from the diagram alongside that with 10° rise in temperature, the area showing the fraction of molecules having energy equal to or greater than activation energy gets almost double leading to almost doubling of the rate of reaction.

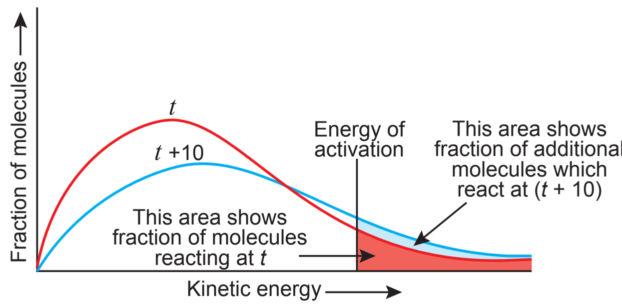


Fig. 4.10: Distribution curve showing temperature dependence of rate of a reaction

15. Catalyst: A catalyst is a substance which alters the rate of reaction without itself undergoing any chemical change at the end of the reaction.

For example, catalyst MnO_2 increases the rate of decomposition of potassium chlorate to a great extent.

$$2KClO_3 \xrightarrow[\text{Heat}]{MnO_2} 2KCl + 3O_2$$

According to intermediate complex theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.

$$\underset{\text{Reactants}}{A + B} + \underset{\text{Catalyst}}{X} \longrightarrow \underset{\text{Intermediate complex}}{A \cdots B \cdots X} \longrightarrow \underset{\text{Products}}{A\text{—}B} + \underset{\text{Catalyst (Regenerated)}}{X}$$

It is believed that the catalyst provides an alternate pathway by reducing the activation energy between reactants and products hence lowering the potential energy barrier as shown in Fig. 4.11.

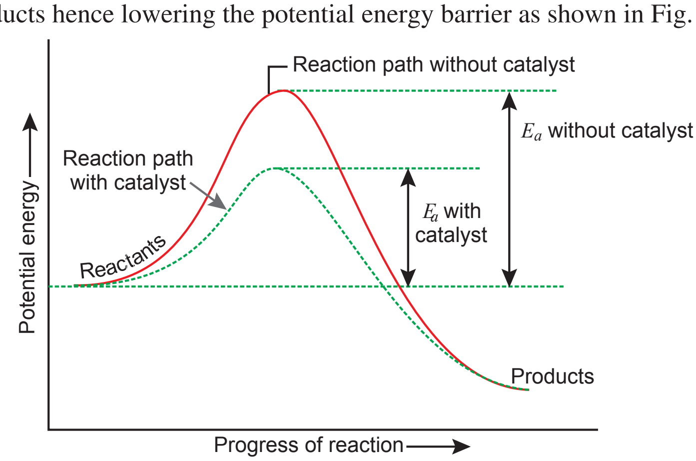


Fig. 4.11: Effect of catalyst on activation energy

It is clear from the Arrhenius equation $(k = Ae^{-E_a/RT})$ that lower the value of activation energy faster will be the rate of reaction.

For example, SO_2 is oxidised to SO_3 in the presence of nitric oxide as catalyst.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3$$

$$\underset{\text{Reactant}}{O_2(g)} + \underset{\text{Catalyst}}{2NO(g)} \longrightarrow \underset{\text{Intermediate}}{2NO_2(g)}$$

$$\underset{\text{Intermediate}}{NO_2(g)} + \underset{\text{Reactant}}{SO_2(g)} \longrightarrow \underset{\text{Product}}{SO_3(g)} + \underset{\text{Catalyst}}{NO(g)}$$

Characteristics of a catalyst

(*i*) It can only catalyse the spontaneous reaction but not the non-spontaneous reaction.

(*ii*) It does not change the equilibrium constant, but only helps in attaining equilibrium faster.

(*iii*) It can catalyse both forward and backward reactions to the same extent to maintain the equilibrium state in case of reversible reaction.

(*iv*) It does not alter the free energy change (ΔG) of a reaction.

(*v*) A small amount of the catalyst can catalyse a large amount of reactions.

16. Collision Theory of Chemical Reactions:

(*i*) Only effective collisions bring about a chemical reaction. The collisions in which molecules collide with sufficient kinetic energy (threshold energy) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collisions.

(*ii*) In collision theory, activation energy and proper orientation of the molecules together determine the criteria of an effective collision and hence the rate of chemical reaction.

$$\text{Rate} = PZ_{AB}e^{-E_a/RT}$$

Where, Z_{AB} = The collision frequency of reactants A and B

P = Probability factor or steric factor

(It take into accounts the fact that in a collision, molecules must be properly oriented)

$e^{-Ea/RT}$ = Fraction of molecules with energies equal to or greater than E_a.

Important Formulae

1. Integrated Rate Equations

(*i*) For a zero order reaction:

$$t = \frac{[R]_0 - [R]}{k} \quad \text{and} \quad t_{1/2} = \frac{[R]_0}{2k}$$

(*ii*) For a first order reaction:

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} \quad \text{and} \quad t_{1/2} = \frac{0.693}{k}$$

Amount of the substance left after n half lives of Ist order reaction = $\frac{[R]_0}{2^n}$.

2. Arrhenius Equation

(*i*) $k = A\,e^{-E_a/RT}$

where k = Rate constant, A = Arrhenius factor or frequency factor, E_a = Activation energy, R = Gas constant, T = Temperature in Kelvin

(*ii*) $$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

where k_1 = Rate constant at T_1 and k_2 = Rate constant at T_2

(*iii*) $E_a = -\,2.303 \times R \times \text{slope}\left(\text{in a plot of }\log\,k\ vs\ \frac{1}{T}\right)$

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. For the reaction $R \rightarrow P$ the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

Ans. The average rate $= -\dfrac{\Delta[R]}{\Delta t} = -\dfrac{[R_2]-[R_1]}{t_2 - t_1}$

$$= -\frac{0.02\text{ M} - 0.030\text{ M}}{25\text{ min}} = -\frac{-0.01\text{ M}}{25\text{ min}} = 4 \times 10^{-4}\text{ M min}^{-1}$$

or $$= \frac{0.01\text{ M}}{25 \times 60\text{ s}} = \mathbf{6.66 \times 10^{-6}\ M\ s^{-1}}.$$

Q. 2. In a reaction 2A $\rightarrow$ Products, concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval.

Ans. Rate of reaction = Rate of disappearance of A

$$= -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = -\frac{1}{2}\frac{(0.4 - 0.5)\text{ mol L}^{-1}}{10\text{ min}} = \mathbf{0.005\ mol\ L^{-1}\ min^{-1}}$$

Q. 3. For a reaction, A + B $\rightarrow$ Product, the rate law is given by $r = k[A]^{1/2}[B]^2$. What is the order of the reaction?

Ans. Order of reaction $= \dfrac{1}{2} + 2 = \mathbf{\dfrac{5}{2}}$.

Q. 4. The conversion of molecule X to Y follows second order kinetics. If concentration of X is increased to three times, how will it affect the rate of formation of Y?

Ans. Rate $= k[X]^2$

$r_1 = k[X]^2$ ...(*i*)

$r_2 = k[3X]^2$ ...(*ii*)

Dividing (*ii*) by (*i*), $\dfrac{r_2}{r_1} = \dfrac{9k[X]^2}{k[X]^2}$

$r_2 = 9r_1$

Thus, rate of formation of Y will increase by **nine times**.

Q. 5. A first order reaction has a rate constant $1.15 \times 10^{-3}\ s^{-1}$. How long will 5 g of this reactant take to reduce to 3 g?

Ans. Given $[R]_0 = 5$ g, $[R] = 3$g, $k = 1.15 \times 10^{-3}\text{ s}^{-1}$. As the reaction is of first order,

$$\therefore \quad t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} = \frac{2.303}{1.15 \times 10^{-3}\text{ s}^{-1}}\log\frac{5\text{ g}}{3\text{ g}} = 2.00 \times 10^3\ (\log 1.667)\text{ s}$$

$= 2.0 \times 10^3 \times 0.2219$ s = 443.8 s = **444 s**

Q. 6. Time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Ans. For a first order reaction, $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{60\text{ min}} = \mathbf{1.155 \times 10^{-2}\ min^{-1}}$

Q. 7. What will be the effect of temperature on rate constant?

Ans. The rate constant of a reaction is nearly doubled with rise in temperature by 10°. The exact dependence of the rate constant on temperature is given by Arrhenius equation, $k = Ae^{-E_a/RT}$ where A is called frequency factor and E_a is the activation energy of the reaction.

Q. 8. The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate E_a.

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

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

$$= (2.303)\,(8.314\text{ J K}^{-1}\text{ mol}^{-1})\left(\log \frac{2}{1}\right) \times \left(\frac{298\text{ K} \times 308\text{ K}}{308\text{ K} - 298\text{ K}}\right)$$

$$= 52898\text{ J mol}^{-1} = \mathbf{52.9\text{ kJ mol}^{-1}}$$

Q. 9. The activation energy for reaction, $2HI(g) \longrightarrow H_2(g) + I_2(g)$, is 209.5 kJ mol^{-1} at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy.

Ans. Fraction of molecules having energy equal to or greater than activation energy,

$$x = \frac{n}{N} = e^{-E_a/RT}$$

$\therefore$
$$\ln x = -\frac{E_a}{RT} \quad \text{or} \quad \log x = -\frac{E_a}{2.303\,RT}$$

or
$$\log x = -\frac{209.5 \times 10^3\text{ J mol}^{-1}}{2.303 \times 8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 581\text{ K}} = -18.8323$$

$$x = \text{Antilog}\,(-18.8323)$$
$$= \text{Antilog}\,(\overline{19}.1677) = \mathbf{1.471 \times 10^{-19}}$$

NCERT Textbook Exercises

Q. 1. From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants:

(*a*) $3NO(g) \longrightarrow N_2O(g) + NO_2(g)$ — rate $= k[NO]^2$

(*b*) $H_2O_2\,(aq) + 3I^-\,(aq) + 2H^+ \longrightarrow 2H_2O\,(l) + I_3^-(aq)$ — rate $= k[H_2O_2][I^-]$

(*c*) $CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$ — rate $= k[CH_3CHO]^{3/2}$

(*d*) $C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$ — rate $= k[C_2H_5Cl]$

Ans. (*a*) Rate $= k[NO]^2$, Order of reaction w.r.t. reactant NO = 2, Order of reaction = 2

Unit of *k*: $k = \dfrac{\text{Rate}}{[NO]^2} = \dfrac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^2} = \text{L mol}^{-1}\text{s}^{-1}$

(*b*) Rate $= k[H_2O_2][I^-]$, Order of reaction w.r.t. reactant H_2O_2 = 1, Order of reaction w.r.t. reactant I^- = 1,

Order of reaction = 1 + 1 = 2.

Unit of *k*: $k = \dfrac{\text{Rate}}{[H_2O_2][I^-]} = \dfrac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})\,(\text{mol L}^{-1})} = \text{L mol}^{-1}\text{ s}^{-1}$

(*c*) Rate $= k[CH_3CHO]^{3/2}$, Order of reaction w.r.t. reactant $CH_3CHO = \dfrac{3}{2}$, Order of reaction $= \dfrac{3}{2}$

Unit of *k*: $k = \dfrac{\text{Rate}}{[CH_3CHO]^{3/2}} = \dfrac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^{3/2}} = \text{mol}^{-1/2}\text{L}^{1/2}\text{s}^{-1}$

(*d*) Rate $= k[C_2H_5Cl]$, Order of reaction w.r.t. reactant $C_2H_5Cl = 1$, Order of reaction = 1.

Unit of *k*: $k = \dfrac{\text{Rate}}{[C_2H_5Cl]} = \dfrac{\text{mol L}^{-1}\text{s}^{-1}}{\text{mol L}^{-1}} = \text{s}^{-1}$

Q. 2. For the reaction $2A + B \rightarrow A_2B$, the rate $= k\,[A][B]^2$ with $k = 2.0 \times 10^{-6}$ mol^{-2} L^2 s^{-1}. Calculate the initial rate of the reaction when $[A] = 0.1$ mol L^{-1} and $[B] = 0.2$ mol L^{-1}. Calculate the rate of reaction after $[A]$ is reduced to 0.06 mol L^{-1}.

Ans. Initial rate $= k\,[A][B]^2 = (2.0 \times 10^{-6}\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1})\ (0.1\ \text{mol L}^{-1})\ (0.2\ \text{mol L}^{-1})^2$

$= \mathbf{8 \times 10^{-9}\ mol\ L^{-1}\ s^{-1}}$

When $[A]$ is reduced from 0.10 mol L^{-1} to 0.06 mol L^{-1}, *i.e.*, 0.04 mol L^{-1} of A has reacted,

$$B \text{ reacted} = \frac{1}{2} \times 0.04\ \text{mol L}^{-1} = 0.02\ \text{mol L}^{-1}$$

Now $[B] = 0.2 - 0.02 = 0.18$ mol L^{-1}

Rate $= (2.0 \times 10^{-6}\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1})\ (0.06\ \text{mol L}^{-1})\ (0.18\ \text{mol L}^{-1})^2$

$= \mathbf{3.89 \times 10^{-9}\ mol\ L^{-1}\ s^{-1}}$

Q. 3. The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}?

Ans.
$$2NH_3 \longrightarrow N_2 + 3H_2$$

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

For zero order reaction, rate $= k$

$$\therefore \quad -\frac{1}{2}\frac{d\,[NH_3]}{dt} = \frac{d\,[N_2]}{dt} = \frac{1}{3}\frac{d\,[H_2]}{dt}$$

$$= 2.5 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

$$\text{Rate of production of } N_2 = \frac{d\,[N_2]}{dt} = \mathbf{2.5 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}}$$

$$\text{Rate of production of } H_2 = \frac{d\,[H_2]}{dt}$$

$$= 3 \times (2.5 \times 10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}) = \mathbf{7.5 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}}$$

Q. 4. The decomposition of dimethyl ether leads to the formation of CH_4, H_2 and CO and the reaction rate is given by

$$\textbf{Rate} = k\,[CH_3OCH_3]^{3/2}.$$

The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, *i.e.,*

$$\textbf{Rate} = k[P_{CH_3OCH_3}]^{3/2}$$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant?

Ans. In terms of pressure, unit of rate = bar min^{-1}

$$\text{Unit of } k = \frac{\text{Rate}}{[P_{CH_3OCH_3}]^{3/2}} = \frac{\text{bar min}^{-1}}{(\text{bar})^{3/2}} = \mathbf{bar^{-1/2}\ min^{-1}}$$

Q. 5. Mention the factors that affects the rate of a chemical reaction.

Ans. Refer to Basic Concepts Point 5.

