Chemical Kinetics

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) $\Delta t \to 0$

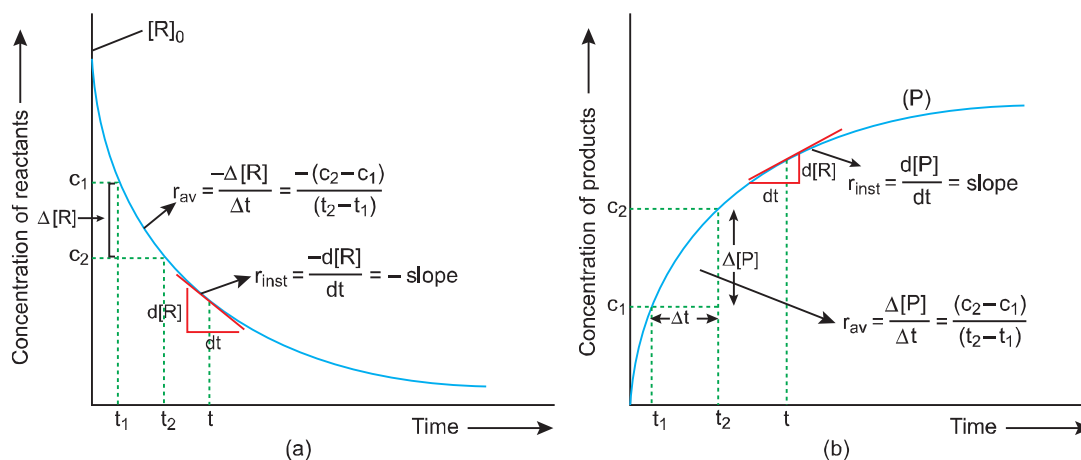   For a general reaction, $\qquad R \longrightarrow P$

Fig. 4.1: Instantaneous and average rate of reaction

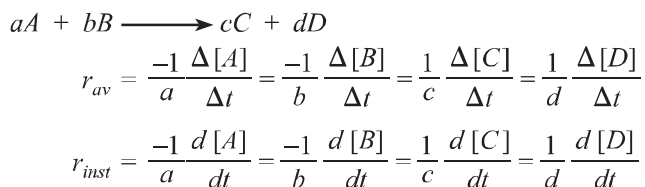$$\text{Instantaneous rate} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

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
$$[A] = [B] = 1 \text{ mol L}^{-1} \text{ then}$$

$$\text{Rate} = k$$

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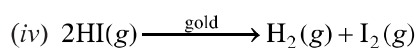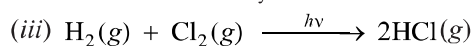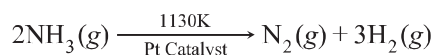
$$\text{Rate} = k[A]^n$$

or

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

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

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

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

(b) **Examples of 1st order reactions**

    (i) All radioactive disintegrations are of the first order.
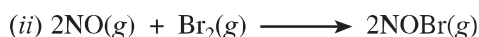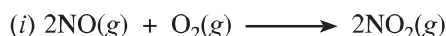
    (ii) Decomposition of sulphuryl chloride.

$$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$$

    Unit of $k = s^{-1}$. 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 $k = \text{litre mol}^{-1} \text{second}^{-1}$

(d) **Examples of 3rd order reactions**

    (i) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$
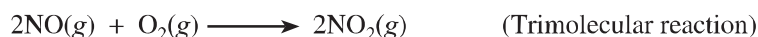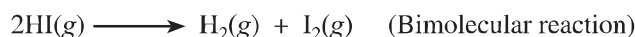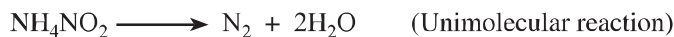
    (ii) $2NO(g) + Br_2(g) \longrightarrow 2NOBr(g)$

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

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:

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O \qquad \text{(Unimolecular reaction)}$$
$$2HI(g) \longrightarrow H_2(g) + I_2(g) \qquad \text{(Bimolecular reaction)}$$
$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \qquad \text{(Trimolecular reaction)}$$

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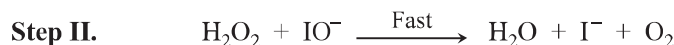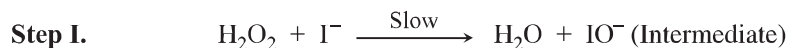
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(*d*) **Mechanism of reaction:** A series of elementary reactions proposed to account for the overall reaction is called mechanism of reaction. The overall rate of the reaction is controlled by the slowest step in a reaction and is called the **rate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

Consider the reaction, $2H_2O_2 \xrightarrow[\text{Alkaline medium}]{I^-} 2H_2O + O_2$
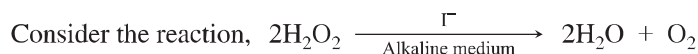
The rate equation for this reaction is found to be

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

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

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

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

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.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
$$\text{Rate} = k\,[C_{12}H_{22}O_{11}]$$
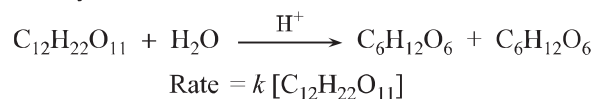
10. **Zero Order Reactions:** In such reactions, the rate remains constant throughout the course of reaction, *i.e.*, the rate does not change with the change in concentration of reactants.