Q. 6. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (*i*) doubled (*ii*) reduced to half?

Ans. Rate $= k\,[A]^2 = ka^2$

If $[A] = 2a$, Rate $= k\,[2a]^2 = 4ka^2 =$ **4 times of the initial rate**

If $[A] = \frac{1}{2}a$, Rate $= k\left(\frac{a}{2}\right)^2 = \frac{1}{4}ka^2 = \mathbf{\frac{1}{4}}$ **times of the initial rate**

Q. 7. What is the effect of temperature on the rate constant of a reaction? How can this effect of temperature on rate constant be represented quantitatively?

Ans. The rate constant of a reaction increases with increase in temperature and becomes nearly double for every 10°C rise of temperature. The effect can be represented quantitatively by Arrhenius equation,

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

where E_a is the activation energy of the reaction and A is the frequency factor.

Q. 8. In a pseudo first order hydrolysis of an ester in water, the following results were obtained:

t/s	0	30	60	90
[A]/mol L^{-1}	0.55	0.31	0.17	0.085

Calculate the average rate of reaction between the time interval 30 to 60 seconds.

Ans. Average rate of reaction between the interval 30–60 s.

$$= -\frac{C_2 - C_1}{t_2 - t_1}$$

$$= -\frac{(0.17 - 0.31)}{60 - 30} = \frac{0.14}{30} \text{ mol L}^{-1}\text{ s}^{-1}$$

$$= \mathbf{4.67 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}}$$

Q. 9. A reaction is first order in *A* and second order in *B*.

(i) Write the differential rate equation.

(ii) How is the rate affected on increasing the concentration of *B* three times?

(iii) How is the rate affected when concentration of both *A* and *B* are doubled?

Ans. (i) Rate $= \dfrac{-d[R]}{dt} = k[A][B]^2$

(ii) If the concentration of B is tripled, then

Rate $= k[A][3B]^2 = 9k[A][B]^2$, *i.e.*, the rate of reaction becomes 9 times.

(iii) If the concentration of both A and B are doubled, then

Rate $= k[2A][2B]^2 = 8k[A][B]^2$, *i.e.*, the rate of reaction becomes 8 times.

Q. 10. In a reaction between *A* and *B*, the initial rate of reaction (r_0) was measured for different initial concentrations of *A* and *B* as given below:

A/mol L^{-1}	0.20	0.20	0.40
B/mol L^{-1}	0.30	0.10	0.05
r_0/mol L^{-1} s^{-1}	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

What is the order of reaction with respect to *A* and *B*?

Ans. Let the rate law be $r_0 = k[A]^m\,[B]^n$

$$(r_0)_1 = 5.07 \times 10^{-5} = k\,(0.20)^m\,(0.30)^n \quad ...(i)$$

$$(r_0)_2 = 5.07 \times 10^{-5} = k\,(0.20)^m\,(0.10)^n \quad ...(ii)$$

$$(r_0)_3 = 1.43 \times 10^{-4} = k\,(0.40)^m\,(0.05)^n \quad ...(iii)$$

Dividing (*i*) by (*ii*), $\dfrac{(r_0)_1}{(r_0)_2} = \dfrac{5.07\times10^{-5}}{5.07\times10^{-5}} = \dfrac{k(0.20)^m(0.30)^n}{k(0.20)^m(0.10)^n}$

$$1 = 3^n \text{ or } 3^0 = 3^n \quad \Rightarrow \quad n = 0$$

Dividing (*iii*) by (*ii*), $\dfrac{(r_0)_3}{(r_0)_2} = \dfrac{1.43\times10^{-4}}{5.07\times10^{-5}} = \dfrac{k(0.40)^m(0.05)^n}{k(0.20)^m(0.10)^n}$

$$2.821 = 2^m \times (1/2)^0$$

$$\Rightarrow \quad \log 2.821 = m \log 2$$

$$\Rightarrow \quad m = \frac{\log 2.821}{\log 2} = 1.496 = 1.5$$

Thus, order of reaction w.r.t. A = **1.5** and order of reaction w.r.t. B = **0**.

Q. 11. The following results have been obtained during the kinetic studies of the reaction:

$$2A + B \longrightarrow C + D$$

Experiment	[A]/mol L^{-1}	[B]/mol L^{-1}	Initial rate of formation of D/mol L^{-1} min^{-1}
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

Ans. Suppose order of reaction w.r.t. reactant A is m and with respect to B is n. Then the rate law will be

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

Substituting the values of experiments I to IV, we have

$$(\text{Rate})_{\text{expt } I} = 6.0 \times 10^{-3} = k\,(0.1)^m\,(0.1)^n \quad ...(i)$$

$$(\text{Rate})_{\text{expt } II} = 7.2 \times 10^{-2} = k\,(0.3)^m\,(0.2)^n \quad ...(ii)$$

$$(\text{Rate})_{\text{expt } III} = 2.88 \times 10^{-1} = k\,(0.3)^m\,(0.4)^n \quad ...(iii)$$

$$(\text{Rate})_{\text{expt } IV} = 2.4 \times 10^{-2} = k\,(0.4)^m\,(0.1)^n \quad ...(iv)$$

$$\therefore \quad \frac{(\text{Rate})_{\text{expt } I}}{(\text{Rate})_{\text{expt } IV}} = \frac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}} = \frac{k\,(0.1)^m\,(0.1)^n}{k\,(0.4)^m (0.1)^n}$$

$$\text{or} \quad \frac{1}{4} = \frac{(0.1)^m}{(0.4)^m} = \left(\frac{1}{4}\right)^m, \quad m = 1$$

$$\frac{(\text{Rate})_{\text{expt } II}}{(\text{Rate})_{\text{expt } III}} = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{k\,(0.3)^m\,(0.2)^n}{k\,(0.3)^m (0.4)^n}$$

$$\text{or} \quad \frac{1}{4} = \frac{(0.2)^n}{(0.4)^n} = \left(\frac{1}{2}\right)^n$$

$$\text{or} \quad \left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^n \quad \text{or} \quad n = 2$$

$\therefore$ Rate law expression is given by

$$\textbf{Rate} = \boldsymbol{k\,[A]\,[B]^2}$$

Order of reaction w.r.t. A = **1**;

Order of reaction w.r.t. B = **2**.

Overall order of reaction = 1 + 2 = **3**

$$k = \frac{\text{Rate}}{[A][B]^2} = \frac{6.0 \times 10^{-3}\ \text{mol L}^{-1}\ \text{min}^{-1}}{(0.1\ \text{mol L}^{-1})\,(0.1\ \text{mol L}^{-1})^2}$$

$$= \mathbf{6.0\ mol^{-2}\ L^2\ min^{-1}}$$

Q. 12. The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

Experiment	[A]/ mol L^{-1}	[B]/ mol L^{-1}	Initial rate/ mol L^{-1} min^{-1}
I	0.1	0.1	2.0×10^{-2}
II	—	0.2	4.0×10^{-2}
III	0.4	0.4	—
IV	—	0.2	2.0×10^{-2}

[CBSE 2019 (56/5/2)]

Ans. The rate expression for the reaction is given as

$$\text{Rate} = k\,[A]^1\,[B]^0 = k[A]$$

For experiment I, Rate $= 2.0 \times 10^{-2}$ mol L^{-1} min^{-1} $= k\,(0.1\text{ M})$ or $k = \mathbf{0.2\ min^{-1}}$

For experiment II, Rate $= 4.0 \times 10^{-2}$ mol L^{-1} min^{-1} $= (0.2\text{ min}^{-1})\,[A]$ or $[A] = \mathbf{0.2\ mol\ L^{-1}}$

For experiment III, Rate $= (0.2\text{ min}^{-1})\,(0.4\text{ mol L}^{-1}) = \mathbf{0.08\ mol\ L^{-1}\ min^{-1}}$

For experiment IV, Rate $= 2.0 \times 10^{-2}$ mol L^{-1} min^{-1} $= 0.2\text{ min}^{-1}\,[A]$ or $[A] = \mathbf{0.1\ mol\ L^{-1}}$

Q. 13. Calculate the half-life of a first order reaction from their rate constants given below:

***(i)* 200 s^{-1}** ***(ii)* 2 min^{-1}**

***(iii)* 4 $years^{-1}$**

Ans. Half-life period of a first order reaction, $t_{1/2} = \dfrac{0.693}{k}$

(*i*) $t_{1/2} = \dfrac{0.693}{200\text{ s}^{-1}} = 0.346 \times 10^{-2}\text{ s} = \mathbf{3.46 \times 10^{-3}\ s}$

(*ii*) $t_{1/2} = \dfrac{0.693}{2\text{ min}^{-1}} = 0.346\text{ min} = \mathbf{3.46 \times 10^{-1}\ min}$

(*iii*) $t_{1/2} = \dfrac{0.693}{4\text{ year}^{-1}} = 0.173\text{ year} = \mathbf{1.73 \times 10^{-1}\ year}$

Q. 14. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

Ans. Radioactive decay follows first order kinetics.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730}\text{ year}^{-1} = 1.21 \times 10^{-4}\text{ year}^{-1}$$

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} = \frac{2.303}{(1.21 \times 10^{-4}\text{ year}^{-1})}\log\frac{100}{80}$$

$$= \frac{2.303}{1.21 \times 10^{-4}\text{ year}^{-1}} \times 0.09691$$

$$= \mathbf{1845\ years\ (approx.)}$$

Q. 15. The experimental data for the decomposition of N_2O_5

$$[2N_2O_5 \longrightarrow 4NO_2 + O_2]$$

in gas phase at 318 K are given below:

t (*s*)	0	400	800	1200	1600	2000	2400	2800	3200
$10^5 \times [N_2O_5]$/mol L^{-1}	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(*i*) Plot $[N_2O_5]$ against t.

(*ii*) Find the half-life period for the reaction.

(*iii*) Draw a graph between log $[N_2O_5]$ and t.

(*iv*) What is rate law?

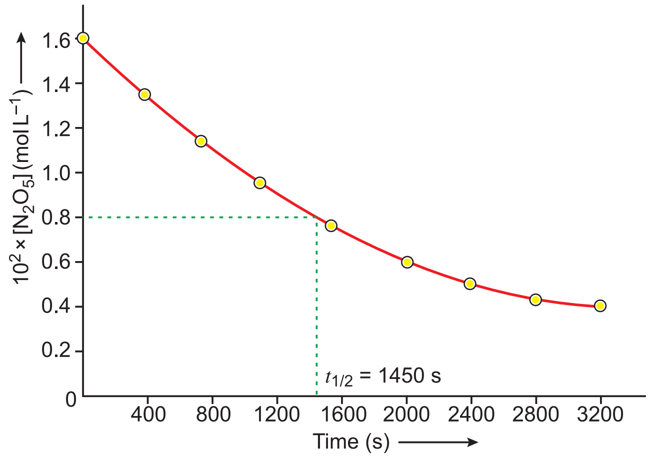
(*v*) **Calculate the rate constant.**

(*vi*) **Calculate the half-life period from k and compare it with (*ii*).**

Ans.

t (s)	0	400	800	1200	1600	2000	2400	2800	3200
$10^5 \times [N_2O_5]$/mol L^{-1}	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35
log $[N_2O_5]$	– 1.79	– 1.87	– 1.94	– 2.03	– 2.11	– 2.19	– 2.28	– 2.37	– 2.46

(*i*) **Plot of $[N_2O_5]$ versus time**

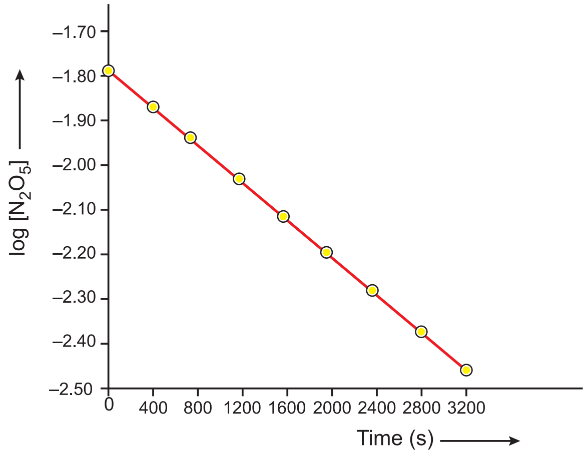


(*ii*) Initial concentration of $[N_2O_5] = 1.63 \times 10^2$ M

Half of the concentration = 0.815×10^2 M

Time corresponding to this concentration = 1450 s. Hence, $t_{1/2}$ = **1450 s**.

(*iii*) **Plot of log $[N_2O_5]$ versus time**



(*iv*) As plot of log $[N_2O_5]$ vs time is a straight line, hence it is a reaction of first order.

∴ Rate law is,

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

(*v*) Slope of the line $= -\dfrac{k}{2.303}$ ...(*i*)

$$\text{Slope} = \frac{-2.46-(-1.79)}{3200-0} = -\frac{0.67}{3200} \quad ...(ii)$$

From equation (*i*) and (*ii*), we get

$$-\frac{k}{2.303} = \frac{-0.67}{3200} \quad \text{or} \quad k = \frac{0.67 \times 2.303}{3200}$$

or $k = \mathbf{4.82 \times 10^{-4}\ s^{-1}}$

(vi) $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.82 \times 10^{-4}\,\text{s}^{-1}} = \mathbf{1438\ s}$$

The two values are almost same within limits of possible error.

Q. 16. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?

Ans. $$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} \quad \text{as} \quad [R] = \frac{[R]_0}{16}$$

$$t = \frac{2.303}{k} \log \frac{[R]_0}{\frac{[R]_0}{16}} = \frac{2.303}{60} \times 4 \log 2$$

$$= \frac{2.303}{60} \times 4 \times 0.3010 = \mathbf{4.62 \times 10^{-2}\ s}$$

Q. 17. During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1 μg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically?

Ans. As radioactive disintegration follows first order kinetics,

$\therefore$ Decay constant of ^{90}Sr, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} = 2.466 \times 10^{-2}\ y^{-1}$

To calculate the amount left after 10 years:

$[R]_0 = 1$ μg, $t = 10$ years, $k = 2.466 \times 10^{-2}\ y^{-1}$, $[R] = ?$

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

$$2.466 \times 10^{-2} = \frac{2.303}{10} \log \frac{1}{[R]}$$

or $\log [R] = -0.1071$

or $[R] = \text{Antilog } \bar{1}.8929 = \mathbf{0.7814\ \mu g}$

To calculate the amount left after 60 years:

$$2.466 \times 10^{-2} = \frac{2.303}{60} \log \frac{1}{[R]}$$

or $\log [R] = -0.6425$

or $[R] = \text{Antilog } \bar{1}.3575 = \mathbf{0.2278\ \mu g}$

Q. 18. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction. **[*CBSE 2019 (56/5/2)*]**

Ans. For a first order reaction,

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

When the reaction is 99% completed, $[R] = [R]_0 - 0.99\,[R]_0 = 0.01\,[R]_0$

When the reaction is 90% completed, $[R] = [R]_0 - 0.9[R]_0 = 0.1[R]_0$

$$\frac{t_{99\%}}{t_{90\%}} = \frac{\frac{2.303}{k} \log \frac{[R]_0}{0.01[R]_0}}{\frac{2.303}{k} \log \frac{[R]_0}{0.1[R]_0}} = \frac{\log 10^2}{\log 10} = \frac{2 \log 10}{\log 10} = 2$$

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

Q. 19. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

Ans. For a first order reaction

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

When $t = 40$ minutes, $\frac{[R]_0}{[R]} = \frac{100}{100-30} = \frac{10}{7}$

$$k = \frac{2.303}{40} \log \frac{10}{7}$$

$$k = \frac{2.303}{40} \log 1.428 = \frac{2.303}{40} \times 0.1547$$

$$k = 8.91 \times 10^{-3} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.91 \times 10^{-3}}$$

$$t_{1/2} = \mathbf{77.78 \text{ min}}$$

Q. 20. For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained:

***t* (s)**	**0**	**360**	**720**
***P* (mm of Hg)**	**35.0**	**54.0**	**63.0**

Calculate the rate constant.

Ans.

	$(CH_3)_2CHN{=}NCH(CH_3)_2(g) \longrightarrow$	$N_2(g)$ +	$C_6H_{14}(g)$
Initial pressure	P_0	0	0
After time t	$P_0 - p$	p	p

Total pressure after time t $(P_t) = (P_0 - p) + p + p = P_0 + p$ *or* $p = P_t - P_0$

$a \propto P_0$ and $(a - x) \propto P_0 - p$ or substituting the value of p,

$a - x \propto P_0 - (P_t - P_0)$, *i.e.*, $(a - x) \propto 2P_0 - P_t$

For a first order reaction

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

$$= \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

When $t = 360$ s $\quad k = \frac{2.303}{360\text{s}} \log \frac{35.0}{2 \times 35.0 - 54.0} = \frac{2.303}{360 \text{ s}} \log \frac{35}{16}$

$$= \frac{2.303}{360 \text{ s}} (0.3400) = 2.175 \times 10^{-3} \text{ s}^{-1}$$

When $t = 720$ s, $\quad k = \frac{2.303}{720 \text{ s}} \log \frac{35.0}{2 \times 35.0 - 63.0} = \frac{2.303}{720 \text{ s}} \log 5$

$$= \frac{2.303}{720 \text{ s}} (0.6990) = 2.235 \times 10^{-3} \text{ s}^{-1}$$

Average value of $k = \frac{2.175 + 2.235}{2} \times 10^{-3} \text{ s}^{-1} = \mathbf{2.20 \times 10^{-3} \text{ s}^{-1}}$

Q. 21. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	**Time/s**	**Total pressure/atm**
1	0	0.5
2	100	0.6

Calculate the rate of reaction when total pressure is 0.65 atm.

Ans. $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$

$$k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

When $t = 100$ s, $\quad k = \frac{2.303}{100 \text{ s}} \log \frac{0.5}{2 \times 0.5 - 0.6} = \frac{2.303}{100 \text{ s}} \log (1.25)$

$= \frac{2.303}{100 \text{ s}} (0.0969) = \mathbf{2.2316 \times 10^{-3}\ s^{-1}}$

When $P_t = 0.65$ atm, *i.e.*, $P_0 + p = 0.65$ atm

$\therefore \quad p = 0.65 - P_0 = 0.65 - 0.50 = 0.15$ atm

Pressure of SO_2Cl_2 at time t ($p_{SO_2Cl_2}$) $= P_0 - p = 0.50 - 0.15$ atm $= 0.35$ atm

$\therefore \quad \text{Rate} = k \times p_{SO_2Cl_2} = (2.2316 \times 10^{-3}\ s^{-1})\ (0.35\ \text{atm})$

$= \mathbf{7.8 \times 10^{-4}\ atm\ s^{-1}}$

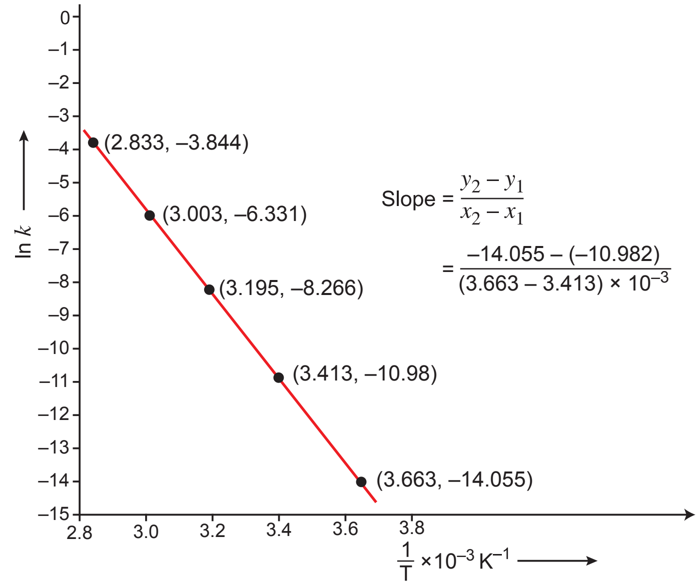
Q. 22. The rate constant for the decomposition of N_2O_5 at various temperatures is given below:

T°C	0	20	40	60	80
$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between ln k and $1/T$ and calculate the values of A and E_a. Predict the rate constant at 30°C and 50°C.

Ans. To draw the graph of ln k versus $\frac{1}{T}$, we can re-write the given data as follows:

T (K)	273	293	313	333	353
$1/T$ (K^{-1})	0.003663	0.003413	0.00319	0.003003	0.002833
ln k	– 14.055	– 10.982	– 8.266	– 6.331	– 3.844



Graph of ln k vs 1/T

From the graph, we find that

$$\text{Slope} = \frac{-E_a}{R} = \frac{-(-3.073)}{0.25 \times 10^{-3}}$$

$\therefore$ Activation energy, $E_a = \frac{3.073}{0.25 \times 10^{-3}} \times 8.314 = 102195.7\ \text{J mol}^{-1} =$ **102.20 kJ/mol**

We know that $\quad \ln k = \ln A - \frac{E_a}{RT}$

or $\quad \ln A = \left(\frac{E_a}{R}\right)\frac{1}{T} + \ln k$

At $T = 273$ K, ln $k = -14.055$

$$\therefore \quad \ln A = \frac{102.20}{8.314 \times 10^{-3} \times 273} - 14.055 = 30.973$$

Frequency factor, $A = 2.83 \times 10^{13}$

The value of rate constant at two different temperatures can be determined as follows:

T	$1/T$	Value of ln k (from graph)	Value of k
303	0.003300	– 9.7	$6.13 \times 10^{-5}\ s^{-1}$
323	0.003096	– 6.3	$1.84 \times 10^{-3}\ s^{-1}$

Q. 23. The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5}\ s^{-1}$ at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor?

Ans. Given, $k = 2.418 \times 10^{-5}\ s^{-1}$, $E_a = 179.9\ kJ\ mol^{-1}$, $T = 546$ K.

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

or $$\log A = \log k + \frac{E_a}{2.303\ RT}$$

$$\log A = \log (2.418 \times 10^{-5}\ s^{-1}) + \frac{179.9\ kJ\ mol^{-1}}{2.303 \times 8.314 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1} \times 546\ K}$$

$$= (-5 + 0.3834)\ s^{-1} + 17.2081$$

$$= 12.5915\ s^{-1}$$

or $$A = \text{Antilog}\ (12.5915)\ s^{-1}$$

$$= \mathbf{3.904 \times 10^{12}\ s^{-1}}$$

Q. 24. Consider a certain reaction $A \longrightarrow$ Products with $k = 2.0 \times 10^{-2}\ s^{-1}$. Calculate the concentration of A remaining after 100 s if the initial concentration of A is 1.0 mol L^{-1}.

Ans. The units of k show that the reaction is of first order. Hence, $k = \dfrac{2.303}{t} \log \dfrac{[R]_0}{[R]}$

$\therefore$ $$2.0 \times 10^{-2}\ s^{-1} = \frac{2.303}{100\ s} \log \frac{1.0\ mol\ L^{-1}}{[A]} \quad \text{or } \log [A] = -0.8684$$

$\therefore$ $$[A] = \text{Antilog}\ (-0.8684) = \text{Antilog}\ (\bar{1}.1316) = \mathbf{0.1354\ mol\ L^{-1}}$$

Q. 25. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law with $t_{1/2} = 3.00$ hours. What fraction of sample of sucrose remains after 8 hours?

Ans. Since sucrose decomposes according to first order rate law,

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

As $t_{1/2} = 3.0$ hours,

$\therefore$ $$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3h} = 0.231\ h^{-1}$$

$$0.231\ h^{-1} = \frac{2.303}{8h} \log \frac{[R]_0}{[R]}$$

or $$\log \frac{[R]_0}{[R]} = 0.8024$$

or $$\frac{[R]_0}{[R]} = \text{Antilog}\ (0.8024) = 6.345$$

or $$\frac{[R]}{[R]_0} = \frac{1}{6.345} = \mathbf{0.158}$$

Q. 26. The decomposition of hydrocarbon follows the equation: $k = (4.5 \times 10^{11}\ s^{-1})\ e^{-(28000\ K)/T}$. Calculate E_a.

Ans. From Arrhenius equation, $k = A\ e^{-E_a/RT}$

$\therefore$ $$-\frac{E_a}{RT} = -\frac{28000\ K}{T}$$

or $$E_a = 28000\ K \times R = 28000\ K \times 8.314\ J\ K^{-1}\ mol^{-1}$$

$$= \mathbf{232.79\ kJ\ mol^{-1}}$$

Q. 27. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.34 - 1.25 \times 10^4 \text{ K/T}$$

Calculate E_a for this reaction and at what temperature will its half-period be 256 minutes.

Ans. Given, $\log k = 14.34 - \dfrac{1.25\times10^4}{T}$

Comparing with the equation, $\log k = \log A - \dfrac{E_a}{2.303\,RT}$, we get

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

or $$E_a = 1.25 \times 10^4 \times 2.303 \times 8.314$$
$$= 23.934 \times 10^4 \text{ J mol}^{-1}$$
$$E_a = \mathbf{239.34\ kJ\ mol^{-1}}$$

Given, $t_{1/2} = 256 \text{ min} = 256 \times 60 \text{ s}$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{256\times60} = 4.5 \times 10^{-5}\ \text{s}^{-1}$$

Substituting the value of k in given equation, we get

$$\log(4.51 \times 10^{-5}) = 14.34 - \frac{1.25\times10^4}{T}$$

$$\log 4.51 + \log 10^{-5} = 14.34 - \frac{1.25\times10^4}{T}$$

or $$\log 4.51 - 5\log 10 = 14.34 - \frac{1.25\times10^4}{T}$$

$$0.6542 - 5 = 14.34 - \frac{1.25\times10^4}{T} \quad \text{or} \quad \frac{1.25\times10^4}{T} = 18.6858$$

or $$T = \frac{1.25\times10^4}{18.6858} = \mathbf{669\ K\ (approx.)}$$

Q. 28. The decomposition of A into product has value of k as $4.5 \times 10^3\ s^{-1}$ at 10°C and energy of activation is 60 kJ mol^{-1}. At what temperature would k be $1.5 \times 10^4\ s^{-1}$?

Ans. $k_1 = 4.5 \times 10^3\ \text{s}^{-1}$, $T_1 = 10 + 273 \text{ K} = 283 \text{ K}$; $k_2 = 1.5 \times 10^4\ \text{s}^{-1}$, $T_2 = ?$, $E_a = 60 \text{ kJ mol}^{-1}$

From Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_2T_1}\right]$$

$$\log\frac{1.5\times10^4}{4.5\times10^3} = \frac{60000 \text{ J mol}^{-1}}{2.303\times8.314 \text{ JK}^{-1}\text{ mol}^{-1}}\left(\frac{T_2 - 283}{283T_2}\right)$$

or $$\log 3.333 = 3133.63\left(\frac{T_2-283}{283T_2}\right) \quad \text{or} \quad \frac{0.5228}{3133.63} = \frac{T_2-283}{283T_2}$$

or $$0.0472\,T_2 = T_2 - 283$$

or $$0.9528\,T_2 = 283$$

or $$T_2 = \frac{283}{0.9528} = 297 \text{ K} = 297 - 273\text{°C} = \mathbf{24°C}$$

Q. 29. 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 value of A is $4 \times 10^{10}\ s^{-1}$, calculate k at 318 K and E_a.

Ans. $$k_1 = \frac{2.303}{t_1}\log\frac{[R]_0}{[R]_0 - 0.10\,[R]_0} = \frac{2.303}{t_1}\log\frac{100}{90}$$

$$= \frac{2.303}{t_1}(0.0458) = \frac{0.1055}{t_1} \quad \text{or} \quad t_1 = \frac{0.1055}{k_{298\text{K}}}$$

$$k_2 = \frac{2.303}{t_2} \log \frac{[R]_0}{[R]_0 - 0.25\,[R]_0} = \frac{2.303}{t_2} \log \frac{100}{75}$$

$$= \frac{2.303}{t_2}(0.125) = \frac{0.2879}{t_2} \quad \text{or} \quad t_2 = \frac{0.2879}{k_{308\text{K}}}$$

But $t_1 = t_2$. Hence, $\dfrac{0.1055}{k_1} = \dfrac{0.2879}{k_2}$ or $\dfrac{k_2}{k_1} = 2.7289$

Now, from Arrhenius equation, $\log \dfrac{k_2}{k_1} = \dfrac{E_a}{2.303\,R}\left[\dfrac{T_2 - T_1}{T_2 T_1}\right]$

$$\therefore \qquad \log(2.7289) = \frac{E_a}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \frac{(308 - 298)\text{ K}}{298 \text{ K} \times 308 \text{ K}}$$

$$0.4360 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{298 \times 308}$$

or $\qquad E_a = \mathbf{76.623\ kJ\ mol^{-1}}$

Calculation of k at 318 K:

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$

$$= \log(4 \times 10^{10}) - \frac{76.623 \text{ kJ mol}^{-1}}{2.303 \times 8.314 \times 10^{-3} \text{ kJ K}^{-1}\text{mol}^{-1} \times 318 \text{ K}}$$

$$= 10.6021 - 12.5843 = -1.9822$$

or $\qquad k = \text{Antilog}(-1.9822) = \text{Antilog}(\bar{2}.0178)$

$$= \mathbf{1.042 \times 10^{-2}\ s^{-1}}$$

Q. 30. The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

[CBSE 2019 (56/4/1)]