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

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

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

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

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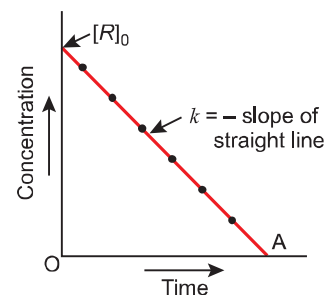
$$-[R] = kt - [R]_0$$
$$kt = [R]_0 - [R]$$

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

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

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.

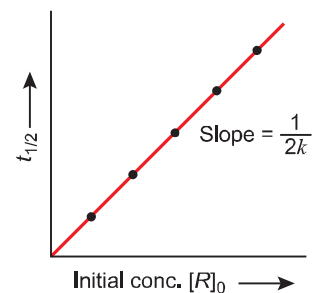**Half-life period of a zero order reaction:**

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

Substituting these values in equation (ii), we get

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

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

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

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,

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

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

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

Integrating both sides, we get

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

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

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

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

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

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

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

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

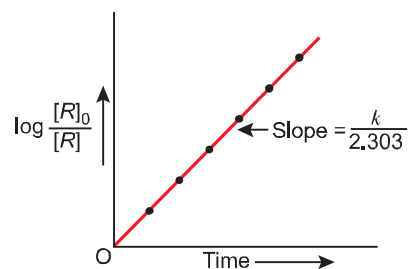When $\qquad t = t_{1/2}, \quad [R] = \dfrac{[R]_0}{2}$

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

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

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

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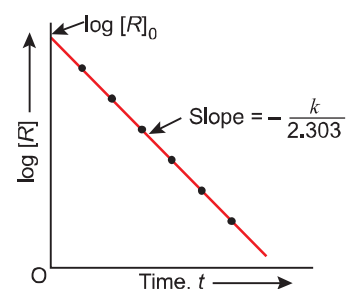
12. **Integrated Rate Equation for a Gaseous System:** Consider a typical first order gas phase reaction.
$$A(g) \longrightarrow B(g) + C(g)$$
Let P_i be the initial pressure of A and P_t the total pressure at time 't' and P_A, P_B and P_C be the partial pressures of A, B and C respectively at time t.

Total pressure, $P_t = P_A + P_B + P_C$ (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

$$P_t = (P_i - x) + x + x = P_i + x \quad or \quad x = P_t - P_i$$
$$P_A = P_i - x = P_i - (P_t - P_i) = 2P_i - P_t$$
$$k = \frac{2.303}{t} \log \frac{P_i}{P_A} = \frac{2.303}{t} \log \frac{P_i}{(2P_i - P_t)}$$
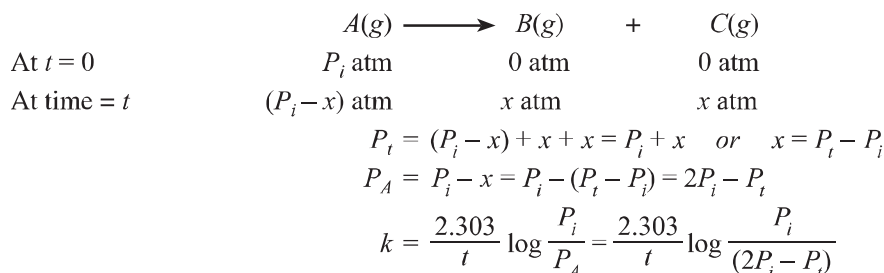
13. **Determination of Order of Reaction:**

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.
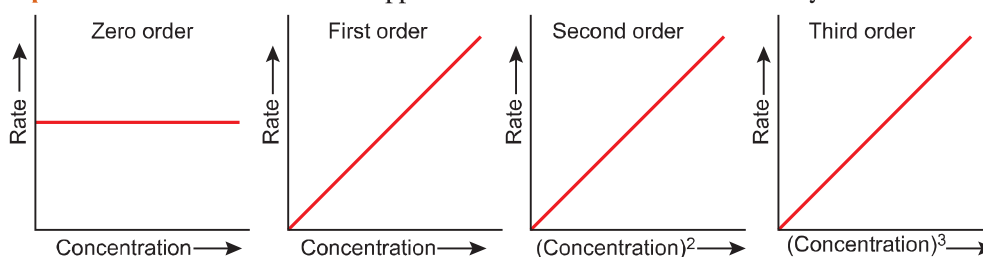
Fig. 4.6