Ans. $\qquad k_2 = 4k_1 \quad \Rightarrow \quad \dfrac{k_2}{k_1} = 4$

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

$$\Rightarrow \qquad \log 4 = \frac{E_a}{2.303 \times 8.314}\left(\frac{313 - 293}{293 \times 313}\right)$$

$$2 \times \log 2 = \frac{E_a}{19.147}\left(\frac{20}{91709}\right)$$

$$E_a = \frac{2 \times 0.3010 \times 19.147 \times 91709}{20} = \mathbf{52.85\ kJ/mol}$$

Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. In the reaction,

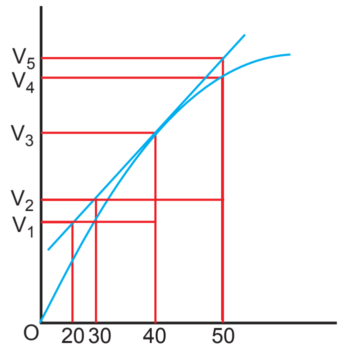
$$\mathbf{BrO_3^-(aq) + 5Br^-(aq) + 6H^+ \longrightarrow 3Br_2(l) + 3H_2O(l)}$$

The rate of appearance of bromine is related to rate of disappearance of bromide ion as

(*a*) $\dfrac{d[Br_2]}{dt} = \dfrac{-5}{3}\dfrac{d[Br^-]}{dt}$ (*b*) $\dfrac{d[Br_2]}{dt} = \dfrac{5}{3}\dfrac{d[Br^-]}{dt}$

(*c*) $\dfrac{d[Br_2]}{dt} = \dfrac{3}{5}\dfrac{d[Br^-]}{dt}$ (*d*) $\dfrac{d[Br_2]}{dt} = \dfrac{-3}{5}\dfrac{d[Br^-]}{dt}$

2. A graph of volume of hydrogen released vs time for the reaction between zinc and dil. HCl is given in figure. On the basis of this mark the correct option. [*NCERT Exemplar*]



(*a*) Average rate upto 40 seconds is $\dfrac{V_3 - V_2}{40}$

(*b*) Average rate upto 40 seconds is $\dfrac{V_3 - V_2}{40 - 30}$

(*c*) Average rate upto 40 seconds is $\dfrac{V_3}{40}$

(*d*) Average rate upto 40 seconds is $\dfrac{V_3 - V_1}{40 - 20}$

3. Consider the graph given in the above question. Which of the following options does not show instantaneous rate of reaction at 40th second? [*NCERT Exemplar*]

(*a*) $\dfrac{V_5 - V_2}{50 - 30}$ (*b*) $\dfrac{V_4 - V_2}{50 - 30}$ (*c*) $\dfrac{V_3 - V_2}{40 - 30}$ (*d*) $\dfrac{V_3 - V_1}{40 - 20}$

4. The rate constant of reaction is 2.0×10^{-6} mol^{-2} L^{2} s^{-1}. The order of the reaction is

(*a*) 0 (*b*) 2 (*c*) 1 (*d*) 3

5. The rate of a gaseous reaction is given by the expression, rate = $k[A]$ $[B]$. If the volume of the reaction vessel is suddenly reduced to 1/4 of the initial volume, the reaction rate related to original rate will be

(*a*) 1/16 (*b*) $\dfrac{1}{8}$ (*c*) 8 (*d*) 16

6. Which of the following is not correct about order of a reaction? [*NCERT Exemplar*]

(*a*) The order of a reaction can be a fractional number.

(*b*) Order of a reaction is experimentally determined quantity.

(*c*) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.

(*d*) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.

7. Which of the following statements are applicable to a balanced chemical equation of an elementary reaction? [*NCERT Exemplar*]

(*a*) Order is same as molecularity. (*b*) Order is less than the molecularity.

(*c*) Order is greater than the molecularity. (*d*) Molecularity can never be zero.

8. For the reaction,

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

The experimental data suggests,

$$\text{Rate} = k[H_2][Br_2]^{\frac{1}{2}}$$

The molecularity and order for the reaction is

(*a*) 2 and 2 (*b*) 2 and $1\frac{1}{2}$ (*c*) $1\frac{1}{2}$ and 2 (*d*) $1\frac{1}{2}$ and $1\frac{1}{2}$

9. The unit of rate constant of a zero order reaction is

(*a*) litre second^{-1} (*b*) litre mole^{-1} second^{-1} (*c*) mole litre^{-1} second^{-1} (*d*) mole second^{-1}

10. Rate law cannot be determined from balanced chemical equation if __________. [*NCERT Exemplar*]

(*a*) reverse reaction is involved (*b*) it is an elementary reaction

(*c*) it is a sequence of elementary reactions (*d*) any of the reactants is in excess

11. In the reaction, A $\longrightarrow$ B, the rate of reaction increases two times on increasing the concentration of A four times, the order of reaction is

(*a*) 2 (*b*) 0 (*c*) $\dfrac{1}{2}$ (*d*) 3

12. Which of the following is a zero order reaction?

(*a*) Decomposition of N_2O_5 (*b*) Decomposition of NH_3

(*c*) Decomposition of N_2O (*d*) Radioactive decay of unstable nuclei

13. Diazonium salt decomposes as

$$C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$$

at 0° C. The evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore it is

(*a*) a first order reaction

(*b*) a second order reaction

(*c*) independent of the initial concentration of the salt

(*d*) a zero order reaction

14. In the graph plotted between ln [*R*] and *t* for a first order reaction, the intercept on *y*-axis is

(*a*) $-k$ (*b*) $[R]_0$ (*c*) $\ln [R]_0$ (*d*) $k/2.303$

15. If 75% of the first-order reaction was completed in 32 minutes, 50% of the same reaction would be completed in:

(*a*) 8 min (*b*) 4 min (*c*) 16 min (*d*) 24 min

16. The half life of a first order reaction is 69.35 sec. The value of rate constant of the reaction is

(*a*) 1.0 s^{-1} (*b*) 0.1 s^{-1} (*c*) 0.01 s^{-1} (*d*) 0.001 s^{-1}

17. Consider a first order gas phase decomposition reaction given below: **[*NCERT Exemplar*]**

$$A(g) \longrightarrow B(g) + C(g)$$

The initial pressure of the system before decomposition of A was p_i. After lapse of time '*t*', total pressure of the system increased by *x* units and became 'p_t'. The rate constant *k* for the reaction is given as ______________.

(*a*) $k = \dfrac{2.303}{t}\log\dfrac{p_i}{p_i - x}$ (*b*) $k = \dfrac{2.303}{t}\log\dfrac{p_i}{2p_i - p_t}$

(*c*) $k = \dfrac{2.303}{t}\log\dfrac{p_i}{2p_i + p_t}$ (*d*) $k = \dfrac{2.303}{t}\log\dfrac{p_i}{p_i + x}$

18. The activation energy of a reaction is zero. The rate of the reaction

(*a*) increases with increase of temperature (*b*) decreases with decrease of temperature

(*c*) decreases with increase of temperature (*d*) is nearly independent of temperature

19. The activation energy of a reaction can be determined from the slope of which of the following graphs?

(*a*) $\ln k$ vs $\dfrac{1}{T}$ (*b*) $\dfrac{T}{\ln k}$ vs $\dfrac{1}{T}$

(*c*) $\ln k$ vs T (*d*) $\dfrac{\ln k}{T}$ vs T

20. Consider figure and mark the correct option.

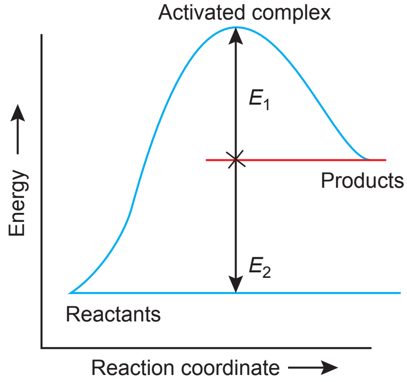
[*NCERT Exemplar*]

(*a*) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.

(*b*) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant.

(*c*) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product.

(*d*) Activation energy of backward reaction is E_1 and product is more stable than reactant.



21. **The role of a catalyst is to change ________________.** [*NCERT Exemplar*]

(*a*) gibbs energy of reaction (*b*) enthalpy of reaction

(*c*) activation energy of reaction (*d*) equilibrium constant

22. **In the presence of a catalyst, the heat evolved or absorbed during the reaction ________________.** [*NCERT Exemplar*]

(*a*) increases (*b*) decreases

(*c*) remains unchanged (*d*) may increase or decrease

Answers

1. (*d*) **2.** (*c*) **3.** (*b*) **4.** (*d*) **5.** (*d*) **6.** (*c*) **7.** (*a*), (*d*) **8.** (*b*) **9.** (*c*) **10.** (*a,c,d*)
11. (*c*) **12.** (*b*) **13.** (*a*) **14.** (*c*) **15.** (*c*) **16.** (*c*) **17.** (*b*) **18.** (*d*) **19.** (*a*) **20.** (*a*)
21. (*c*) **22.** (*c*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(*a*) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*

(*b*) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*

(*c*) *Assertion (A) is correct, but Reason (R) is incorrect statement.*

(*d*) *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. **Assertion (*A*)** : Instantaneous rate is used to predict the rate of a reaction at a particular moment of time.
   Reason (*R*) : Average rate is constant for the time interval for which it is calculated.
2. **Assertion (*A*)** : For the reaction, $CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$, rate = $k[CHCl_3]\,[Cl_2]^{1/2}$
   Reason (*R*) : Rate law for any reaction can be predicted with the help of a balanced chemical equation.
3. **Assertion (*A*)** : The rate of the reaction is the rate of change of concentration of a reaction or a product.
   Reason (*R*) : Rate of reaction remains constant during the course of reaction.
4. **Assertion (*A*)** : Order of the reaction can be zero or fractional.
   Reason (*R*) : We cannot determine order from balanced chemical equation.
5. **Assertion (*A*)** : Order and molecularity are same.
   Reason (*R*) : Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step.
6. **Assertion (*A*)** : For the reaction
   $$2N_2O_5 \longrightarrow 4NO_2 + O_2;$$
   Rate = $k[N_2O_5]$.
   Reason (*R*) : Rate of decomposition of N_2O_5 is determined by slow step.
7. **Assertion (*A*)** : The inversion of cane sugar,
   $$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
   is a pseudo first order reaction.
   Reason (*R*) : H_2O in this reaction is present in very less amount as compared to $C_{12}H_{22}O_{11}$.
8. **Assertion (*A*)** : For each ten degree rise of temperature the specific rate constant is nearly doubled.
   Reason (*R*) : Energy-wise distribution of molecules in a gas is an experimental function of temperature.
9. **Assertion (*A*)** : If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.
   Reason (*R*) : Lower the activation energy, faster is the reaction.

10. **Assertion (*A*) :** Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.

Reason (*R*) : Reactant molecules undergo chemical change irrespective of their orientation during collision.

11. **Assertion (*A*) :** The enthalpy of reaction remains constant in the presence of a catalyst.

Reason (*R*) : A catalyst participating in the reaction, forms different activated complex and lowers down the activation energy but the difference in energy of reactant and product remains the same.

12. **Assertion (*A*) :** All collision of reactant molecules lead to product formation.

Reason (*R*) : Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.

Answers

1. (*b*) **2.** (*c*) **3.** (*c*) **4.** (*b*) **5.** (*d*) **6.** (*b*) **7.** (*c*) **8.** (*b*) **9.** (*c*) **10.** (*c*)
11. (*a*) **12.** (*d*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

The rate of a chemical reaction 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. Rate of the reaction depends upon the nature of reactants, concentration of reactants, temperature, presence of catalyst, surface area of the reactants and presence of light. Rate of reaction is directly related to the concentration of reactant. Rate law states that the rate of reaction depends upon the concentration terms on which the rate of reaction actually depends, as observed experimentally. The sum of powers of the concentration of the reactants in the rate law expression is called order of reaction while the number of reacting species taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction is called molecularity of the reaction.

1. **Express the rate of the following reaction in terms of different reactants and products.**

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO_2(g) + 6H_2O(g)$$

Ans. Rate of reaction $= -\frac{1}{4}\frac{d[NH_3]}{dt}$

$$= -\frac{1}{5}\frac{d[O_2]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = +\frac{1}{6}\frac{d[H_2O]}{dt}$$

2. **Why do pieces of wood burn faster than a log of wood of the same mass?**

Ans. Pieces of wood have larger surface area than the log of wood of the same mass. Greater the surface area, faster is the reaction.

3. **Why does the rate of any reaction generally decrease during the course of the reaction?**

Ans. The rate of reaction depends on the concentration of reactants. As the reaction progresses, reactants start getting converted to products so the concentration of reactants decreases hence the rate of reaction decreases.

4. **Why is molecularity applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?**

Ans. A complex reaction proceeds through several elementary reactions. Number of molecules involved in each elementary reaction may be different, *i.e.*, the molecularity of each step may be different. Therefore, discussion of the molecularity of overall complex reaction is meaningless. On the other hand, order of a complex reaction is determined by the slowest step in its mechanism and is not meaningless even in the case of complex reactions.

5. **The kinetics of the reaction**

$$mA + nB + pC \longrightarrow m'X + n'Y + p'Z$$

obey the rate expression $dx/dt = k[A]^m[B]^n$

Calculate total order and molecularity of the reaction.

Ans. The total order of reaction = $m + n$

The molecularity of the reaction = $m + n + p$

PASSAGE–2

Temperature has a marked effect on the rate of reaction. For most of the reactions,the rate of reaction becomes nearly double for every 10 degree rise in temperature. The effect of temperature is usually expressed in terms of temperature coefficient. The quantitative dependence of reaction rate on temperature was first explained by Swante Arrhenius. Arrhenius proposed a simple equation known as Arrhenius equation

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

This equation provides a relationship between the rate constant (k) of a reaction and the temperature of the system. A is the Arrhenius factor or pre-exponential factor, E_a is the activation energy and R is the gas constant.

1. **Define 'activation energy' of a reaction.** *[CBSE (AI) 2011]*

Ans. The energy required to form the intermediate called activated complex is known as activation energy.

Activation energy = Threshold energy – Average energy of the reactants

2. **How does a catalyst affect the rate of a reaction? Explain with respect to the Arrhenius equation.**

Ans. A catalyst decreases the activation energy. According to Arrhenius equation, lower the activation energy, greater will be the rate constant and thus the rate of reaction increases.

3. **Can a reaction have zero activation energy? Justify.**

Ans. No, $E_a \neq 0$.

If $E_a = 0$, then according to Arrhenius equation,

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

$$k = Ae^0 = \text{A},$$

i.e., Rate constant = Collision frequency

This means every collision results into a chemical reaction which cannot be true.

4. **The plot of log k vs X is linear with slope = $-E_a/2.303R$. What is X?**

Ans. $1/T$

5. **What is the fraction of molecules having energy greater than activation energy, E_a?**

Ans. $e^{-Ea/RT}$ at temperature T.

Very Short Answer Questions [1 mark]

Q. 1. For the assumed reaction $X_2 + 3Y_2 \longrightarrow 2XY_3$, write the rate of equation in terms of rate of disappearance of Y_2. *[HOTS]*

Ans. Rate $= -\dfrac{d[X_2]}{dt} = -\dfrac{1}{3}\dfrac{d[Y_2]}{dt} = +\dfrac{1}{2}\dfrac{d[XY_3]}{dt}$

Rate of disappearance of $Y_2 = -\dfrac{d[\text{Y}_2]}{dt} = -3\dfrac{d[\text{X}_2]}{dt} = +\dfrac{3}{2}\dfrac{d[\text{XY}_3]}{dt}$

Q. 2. Why does the rate of a reaction increase with rise in temperature? *[NCERT Exemplar]*

Ans. At higher temperatures, larger fraction of colliding particles can cross the energy barrier (*i.e.*, the activation energy), which leads to faster rate.

Q. 3. Define 'order of a reaction'. *[CBSE 2019 (56/2/1)]*

Ans. Order of a reaction may be defined as the sum of the powers of the concentration terms of the reactants in the rate law expression.

Q. 4. Identify the order of reaction from the following unit for its rate constant:
$L\ mol^{-1}s^{-1}$ [*CBSE (F) 2010*]

Ans. Second order.

Q. 5. For the reaction $A \longrightarrow B$, the rate of reaction becomes three times when the concentration of A is increased by nine times. What is the order of reaction? [*HOTS*]

Ans. Let, $r = k\,[A]^n$ ...(*i*)

Given, $3r = k\,[9A]^n$ ...(*ii*)

Dividing equation (*ii*) by (*i*), we get

$$\frac{3r}{r} = \frac{k[9A]^n}{k[A]^n} = \frac{9^n k[A]^n}{k[A]^n}$$

$$3 = 9^n \quad \text{or} \quad 3^1 = 3^{2n}$$

$$\Rightarrow \quad 2n = 1 \quad \text{or} \quad n = \frac{1}{2}$$

$$\therefore \quad \text{Rate, } r = k[A]^{1/2}$$

$$\text{Order of reaction} = \mathbf{\frac{1}{2}}$$

Q. 6. For which type of reactions, order and molecularity have the same value? [*NCERT Exemplar*]

Ans. If the reaction is an elementary reaction, order is same as molecularity.

Q. 7. Why is the probability of reaction with molecularity higher than three very rare? [*NCERT Exemplar*]

Ans. The probability of more than three molecules colliding simultaneously is very small. Hence, possibility of molecularity being three is very low.

Q. 8. For a reaction, $A + B \longrightarrow$ Products, the rate law is Rate = $k[A][B]^{3/2}$. Can the reaction be an elementary reaction? Explain. [*HOTS*]

Ans. During an elementary reaction, the number of atoms or ions colliding to react is referred to as molecularity. Had this been an elementary reaction the order of reaction with respect to B would have been 1, but in the given rate law it is $\frac{3}{2}$. This indicates that the reaction is not an elementary reaction.

Q. 9. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of the reaction? [*HOTS*]

Ans. As $t_{75\%} = 2t_{50\%}$

Therefore, it is a first order reaction.

Q. 10. What is the effect of adding a catalyst on
(*i*) Activation energy (E_a), and
(*ii*) Gibbs energy (ΔG) of a reaction? [*CBSE Delhi 2017; (AI) 2017*]

Ans. (*i*) Decreases

(*ii*) No effect

Q. 11. Define threshold energy of a reaction.

Ans. Threshold energy is the minimum energy which must be possessed by reacting molecules in order to undergo effective collision which leads to formation of product molecules.

Q. 12. Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction. Explain with the help of one example. [*NCERT Exemplar*]

Ans. Thermodynamically the conversion of diamond to graphite is highly feasible but this reaction is very slow because its activation energy is high.

Q. 13. In some cases, it is found that a large number of colliding molecules have energy more than threshold value, yet the reaction is slow. Why? [*CBSE Delhi 2013*]

Ans. This is due to improper orientation of the colliding molecules at the time of collision.

Short Answer Questions–I [2 marks]

Q. 1. For the reaction $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ the rate of formation of $NO_2(g)$ is 2.8×10^{-3} Ms^{-1}. Calculate the rate of disappearance of $N_2O_5(g)$. *[CBSE 2018]*

Ans. Rate $= \frac{-1}{2}\frac{\Delta(N_2O_5)}{\Delta t} = +\frac{1}{4}\frac{\Delta(NO_2)}{\Delta t} = +\frac{\Delta(O_2)}{\Delta t}$

$$\text{Rate of disappearance of } N_2O_5 = -\frac{\Delta(N_2O_5)}{\Delta t} = \frac{1}{2}\frac{\Delta(NO_2)}{\Delta t}$$

$$= \frac{1}{2} \times 2.8 \times 10^{-3}\ Ms^{-1} = \mathbf{1.4 \times 10^{-3}\ Ms^{-1}}$$

Q. 2. The rate law for the reaction: Ester + H^+ $\longrightarrow$ Acid + Alcohol is:

$$\frac{dx}{dt} = k\,[\text{Ester}]\,[H^+]^0$$

What would be the effect on the rate if (*i*) concentration of the ester is doubled? (*ii*) concentration of H^+ is doubled?

Ans. (*i*) The rate of reaction will be doubled. (*ii*) No effect on rate.

Q. 3. Differentiate between rate of reaction and reaction rate constant.

Ans.

S. No.	Rate of Reaction	Reaction Rate Constant
(*i*)	Rate of reaction is the change in concentration of a reactant or product in a unit interval of time.	It is the rate of reaction when the molar concentration of each of the reactants is unity.
(*ii*)	The rate of reaction at any instant of time depends upon the molar concentrations of the reactants at that time.	The rate constant does not depend upon the concentrations of the reactants.
(*iii*)	Its units are always mol litre^{-1} time^{-1}.	Its units depend upon the order of reaction.

Q. 4. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is reduced to half? What is the unit of rate constant for such a reaction? *[CBSE (AI) 2011]*

Ans. Consider the reaction $nR \longrightarrow$ Products

As the reaction is of second order

$\therefore$ Rate, $r = k\,[R]^2$ ...(*i*)

If the concentration of the reactant reduced to half, then

Rate, $r' = k\left[\frac{R}{2}\right]^2$ ...(*ii*)

Dividing equation (*ii*) by (*i*), we get

$$\frac{r'}{r} = \frac{k\,[R]^2}{4k\,[R]^2} = \frac{1}{4}$$

$r' = \frac{1}{4}r$, *i.e.*, rate of reaction becomes $\frac{1}{4^{th}}$ of the initial rate.

The unit of rate constant is **mol^{-1} L s^{-1}**.

Q. 5. What do you understand by the rate law and rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are: *[CBSE (AI) 2011]*

(*i*) L^{-1} mol s^{-1} (*ii*) L mol^{-1} s^{-1}.

Ans. An experimentally determined expression which relates the rate of reaction with the concentration of reactants is called rate law while the rate of reaction when concentration of each reactant is unity in a rate law expression is called rate constant.

(*i*) Comparing power of mole in L^{-1} mol s^{-1} and $(\text{mol } L^{-1})^{1-n}\,s^{-1}$,

We get

$$1 = 1 - n \quad \Rightarrow \quad n = 0 \text{ } i.e., \text{ zero order reaction}$$

(*ii*) Again comparing power of mole in L $mol^{-1}s^{-1}$ and $(\text{mol } L^{-1})^{1-n}s^{-1}$, we get

$$-1 = 1 - n \quad \Rightarrow \quad n = 2, \ i.e., \text{ second order reaction}$$

Q. 6. Calculate the overall order of a reaction which has the rate expression,

(i) Rate = $k[A]^{1/2}[B]^{3/2}$ (ii) Rate = $k[A]^{3/2}[B]^{-1}$

Ans. (i) Order = $\frac{1}{2}+\frac{3}{2}=2$, *i.e.*, second order.

(ii) Order = $\frac{3}{2}+(-1)=\frac{1}{2}$, *i.e.*, half order.

Q. 7. Write two differences between 'order of reaction' and 'molecularity of reaction'.[*CBSE Delhi 2014*]

Ans. Differences between order and molecularity of reaction:

S.No.	Order	Molecularity
(*i*)	It is the sum of the powers of the concentration of the reactants in the rate law expression.	It is the number of reacting species taking part in an elementary reaction, which must collide simultaneously so as to result into a chemical reaction.
(*ii*)	It is determined experimentally.	It is a theoretical concept.
(*iii*)	It can be zero or a fraction.	It cannot be zero or a fraction.
(*iv*)	Order is applicable to elementary as well as complex reactions.	Molecularity is applicable only for elementary reactions. For complex reactions it has no meaning.

(*Any two*)

Q. 8. For a reaction: $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$

Rate = k

(i) Write the order and molecularity of this reaction.

(ii) Write the unit of k. [*CBSE South 2016*]

Ans. (*i*) Zero order, bimolecular

(*ii*) mol L^{-1} s^{-1}

Q. 9. Why is molecularity applicable only for elementary reactions and order is applicable for elementary as well as complex reactions? [*NCERT Exemplar*]

Ans. A complex reaction proceeds through several elementary reactions. Number of molecules involved in each elementary reaction may be different, *i.e.*, the molecularity of each step may be different. Therefore, discussion of molecularity of overall complex reaction is meaningless. On the other hand, order of a complex reaction is determined by the slowest step in its mechanism and is not meaningless even in the case of complex reactions.

Q. 10. Consider the decomposition of hydrogen peroxide in alkaline medium which is catalysed by iodide ions.

$$2H_2O_2 \xrightarrow{OH^-} 2H_2O + O_2$$

This reaction takes place in two steps as given below:

Step-I $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ **(slow)**

Step-II $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ **(fast)**

(i) Write the rate law expression and determine the order of reaction w.r.t. H_2O_2.

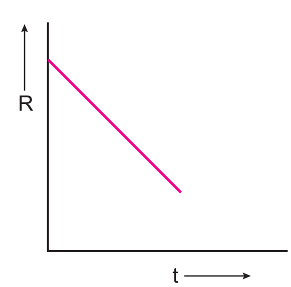
(ii) What is the molecularity of each individual step?

Ans. (*i*) Rate = $k\,[H_2O_2]^1\,[I^-]^1$

Order of reaction w.r.t $H_2O_2 = 1$

(*ii*) Molecularity of step I = 2 and step II = 2.

Q. 11. For a chemical reaction $R \rightarrow P$, the variation in the concentration (R) vs. time (t) plot is given alongside.



(i) Predict the order of the reaction.

(ii) What is the slope of the curve? [*CBSE (AI) 2014*]

Ans. (*i*) Order of the reaction is zero.

(*ii*) Slope = $\frac{d[R]}{dt} = -k$

Q. 12. The rate constant for a reaction of zero order in A is 0.0030 mol L^{-1} s^{-1}. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M?

Ans. k = 0.0030 mol $L^{-1}s^{-1}$, $[R]_0$ = 0.10 M, $[R]$ = 0.075 M

We know that

$$[R] = -kt + [R]_0$$

$$0.075 = -0.0030t + 0.10$$

$$\Rightarrow \quad 3t = 100 - 75 \quad \Rightarrow \quad t = \mathbf{8.33\ seconds}$$

Q. 13. Define the following terms:

(*i*) Pseudo first order reaction

(*ii*) Half life period of reaction ($t_{1/2}$) **[*CBSE Delhi 2014*]**

Ans. (*i*) A reaction which is not truely of first order but under certain conditions becomes a reaction of first order is called pseudo first order reaction, *e.g.*, acid hydrolysis of ethyl acetate.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Rate $\propto [CH_3COOC_2H_5]$ as H_2O is in excess.

(*ii*) The half life ($t_{1/2}$) of a reaction is the time in which the concentration of reactant is reduced to one half of its initial concentration $[R]_0$.

For a first order reaction, $t_{1/2} = \dfrac{0.693}{k}$, *i.e.*, independent of $[R]_0$.

For a zero order reaction, $t_{1/2} = \dfrac{[R]_0}{2k}$, *i.e.*, $t_{1/2} \propto [R]_0$.

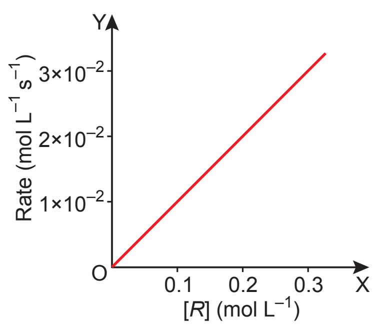
Q. 14. For a reaction: $A + H_2O \longrightarrow B$, Rate $\propto [A]$.

What is its (*i*) molecularity (*ii*) order of reaction?

Ans. (*i*) Pseudo unimolecular

(*ii*) Order = 1.

Q. 15. The rate for the reaction $R \longrightarrow P$ is rate = $k[R]$. It has been shown graphically alongside. What is rate constant for the reaction?



Ans. From the graph

Case I: Rate = $k[A]$

$$1 \times 10^{-2}\ \text{mol L}^{-1}\ \text{s}^{-1} = k\ (0.1\ \text{mol L}^{-1})$$

$$\therefore \quad k = \frac{1 \times 10^{-2}\ \text{mol L}^{-1}\ \text{s}^{-1}}{0.1\ \text{mol L}^{-1}} = 0.1\ \text{s}^{-1}$$

Case II:

$$3 \times 10^{-2}\ \text{mol L}^{-1}\text{s}^{-1} = k\ (0.3\ \text{mol L}^{-1})$$

$$k = \frac{3 \times 10^{-2}\ \text{mol L}^{-1}\ \text{s}^{-1}}{0.3\ \text{mol L}^{-1}} = 0.1\ \text{s}^{-1}$$

Hence, $\mathbf{k = 0.1\ s^{-1}}$

Q. 16. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to $\frac{1}{10}$th of its initial value? **[*CBSE (F) 2013*]**

Ans. $$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} \quad \text{as} \quad [R] = \frac{[R]_0}{10}$$

$$\therefore \quad t = \frac{2.303}{k}\log\frac{[R]_0}{\frac{[R]_0}{10}} = \frac{2.303}{60} \times \log 10 = \frac{2.303}{60} \times 1 = \mathbf{3.838 \times 10^{-2}\ s}$$

Q. 17. **(*i*) For a reaction $A + B \longrightarrow P$, the rate law is given by,**

$$r = k[A]^{1/2}[B]^2.$$

What is the order of this reaction?