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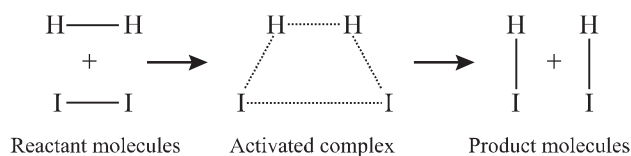
Fig. 4.7: Formation of activated complex from H_2 and I_2 during HI formation

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.
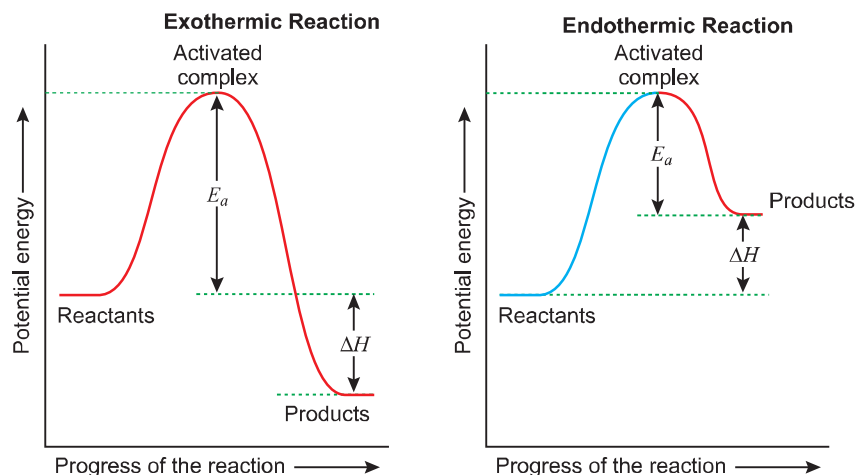
Fig. 4.8: Concept of Activation Energy

(*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 $\log A$.

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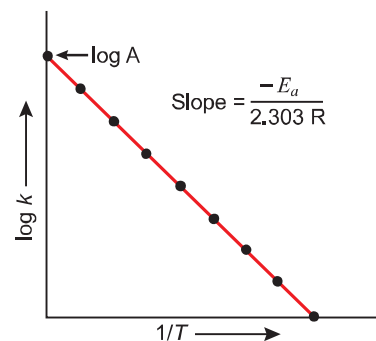

Fig. 4.9: log k vs 1/T

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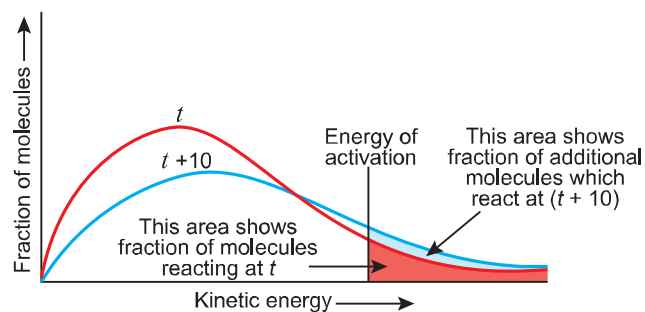
Fig. 4.10: Distribution curve showing temperature dependence of rate of a reaction

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.

$$2KClO_3 \xrightarrow[\text{Heat}]{MnO_2} 2KCl + 3O_2$$
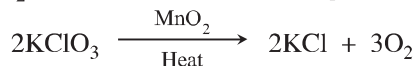
According to intermediate complex theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.
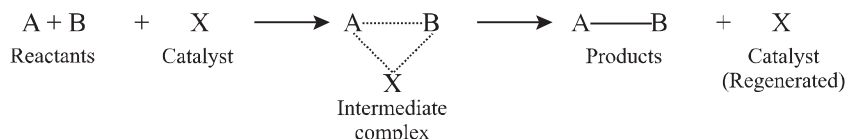
It is believed that the catalyst provides an alternate pathway by reducing the activation energy between reactants and products hence lowering the potential energy barrier as shown in Fig. 4.11.

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.