(*ii*) A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-14}\ s^{-1}$. Find the half life of the reaction. **[*CBSE (AI) 2013*]**

Ans. (*i*) Order of reaction $= \frac{1}{2} + 2 = \mathbf{\frac{5}{2}}$

(*ii*) Radioactive decay follows first order kinetics.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.5 \times 10^{-14}}\ \text{s} = \mathbf{1.26 \times 10^{13}\ s}$$

Q. 18. **87.5% of the substance disintegrated in 45 minutes (first order reaction). What is its half-life?**

Ans. $\left(\frac{1}{2}\right)^n = \frac{12.5}{100}$ because 87.5% has disintegrated, amount left is 12.5%.

$$\left(\frac{1}{2}\right)^n = \left(\frac{1}{8}\right) \quad \Rightarrow \quad \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^3$$

Number of half lives = 3

$$t_{1/2} = \frac{45}{3} = \mathbf{15\ minutes}$$

Q. 19. **After 24 hrs, only 0.125 gm out of the initial quantity of 1 gm of a radioactive isotope remains behind. What is its half life period?** **[*CBSE Sample Paper 2017*]**

Ans. Here, $[R]_0 = 1$ g, $[R] = 0.125$ g, $t = 24$ h

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

$$k = \frac{2.303}{24}\log\frac{1}{0.125} \quad \Rightarrow \quad k = \frac{2.303}{24}\log 8$$

$$k = \frac{2.303}{24} \times 0.9031 \quad \Rightarrow \quad k = 0.0866\ \text{h}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} \quad \Rightarrow \quad t_{1/2} = \frac{0.693}{0.0866\ \text{h}^{-1}} \text{ or } t_{1/2} = \mathbf{8\ h}$$

Q. 20. **Show that in a first order reaction, time required for completion of 99.9% is 10 times that of half-life ($t_{1/2}$) of the reaction.** **[*CBSE (F) 2016*]**

Ans. $t = \frac{2.303}{k}\log\frac{[R]_0}{[R]}$

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{\frac{2.303}{k}\log\frac{100}{100-99.9}}{\frac{2.303}{k}\log\frac{100}{100-50}} = \frac{\log\frac{100}{0.1}}{\log\frac{100}{50}} = \frac{\log 10^3}{\log 2} = \frac{3\log 10}{0.3010}$$

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{30}{3.01} \simeq 10$$

$$t_{99.9\%} = 10t_{50\%}$$

Q. 21. **Rate constant k for first order reaction has been found to be $2.54 \times 10^{-3}\ s^{-1}$. Calculate its three-fourth life.** **[*CBSE Sample Paper 2013*]**

Ans. $$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} \qquad ...(i)$$

$$k = 2.54 \times 10^{-3}\ \text{s}^{-1}; [R] = \frac{[R]_0}{4}$$

Substituting these values in equation (i), we get

$$t_{3/4} = \frac{2.303}{2.54\times10^{-3}}\log\frac{[R]_0}{\frac{[R]_0}{4}} = 0.9066\times10^{3}\log 4$$

$$t_{3/4} = 0.9066 \times 10^3 \times 0.6021 \text{ s}$$

$$= \mathbf{5.46 \times 10^2 \text{ s}}$$

Q. 22. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	Time/second^{-1}	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.

(Given: log 4 = 0.6021, log 2 = 0.3010) **[*HOTS*]**

Ans. $$k = \frac{2.303}{t}\log\frac{P_0}{2P_0 - P_t}$$

Here, $P_0 = 0.4$ atm, $t = 100$ s, $P_t = 0.7$ atm

$\therefore$ $$k = \frac{2.303}{100}\log\frac{0.4}{2\times0.4-0.7}$$

$$= \frac{2.303}{100}\log\frac{0.4}{0.1} = \frac{2.303}{100}\log 4$$

$$= \frac{2.303}{100}\times 0.6021$$

$$k = \mathbf{1.386 \times 10^{-2}\ s^{-1}}$$

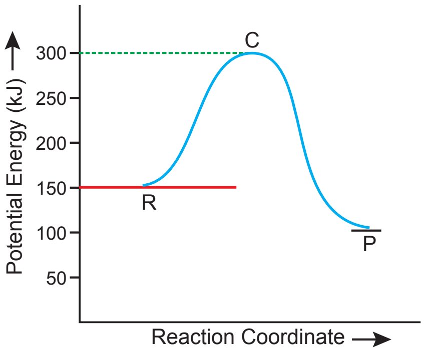
Q. 23. (*i*) Explain why H_2 and O_2 do not react at room temperature.

(*ii*) Write the rate equation for the reaction $A_2 + 3B_2 \longrightarrow 2C$, if the overall order of the reaction is zero. **[*CBSE (AI) 2017*]**

Ans. (*i*) Due to high activation energy for the reaction.

(*ii*) Rate $= k[A_2]^0[B_2]^0$ or Rate $= k$

Q. 24. Answer the following questions on the basis of the given plot of potential energy vs reaction coordinate:



(*i*) What is the threshold energy for the reaction?

(*ii*) What is the activation energy for forward reaction?

(*iii*) What is the activation energy for backward reaction?

(*iv*) What is enthalpy change for the forward reaction?

Ans. (*i*) Threshold energy for the reaction = 300 kJ mol^{-1}

(*ii*) Activation energy for the forward reaction = 300 – 150
= 150 kJ mol^{-1}

(*iii*) Activation energy for the backward reaction = 300 – 100
= 200 kJ mol^{-1}

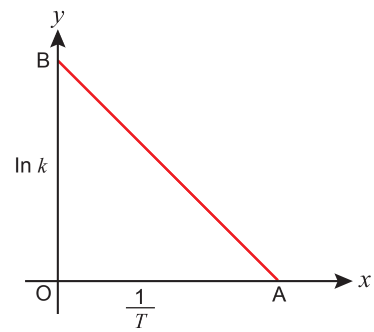
(*iv*) Enthalpy change for the forward reaction Δ_rH = 100 – 150
= – 50 kJ mol^{-1}

Q. 25. **A graph between ln k and $\frac{1}{T}$ for a reaction is given. Here k is rate constant and T is temperature in kelvin. If $OA = a$ and $OB = b$, answer the following:**

(*i*) What is the activation energy (E_a) of the reaction?

(*ii*) What is the frequency factor (A) for the reaction?

[*HOTS*]



Ans. According to Arrhenius equation, $\ln k = -\frac{E_a}{RT} + \ln A$

(*i*) Slope $= -\frac{OB}{OA} = -\frac{b}{a} = -\frac{E_a}{R}$ or $E_a = \frac{b}{a}R$

(*ii*) Intercept on y-axis $= OB = b = \ln A$ or $A = e^b$

Short Answer Questions–II [3 marks]

Q. 1. **$A + 2B \longrightarrow 3C + 2D$. The rate of disappearance of B is 1×10^{-2} mol L^{-1} s^{-1}. What will be (*i*) Rate of the reaction (*ii*) Rate of change in concentration of A and C?**

Ans. (*i*) As $\frac{-d[B]}{dt} = 1 \times 10^{-2}$ mol L^{-1} s^{-1}

$$\therefore \quad \text{Rate} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{2} \times 1 \times 10^{-2} = \mathbf{0.5 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}}$$

(*ii*)
$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = +\frac{1}{3}\frac{d[C]}{dt}$$

Rate of change in concentration of A

$$= -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

$$= \mathbf{0.5 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}}$$

Rate of change in concentration of C

$$= +\frac{d[C]}{dt} = -\frac{3}{2}\frac{d[B]}{dt} = \frac{3}{2} \times 1 \times 10^{-2}$$

$$= \mathbf{1.5 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}}$$

Q. 2. **The rate of reaction, $2NO + Cl_2 \longrightarrow 2NOCl$ is doubled when concentration of Cl_2 is doubled and it becomes eight times when concentration of both NO and Cl_2 are doubled. Deduce the order of the reaction.** **[*HOTS*]**

Ans. Let

$$r = k[NO]^x[Cl_2]^y \quad \ldots(i)$$

$$2r = k[NO]^x[2Cl_2]^y \quad \ldots(ii)$$

$$8r = k[2NO]^x[2Cl_2]^y \quad \ldots(iii)$$

Dividing (*iii*) by (*ii*), we get

$$\frac{8r}{2r} = \frac{k[2NO]^x[2Cl_2]^y}{k[NO]^x[2Cl_2]^y}$$

$$2^2 = [2]^x$$

$$x = 2$$

Putting the value of x in (*i*) and (*ii*), we get

$$r = k[NO]^2[Cl_2]^y$$

$$2r = k[NO]^2[2Cl_2]^y$$

$$\frac{2r}{r} = \frac{[2Cl_2]^y}{[Cl_2]^y}$$

$$2 = [2]^y$$
$$y = 1$$
$$\text{Rate} = k\,[NO]^2\,[Cl_2]^1$$

Overall order of reaction = $x + y = 2 + 1 =$ **3**

Q. 3. Following reaction takes place in one step:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

How will the rate of the above reaction change if the volume of the reaction vessel is reduced to one-third of its original volume? Will there be any change in the order of the reaction with reduced volume? [*HOTS*]

Ans. $$\text{Rate} = k\,[NO]^2\,[O_2]$$

Let initially, moles of NO = a, moles of $O_2 = b$, volume of the vessel = V. Then

$$[NO] = \frac{a}{V}\,\text{M},\ [O_2] = \frac{b}{V}\,\text{M}$$

$$\therefore \qquad \text{Rate}\ (r_1) = k\left(\frac{a}{V}\right)^2\left(\frac{b}{V}\right) = k\frac{a^2 b}{V^3} \qquad \ldots(i)$$

Now, new volume = $\frac{V}{3}$

$\therefore$ New concentrations:
$$[NO] = \frac{a}{V/3} = \frac{3a}{V}$$
$$[O_2] = \frac{b}{V/3} = \frac{3b}{V}$$

$$\therefore \qquad \text{New rate}\ (r_2) = k\left(\frac{3a}{V}\right)^2\left(\frac{3b}{V}\right) = \frac{27ka^2b}{V^3} \qquad \ldots(ii)$$

$$\therefore \qquad \frac{r_2}{r_1} = 27 \qquad \text{or} \qquad r_2 = 27r_1,$$ *i.e.*, rate becomes **27 times**.

Thus, there is no effect on the order of reaction.

Q. 4. Nitric oxide, NO, reacts with oxygen to produce nitrogen dioxide. [*HOTS*]

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

The rate law for this reaction is:

$$\textbf{Rate} = k\,[NO]^2\,[O_2]$$

Propose a mechanism for the reaction.

Ans. The probable proposed mechanism may be,

$NO + O_2 \longrightarrow NO_3$ (fast) Step I

$NO_3 + NO \xrightarrow{k_1} NO_2 + NO_2$ (slow) Step II

Since slowest reaction is the rate determining step, therefore

$$\text{Rate} = k_1\,[NO_3]\,[NO]$$
$$K = \frac{[NO_3]}{[NO][O_2]}$$
$$[NO_3] = K\,[NO]\,[O_2]$$
$$\text{Rate} = k_1K\,[NO]\,[O_2]\,[NO] = K'[NO]^2\,[O_2],\ \text{where } K' = k_1.K$$

Q. 5. The reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ contributes to air pollution whenever a fuel is burnt in air at a high temperature. At 1500 K, equilibrium constant K for it is 1.0×10^{-5}. Suppose in a case $[N_2] = 0.80$ mol L^{-1} and $[O_2] = 0.20$ mol L^{-1} before any reaction occurs. Calculate the equilibrium concentrations of the reactants and the product after the mixture has been heated to 1500 K.

[*CBSE (AI) 2012*] [*HOTS*]

Ans.

	N_2	+ O_2	$\longrightarrow$ 2NO
Initial conc. in mol L^{-1}	0.8	0.2	0
Change in conc. in mol L^{-1}	$-x$	$-x$	$+2x$
Equilibrium conc. in mol L^{-1}	$0.8-x$	$0.2-x$	$2x$

$$K_C = \frac{[NO]^2}{[N_2][O_2]} \qquad \therefore \quad 1\times10^{-5} = \frac{(2x)^2}{(0.8-x)(0.2-x)}$$

As $x << 0.2$, therefore $0.8 - x \approx 0.8$ and $0.2 - x \approx 0.2$

$$\therefore \qquad 1 \times 10^{-5} = \frac{4x^2}{0.16} \qquad \Rightarrow \qquad 4x^2 = 16 \times 10^{-7}$$

$$x = 6.324 \times 10^{-4} \text{ mol L}^{-1}$$

Thus at equilibrium,

$$[NO] = 2x = 2 \times 6.324 \times 10^{-4} = \mathbf{12.648 \times 10^{-4} \text{ mol L}^{-1}}$$

$$[N_2] = 0.8 - 6.324 \times 10^{-4} \text{ mol L}^{-1} = \mathbf{0.799 \text{ mol L}^{-1}}$$

$$[O_2] = 0.2 - 6.324 \times 10^{-4} \text{ mol L}^{-1} = \mathbf{0.199 \text{ mol L}^{-1}}$$

Q. 6. Define order of reaction. How does order of a reaction differ from molecularity for a complex reaction? *[CBSE 2019 (56/3/2), 2020 (56/5/1)]*

Ans.
- The sum of powers of the concentration of the reactants in the rate law expression is known as order of that reaction.

  Consider the general reaction,

  $$aA + bB \longrightarrow cC + dD$$

  Let

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

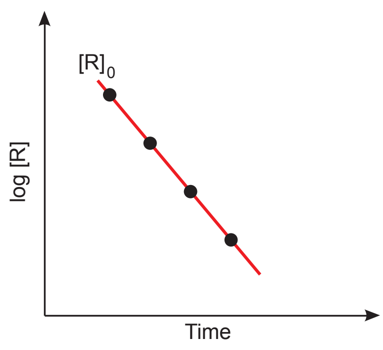
  where x and y represent the order w.r.t. t. The reactants A and B respectively. Overall order of reaction $= x + y$.
- Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions.

  For a complex reaction molecularity has no meaning and order is given by the slowest step. Molecularity of the slowest step is same as the order of the overall reaction.

Q. 7. Observe the graph in diagram and answer the following questions.

(*i*) If slope is equal to -2.0×10^{-6} sec^{-1}, what will be the value of rate constant?

(*ii*) How does the half-life of zero order reaction relate to its rate constant? *[CBSE Sample Paper 2017]*



Ans. (*i*) $\text{Slope} = -\dfrac{k}{2.303}$ or $k = -2.303 \times \text{Slope}$

$$\therefore \qquad k = -2.303 \times (-2.0 \times 10^{-6} \text{ s}^{-1})$$

$$k = \mathbf{4.606 \times 10^{-6} \text{ s}^{-1}}$$

(*ii*) For a zero order reaction

$$t = \frac{[R]_0 - [R]}{k}$$

$$\text{At } t = t_{1/2}, [R] = \frac{[R]_0}{2}$$

$$\therefore \qquad t_{1/2} = \frac{[R]_0 - \dfrac{[R]_0}{2}}{k} \qquad \text{or} \qquad t_{1/2} = \frac{[R]_0}{2k}$$

Q. 8. A solution of H_2O_2 when titrated against $KMnO_4$ solution at different intervals of time gave the following results:

Time (minutes)	0	10	20
Volume of $KMnO_4$ (mL)	23.8	14.7	9.1

Show that decomposition of H_2O_2 is first order reaction.

Ans. (*i*) $k = \dfrac{2.303}{10} \log \dfrac{23.8}{14.7} = \dfrac{2.303}{10} \times 0.2093 = \mathbf{0.048 \text{ min}^{-1}}$

(*ii*) $k = \dfrac{2.303}{20} \log \dfrac{23.8}{9.1} = \dfrac{2.303}{20} \times 0.4176 = \mathbf{0.048 \text{ min}^{-1}}$

Since the value of k comes out to be constant in both the cases, therefore the reaction is of first order.

Q. 9. Define half-life of a reaction. Write the expression of half-life for **[*CBSE (F) 2014*]**

(*i*) zero order reaction and (*ii*) first order reaction.

Ans. The half life ($t_{1/2}$) of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration.

(*i*) $t_{1/2}$ for a zero order reaction $= \dfrac{[R]_0}{2k}$ where $[R]_0$ = initial concentration, k = rate constant

(*ii*) $t_{1/2}$ for a first order reaction $= \dfrac{0.693}{k}$

Q. 10. A first order reaction is 50% complete in 25 minutes. Calculate the time for 80% completion of the reaction. **[*CBSE 2019 (56/3/2)*]**

Ans. $t_{1/2} = \dfrac{0.693}{k} \Rightarrow k = \dfrac{0.693}{t_{1/2}}$

$k = \dfrac{0.693}{25\text{ min}} = 2.772 \times 10^{-2}$ min

$[R] = [R]_0 - 80\%$ of $[R]_0$ or $[R] = [R]_0 - \dfrac{80 \times [R]_0}{100}$ or $[R] = 0.2[R]_0$

Substituting the value of k and $[R]$ in the expression

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}, \text{ we get}$$

$$t = \frac{2.303}{2.772 \times 10^{-2}} \times \log \frac{[R]_0}{0.2[R]_0}$$

$$t = \frac{2.303}{2.772 \times 10^{-2}} \log 5$$

$$t = \frac{2.303 \times 0.699}{2.772 \times 10^{-2}} \quad \text{or} \quad t = \mathbf{58.07\ min}$$

Q. 11. Following data are obtained for the reaction:

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

t/s	0	300	600
$[N_2O_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(*i*) Show that it follows first order reaction.

(*ii*) Calculate the half-life.

(Given log 2 = 0.3010, log 4 = 0.6021) **[*CBSE Delhi 2017*]**

Ans. (*i*) At 300 s,

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

$$= \frac{2.303}{300} \log \frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}} = \frac{2.303}{300} \log 2$$

$$k = \frac{2.303}{300} \times 0.3010 = 2.31 \times 10^{-3}\ s^{-1}$$

At 600 s

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

$$= \frac{2.303}{600} \log \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}} = \frac{2.303}{600} \log 4$$

$$k = \frac{2.303}{600} \times 0.6021 = 2.31 \times 10^{-3}\ s^{-1}$$

k is constant and is equal to $2.31 \times 10^{-3}\ s^{-1}$ when we use first order equation. Hence, it follows first order reaction.

(*ii*) $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{2.31\times10^{-3}\,s^{-1}} = \mathbf{300\ s}$

Q. 12. $^{238}_{92}U$ changes to $^{206}_{92}Pb$ by successive radioactive decay. A sample of uranium ore was analysed and found to contain 1.0 g of ^{238}U and 0.1 g of ^{206}Pb had accumulated due to decay of ^{238}U, find out the age of the ore. (Half-life of $^{238}U = 4.5 \times 10^9$ years) **[*HOTS*]**

Ans. $[A]_0$ = Initial amount of ^{238}U = amount of ^{238}U left at time t + amount of ^{238}U decayed

$$[A]_0 = 1.0 + \text{amount of } ^{238}U \text{ decayed}$$

Now, amount of ^{238}U decayed $= \dfrac{0.1\times 238}{206}\ g = 0.1155\ g$

$\therefore \quad [A]_0 = 1.0\ g + 0.1155\ g = 1.1155\ g$

Determination of k: $\quad k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{4.5\times10^9} = 0.154 \times 10^{-9}\ \text{year}^{-1}$

Determination of time: $\quad t = \dfrac{2.303}{k}\log\dfrac{[A]_0}{[A]}$

Substituting the values of $[A]_0 = 1.1155$ g and $k = 0.154 \times 10^{-9}\ \text{year}^{-1}$

$$t = \frac{2.303}{0.154\times10^{-9}}\log\frac{1.1155}{1}$$
$$= 0.7099 \times 10^9 \text{ year}$$
$$= \mathbf{7.099 \times 10^8\ year}$$

Q. 13. The following data were obtained during the first order thermal decomposition of $N_2O_5(g)$ at a constant volume:

$$\mathbf{2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)}$$

S. No.	Time/s	Total Pressure/atm
1.	0	0.5
2.	100	0.512

Calculate the rate constant. **[*HOTS*]**

Ans. Let the pressure of $N_2O_5(g)$ decrease by $2x$ atm. As two moles of N_2O_5 decompose to give two moles of $N_2O_4(g)$ and one mole of $O_2(g)$, the pressure of $N_2O_4(g)$ increases by $2x$ atm and that of $O_2(g)$ increases by x atm.

	$2N_2O_5(g)$	$\longrightarrow$ $2N_2O_4(g)$	$+ O_2(g)$
At $t = 0$	0.5 atm	0 atm	0 atm
At time t	$(0.5 - 2x)$ atm	$2x$ atm	x atm

$$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$$
$$= (0.5 - 2x) + 2x + x = 0.5 + x$$
$$x = p_t - 0.5$$
$$p_{N_2O_5} = 0.5 - 2x = 0.5 - 2(p_t - 0.5) = 1.5 - 2p_t$$

At $t = 100$ s; $p_t = 0.512$ atm,

$$p_{N_2O_5} = 1.5 - 2 \times 0.512 = 0.476 \text{ atm}$$

Thus, $\quad k = \dfrac{2.303}{t}\log\dfrac{p_i}{p_A}$

$$= \frac{2.303}{100\ s}\log\frac{0.5\ atm}{0.476\ atm}$$
$$= \frac{2.303}{100\ s}\times 0.02136 = \mathbf{4.92 \times 10^{-4}\ s^{-1}}$$

Q. 14. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} \text{K}$$

Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes.

(Given: $R = 8.314$ JK^{-1} mol^{-1}) **[*CBSE Delhi 2016*]**

Ans. Comparing the equation, $\log k = 14.2 - \dfrac{1.0 \times 10^4}{T}$ K with the equation, $\log k = \log A - \dfrac{E_a}{2.303\,RT}$, we get

$$\frac{E_a}{2.303\,RT} = \frac{1.0 \times 10^4 K}{T} \quad \text{or} \quad E_a = 1.0 \times 10^4 \text{ K} \times 2.303 \times R$$

$$E_a = 1.0 \times 10^4 \text{ K} \times 2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 19.1471 \times 10^4 \text{ J mol}^{-1} = \mathbf{191.47\ kJ\ mol^{-1}}$$

For a first order reaction, $t_{1/2} = \dfrac{0.693}{k}$ or $k = \dfrac{0.693}{t_{1/2}}$

$$\therefore \quad k = \frac{0.693}{200 \text{ min}} = \mathbf{3.465 \times 10^{-3}\ min^{-1}}$$

Q. 15. The rate constant of a first order reaction increases from 2×10^{-2} to 4×10^{-2} when the temperature changes from 300 K to 310 K. Calculate the energy of activation (E_a).

(log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021) **[*CBSE Patna 2015*]**

Ans. Substituting $k_1 = 2\times10^{-2}$, $k_2 = 4\times10^{-2}$, $T_1 = 300$ K, $T_2 = 310$ K, $R = 8.314$ J K^{-1}mol^{-1} in the expression

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left(\frac{T_2 - T_1}{T_1 T_2}\right), \text{ we get}$$

$$\log\frac{4\times10^{-2}}{2\times10^{-2}} = \frac{E_a}{2.303 \times 8.314}\left(\frac{310 - 300}{300 \times 310}\right)$$

$$\log 2 = \frac{E_a}{19.147} \times \frac{10}{300 \times 310}$$

$$E_a = 0.3010 \times 19.147 \times 300 \times 31 = 53598 \text{ J mol}^{-1}$$

$$E_a = \mathbf{53.598\ kJ\ mol^{-1}}$$

Q. 16. For a reaction, the energy of activation is zero. What is the value of rate constant at 300 K, if $k = 1.6 \times 10^6$ s^{-1} at 280 K? [$R = 8.31$ J K^{-1} mol^{-1}]

Ans. Given $T_1 = 280$ K, $k_1 = 1.6 \times 10^6$ s^{-1}, $k_2 = ?$, $E_a = 0$, $T_2 = 300$ K.

By Arrhenius equation,

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

As, $E_a = 0$

$$\therefore \quad \log\frac{k_2}{k_1} = 0$$

$$\text{or} \quad \frac{k_2}{k_1} = 1 \quad \text{or} \quad k_2 = k_1$$

Thus, the rate constant at 300 K is $\mathbf{1.6 \times 10^6\ s^{-1}}$.

Q. 17. A certain reaction is 50% complete in 20 minutes at 300 K and the same reaction is again 50% complete in 5 minutes at 350 K. Calculate the activation energy if it is a first order reaction.

[$R = 8.314$ J K^{-1} mol^{-1}; log 4 = 0.602] **[*HOTS*]**

Ans. For a first order reaction, $k = \dfrac{0.693}{t_{1/2}}$

$T_1 = 300$ K, $\quad k_1 = \dfrac{0.693}{20} = 3.456 \times 10^{-2}$ min^{-1}

$T_2 = 350$ K, $\quad k_2 = \frac{0.693}{5} = 1.386 \times 10^{-1}$ min^{-1}

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

$$\log \frac{1.386 \times 10^{-1}}{3.465 \times 10^{-2}} = \frac{E_a}{2.303 \times 8.314}\left(\frac{350 - 300}{350 \times 300}\right)$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314}\left(\frac{50}{350 \times 300}\right)$$

$$0.602 = \frac{E_a}{19.147}\left(\frac{50}{350 \times 300}\right)$$

$$E_a = \frac{0.602 \times 19.147 \times 350 \times 300}{50}$$

$$= 24205.63 \text{ J mol}^{-1}$$

$$= \mathbf{24.206\ kJ\ mol^{-1}}$$

Q. 18. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction. ***[CBSE 2018]***

(Given: log 2 = 0.3010, log 4 = 0.6021, R = 8.314 J K^{-1} mol^{-1})

Ans. For a first order reaction, $k = \frac{0.693}{t_{1/2}}$

So, $k_1 = \frac{0.693}{40}$ min^{-1} and $k_2 = \frac{0.693}{20}$ min^{-1}

$$\frac{k_2}{k_1} = \frac{0.693 \text{ min}^{-1}/20}{0.693 \text{ min}^{-1}/40} = 2$$

Here, $T_1 = 300$ K, $T_2 = 320$ K and $R = 8.314$ J K^{-1} mol^{-1}

Substituting these values in the expression

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left(\frac{T_2 - T_1}{T_1 T_2}\right), \text{ we get}$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1}\text{mol}^{-1}}\left(\frac{320 \text{ K} - 300 \text{ K}}{300 \text{ K} \times 320 \text{ K}}\right)$$

$$0.3010 = \frac{E_a \times 20}{19.147 \text{ J mol}^{-1} \times 300 \times 320}$$

or $$E_a = \frac{0.3010 \times 19.147 \times 300 \times 320 \text{ J mol}^{-1}}{20} = 27663.58 \text{ J mol}^{-1}$$

$$E_a = \mathbf{27.66\ kJ\ mol^{-1}}$$

Long Answer Questions [5 marks]

Q. 1. For the reaction,

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g),$$

the following data were collected. All the measurements were taken at 263 K:

Experiment	Initial [NO] (M)	Initial [Cl_2] (M)	Initial rate of disappearance of Cl_2 (M/min)
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

(*i*) **Write the expression for rate law.**

(*ii*) **Calculate the value of rate constant and specify its units.**

(*iii*) **What is the initial rate of disappearance of Cl_2 in experiment 4?** [*CBSE Delhi 2012*]

Ans. Suppose order w.r.t. NO is m and order w.r.t. Cl_2 is n. Then the rate will be

$$\text{Rate} = k\,[\text{NO}]^m\,[\text{Cl}_2]^n$$

Substituting the values of experiment 1 to 3 in the rate expression, we get

$$0.60 = k(0.15)^m\,(0.15)^n \quad \text{...(i)}$$

$$1.20 = k(0.15)^m\,(0.30)^n \quad \text{...(ii)}$$

$$2.40 = k(0.30)^m\,(0.15)^n \quad \text{...(iii)}$$

Dividing equation (*iii*) by (*i*), we get

$$\frac{2.40}{0.60} = \frac{k\,(0.30)^m\,(0.15)^n}{k\,(0.15)^m(0.15)^n}$$

$$4 = 2^m \text{ or } 2^2 = 2^m \text{ or } m = 2$$

Dividing equation (*ii*) by (*i*), we get

$$\frac{1.20}{0.60} = \frac{k\,(0.15)^m\,(0.30)^n}{k\,(0.15)^m(0.15)^n}$$

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

(*i*) Rate law expression is, Rate = $k[\text{NO}]^2\,[\text{Cl}_2]$

(*ii*) $0.60 \text{ mol L}^{-1}\text{ min}^{-1} = k(0.15 \text{ mol L}^{-1})^2\,(0.15 \text{ mol L}^{-1})$

$$k = \mathbf{177.78\ mol^{-2}\ L^2\ min^{-1}}$$

(*iii*) Rate = $177.78 \text{ mol}^{-2}\text{ L}^2\text{ min}^{-1} \times (0.25 \text{ mol L}^{-1})^2\,(0.25 \text{ mol L}^{-1})$

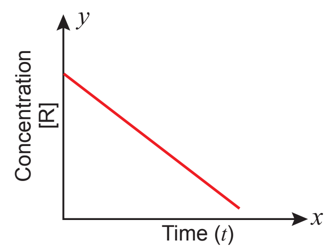
$= \mathbf{2.778\ mol\ L^{-1}\ min^{-1}}$

Q. 2. Consider the reaction $R \xrightarrow{k} P$. The change in concentration of R with time is shown in the following plot: [*CBSE 2019 (56/4/1)*]

(*i*) **Predict the order of the reaction.**

(*ii*) **Derive the expression for the time required for the completion of the reaction.**

(*iii*) **What does the slope of the above line indicate?**



Ans. (*i*) The reaction $R \longrightarrow P$ is a zero order reaction.

(*ii*) For the reaction $R \xrightarrow{k} P$

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

$$d[R] = -k\,dt$$

Integrating both sides,

$$[R] = -kt + C, \quad \text{where } C = \text{constant of integration} \quad \text{...(i)}$$

At $t = 0$, $[R] = [R]_0$

Substituting this in equation (*i*)

$$C = [R]_0$$

Substituting the value of C in equation (*i*)

$$[R] = -kt + [R]_0 \quad \text{...(ii)}$$

$$kt = [R]_0 - [R]$$

$$\Rightarrow \quad t = \frac{[R]_0 - [R]}{k}$$

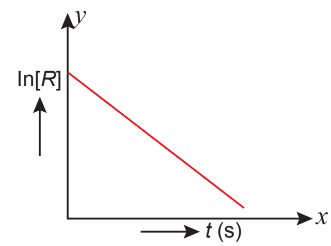
On completion of reactions, $[R] = 0$

$$\therefore \quad t = \frac{[R]_0}{k}$$

(*iii*) From equation (*ii*), we have slope of curve

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

Q. 3. For a certain chemical reaction variation in the concentration ln [R] vs. time plot is given alongside. [*HOTS*]



For this reaction

(*i*) what is the order of the reaction?

(*ii*) what are the units of rate constant k?

(*iii*) give the relationship between k and $t_{1/2}$ (half-life period).

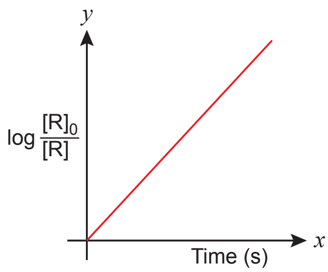
(*iv*) what is the slope of the curve?

(*v*) draw the plot log $[R]_0/[R]$ vs time t(s).

Ans. (*i*) First order (*ii*) time^{-1} (s^{-1})

(*iii*) $k = \frac{0.693}{t_{1/2}}$ (*iv*) slope = – k (rate constant)

(*v*)



Q. 4. Nitrogen pentoxide decomposes according to equation:

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

This first order reaction was allowed to proceed at 40°C and the data below were collected:

$[N_2O_5]$ (M)	Time (min)
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

(*i*) Calculate the rate constant. Include units with your answer.

(*ii*) What will be the concentration of N_2O_5 after 100 minutes?

(*iii*) Calculate the initial rate of reaction. [*CBSE Delhi 2011*]

Ans. (*i*) When t = 20 min, $[R]$ = 0.289 mol L^{-1}

Also, $[R]_0$ = 0.400 mol L^{-1}

For a first order reaction

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

$$\therefore \quad k = \frac{2.303}{20}\log\frac{0.400}{0.289} \Rightarrow k = \frac{2.303}{20}\log\frac{4.00}{2.89}$$

$$\Rightarrow \quad k = \frac{2.303}{20}[\log 4.00 - \log 2.89] \Rightarrow k = \frac{2.303}{20}[0.6021 - 0.4609]$$

$$\Rightarrow \quad k = \frac{2.303}{20}\times 0.1412 \Rightarrow k = 2.303 \times 0.00706 = 0.016259\ \text{min}^{-1}$$

$$\Rightarrow \quad \mathbf{k = 1.6259 \times 10^{-2}\ min^{-1}}$$

(*ii*)
$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]}$$

Here, $[R]_0$ = 0.400 mol^{-1}, t = 100 min, k = 1.626 × 10^{-2} min^{-1}

$$100 = \frac{2.303}{1.626\times 10^{-2}}\log\frac{0.400}{[R]}$$

$$\frac{100 \times 1.626 \times 10^{-2}}{2.303} = \log \frac{0.4}{[R]} \quad \Rightarrow \quad 0.7060 = \log \frac{0.4}{[R]}$$

$$\text{Antilog } (0.7060) = \frac{0.4}{[R]}$$

$$5.082 = \frac{0.4}{[R]} \quad \Rightarrow \quad [R] = \frac{0.4}{5.082} = \mathbf{0.0787\ M}$$

(*iii*) Initial rate, *i.e.*, rate of reaction when $t = 0$

When, $t = 0.00$ min, $[R] = 0.400$ mol L^{-1}

Also, $k = 1.626 \times 10^{-2}$ min^{-1}

$\therefore$ Initial rate $= k\,[R]$

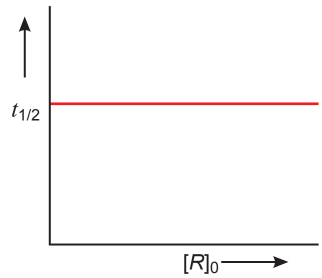
$= 1.626 \times 10^{-2}\ min^{-1} \times 0.400$ mol L^{-1}

$= \mathbf{6.504 \times 10^{-3}\ mol\ L^{-1}\ min^{-1}}$

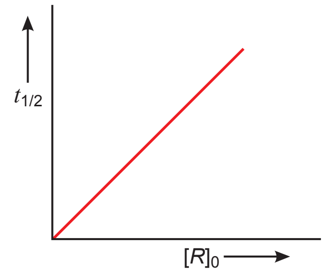
Q. 5. (*i*) **A first order reaction is 75% completed in 40 minutes. Calculate its $t_{1/2}$. [*CBSE (F) 2017*]**

(*ii*) **Predict the order of the reaction in the given plots: [*CBSE 2019 (56/2/1)*]**

(*a*)



(*b*)



where $[R]_0$ is the concentration of reactant.

(Given: log 2 = 0.3010, log 4 = 0.6021)

Ans. (*i*) For a first order reaction, $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

$$\therefore \quad \frac{t_{3/4}}{t_{1/2}} = \frac{\frac{2.303}{k} \log \frac{100}{25}}{\frac{2.303}{k} \log \frac{100}{50}} = \frac{\log 4}{\log 2} = \frac{0.6021}{0.3010}$$

$$\frac{40\text{ min}}{t_{1/2}} = 2 \quad \text{or} \quad t_{1/2} = \mathbf{20\ min.}$$

(*ii*) (*a*) First order (*b*) Zero order

Q. 6. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:

t/s	0	30	60
$[CH_3COOCH_3]$/mol L^{-1}	0.60	0.30	0.15

(*i*) **Show that it follows pseudo first order reaction, as the concentration of water remains constant.**

(*ii*) **Calculate the average rate of reaction between the time interval 30 to 60 seconds.**

(Given log 2 = 0.3010, log 4 = 0.6021) [*CBSE Delhi 2015*]

Ans. (*i*) $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$ ...(*i*)

Substituting $[R]_0 = 0.60$ mol L^{-1}, $[R] = 0.30$ mol L^{-1} and $t = 30$ s in equation (*i*), we get

$$k = \frac{2.303}{30} \log \frac{0.60}{0.30}$$

$$k = \frac{2.303}{30} \log 2 = \frac{2.303}{30} \times 0.3010$$

$$k = 0.0231\ s^{-1}$$

Again substituting, $[R]_0 = 0.60$ mol L^{-1}, $[R] = 0.15$ mol L^{-1} and $t = 60$ in equation (i), we get

$$k = \frac{2.303}{60} \log \frac{0.60}{0.15}$$

$$k = \frac{2.303}{60} \times \log 4 = \frac{2.303}{60} \times 0.6021$$

$$k = 0.0231 \text{ s}^{-1}$$

As the value of k is same in both the cases, therefore, hydrolysis of methylacetate in aqueous solution follows pseudo first order reaction.

(ii) Average rate $= -\dfrac{\Delta[CH_3COOCH_3]}{\Delta t} = \dfrac{-[0.15 - 0.30]}{60 - 30} = \dfrac{0.15}{30}$

Average rate = **0.005 mol L^{-1} s^{-1}**

Q. 7. (i) Write the rate law for a first order reaction. Justify the statement that half life for a first order reaction is independent of the initial concentration of the reactant.

(ii) The activation energy of a reaction is 75.2 kJ mol^{-1} in the absence of a catalyst and it lowers to 50.14 kJ mol^{-1} with a catalyst. How many times will the rate of reaction grow in the presence of a catalyst if the reaction proceeds at 25°C?

Ans. (i) Consider the first order reaction,

$$R \longrightarrow P$$

For this reaction, rate law which relates the rate of reaction to the concentration of reactants can be given as

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

For a first order reaction,

$t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]}$, where $[R]_0$ = initial concentration, $[R]$ = concentration at time t.

At $t_{1/2}$, $[R] = [R]_0/2$

So, the above equation becomes

$$t_{1/2} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_0/2}$$

$$t_{1/2} = \frac{2.303}{k} \log 2 \quad \text{or} \quad t_{1/2} = \frac{2.303}{k} \times 0.3010$$

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

This shows that half life of a first order reaction is independent of the initial concentration of the reactant.

(ii) According to Arrhenius equation,

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

For uncatalysed reaction,

$$\log k_1 = \log A - \frac{E_{a_1}}{2.303\ RT} \quad ...(i)$$

For catalysed reaction,

$$\log k_2 = \log A - \frac{E_{a_2}}{2.303\ RT} \quad ...(ii)$$

A is equal for both reactions.

Subtracting equation (i) from equation (ii),

$$\log \frac{k_2}{k_1} = \frac{E_{a_1} - E_{a_2}}{2.303\ RT} = \frac{(75.2 - 50.14) \text{ kJ mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 4.39$$

$$\frac{k_2}{k_1} = \text{antilog } (4.39) = \mathbf{2.45 \times 10^4}$$

Rate of reaction increases by **2.45×10^4 times.**

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. **(3 × 1 = 3)**

1. Rate law for the reaction $A + 2B \longrightarrow C$ is found to be

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

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be ________.

(*a*) the same (*b*) doubled

(*c*) quadrupled (*d*) halved

2. Which of the following expressions is correct for the rate of reaction given below?

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

(*a*) $\dfrac{\Delta[Br^-]}{\Delta t} = 5\dfrac{\Delta[H^+]}{\Delta t}$ (*b*) $\dfrac{\Delta[Br^-]}{\Delta t} = \dfrac{6}{5}\dfrac{\Delta[H^+]}{\Delta t}$

(*c*) $\dfrac{\Delta[Br^-]}{\Delta t} = \dfrac{5}{6}\dfrac{\Delta[H^+]}{\Delta t}$ (*d*) $\dfrac{\Delta[Br^-]}{\Delta t} = 6\dfrac{\Delta[H^+]}{\Delta t}$

3. Which of the following statement is not correct for the catalyst?

(*a*) It catalyses the forward and backward reaction to the same extent.

(*b*) It alters ΔG of the reaction.

(*c*) It is a substance that does not change the equilibrium constant of a reaction.

(*d*) It provides an alternate mechanism by reducing activation energy between reactants and products.

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. **(3 × 1 = 3)**

4. Assertion (*A*) : Many of photochemical changes have positive sign of ΔG, yet they are spontaneous.

Reason (*R*) : The activation energy in photochemical reactions is provided by light energy.

5. Assertion (*A*) : In a reversible endothermic reaction, E_{act} of the forward reaction is higher than that of the backward reaction.

Reason (*R*) : The threshold energy of the forward reaction is more than that of the backward reaction.

6. Assertion (*A*) : The order of the reaction

$$2NO(g) + 2H_2(g) \longrightarrow 2H_2O(g) + N_2(g) \text{ is } 3.$$

Reason (*R*) : Order of reaction with respect to a given reactant is the power of the reactant's concentration in the rate equation.

Answer the following questions:

7. State a condition under which a bimolecular reaction is kinetically first order. **(1)**

8. Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction. Explain with the help of one example. **(1)**

9. A first order reaction takes 40 minutes for 30% decomposition. Calculate $t_{1/2}$. **(2)**

10. For a zero order reaction will the molecularity be equal to zero? Explain. **(2)**

11. (*i*) The conversion of the molecule X to Y follows second order kinetics. If the concentration X is increased to three times, how will it affect the rate of formation of Y?

    (*ii*) The specific reaction rate of a reaction is 6.2×10^{-3} mol L^{-1} s^{-1}. What is the order of reaction? **(2)**

12. Derive an expression to calculate time required for completion of zero order reaction. **(2)**

13. The rate constant for the decomposition of ethyl iodide

$$C_2H_5I(g) \longrightarrow C_2H_4(g) + HI(g)$$

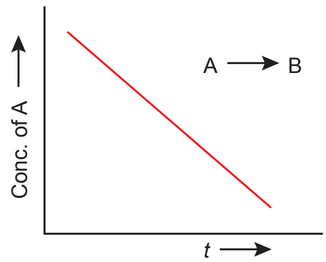
at 600 K is 1.60×10^{-5} s^{-1}. Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700 K. **(3)**

14. For a general reaction A $\longrightarrow$ B, plot of concentration of A vs time is given in figure. Answer the following questions on the basis of this graph.

    (*i*) What is the order of the reaction?

    (*ii*) What is the slope of the curve?

    (*iii*) What are the units of rate constant? **(3)**



15. The following data were obtained for the reaction:

$$A + 2B \longrightarrow C$$

Experiment	[A]/M	[B]/M	Initial rate of formation of C/M min^{-1}
1	0.2	0.3	4.2×10^{-2}
2	0.1	0.1	6.0×10^{-3}
3	0.4	0.3	1.68×10^{-1}
4	0.1	0.4	2.40×10^{-2}

(*i*) Find the order of reaction with respect to A and B.

(*ii*) Write the rate law and overall order of reaction.

(*iii*) Calculate the rate constant (k). **(3)**

16. (*i*) For an elementary reaction

$$2A + B \longrightarrow 3C$$

the rate of appearance of C at time 't' is 1.3×10^{-4} mol L^{-1} s^{-1}.

Calculate at this time

(*a*) rate of the reaction.

(*b*) rate of disappearance of A.

(*ii*) The decomposition of $N_2O_5(g)$ is a first order reaction with a rate constant of 5×10^{-4} s^{-1} at 45°C, *i.e.*, $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$. If initial concentration of N_2O_5 is 0.25 M, calculate its concentration after 2 min. Also, calculate half-life for decomposition of $N_2O_5(g)$. **(5)**

Answers

1. (*a*) **2.** (*c*) **3.** (*b*) **4.** (*b*) **5.** (*c*) **6.** (*a*) **9.** 77.78 min **13.** 6.36×10^{-3} s^{-1}

15. (*iii*) 6.0 L^2 mol^{-1} min^{-1} **16.** (*i*) (*a*) 0.43×10^{-4} mol L^{-1} s^{-1}, (*b*) 0.86×10^{-4} mol L^{-1} s^{-1} (*ii*) 0.235 M, 1386 s