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

$$\underset{\text{Reactant} \quad \text{Catalyst}}{O_2(g) + 2NO(g)} \longrightarrow \underset{\text{Intermediate}}{2NO_2(g)}$$
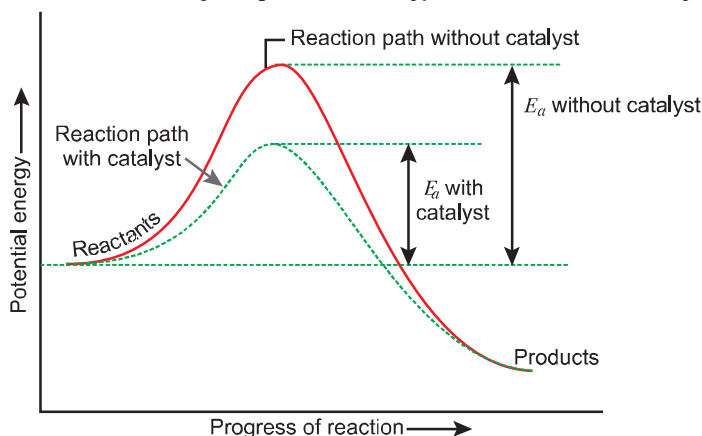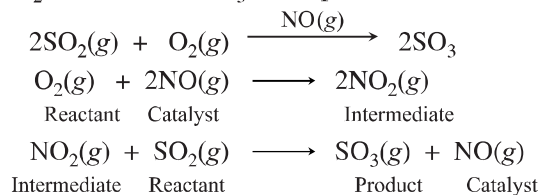
$$\underset{\text{Intermediate} \quad \text{Reactant}}{NO_2(g) + SO_2(g)} \longrightarrow \underset{\text{Product} \quad \text{Catalyst}}{SO_3(g) + NO(g)}$$

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, $\qquad Z_{AB}$ = The collision frequency of reactants A and B

$\qquad\qquad P$ = 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:

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

(ii) For a first order reaction:

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

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

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

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

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

Chemical Kinetics

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 $= -\dfrac{\Delta[R]}{\Delta t} = -\dfrac{[R_2]-[R_1]}{t_2-t_1}$

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

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

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

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

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 $= \dfrac{1}{2} + 2 = \dfrac{5}{2}$.

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. $\quad$ Rate $= k\,[X]^2$

$r_1 = k\,[X]^2 \qquad\qquad\qquad ...(i)$

$r_2 = k\,[3X]^2 \qquad\qquad\qquad ...(ii)$

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

$r_2 = 9r_1$

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, $k = 1.15 \times 10^{-3} s^{-1}$. As the reaction is of first order,

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

$$= 2.0 \times 10^3 \times 0.2219\ s = 443.8\ s = \mathbf{444\ s}$$

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, $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{60\ min} = \mathbf{1.155 \times 10^{-2}\ min^{-1}}$

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,

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

$$\therefore \qquad \ln x = -\frac{E_a}{RT} \quad \text{or} \quad \log x = -\frac{E_a}{2.303 \, RT}$$
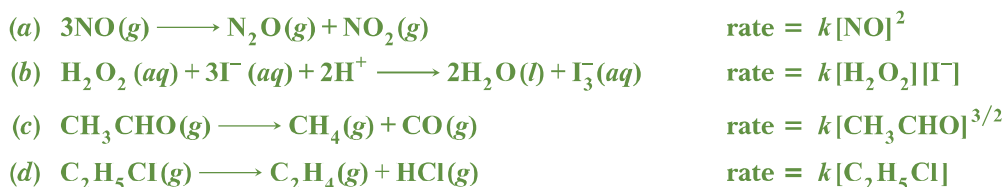
$$\text{or} \qquad \log x = -\frac{209.5 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 581 \text{ K}} = -18.8323$$

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

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

Chemical Kinetics

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.
$$\text{Initial rate} = k\,[A][B]^2 = (2.0 \times 10^{-6}\,mol^{-2}\,L^2\,s^{-1})\,(0.1\,mol\,L^{-1})\,(0.2\,mol\,L^{-1})^2$$
$$= \mathbf{8 \times 10^{-9}\,mol\,L^{-1}\,s^{-1}}$$

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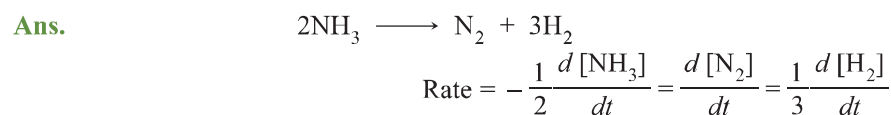
$$B \text{ reacted} = \frac{1}{2} \times 0.04\,mol\,L^{-1} = 0.02\,mol\,L^{-1}$$

Now
$$[B] = 0.2 - 0.02 = 0.18\,mol\,L^{-1}$$
$$\text{Rate} = (2.0 \times 10^{-6}\,mol^{-2}\,L^2\,s^{-1})\,(0.06\,mol\,L^{-1})\,(0.18\,mol\,L^{-1})^2$$
$$= \mathbf{3.89 \times 10^{-9}\,mol\,L^{-1}\,s^{-1}}$$

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 $= k$

$\therefore$
$$-\frac{1}{2}\frac{d\,[NH_3]}{dt} = \frac{d\,[N_2]}{dt} = \frac{1}{3}\frac{d\,[H_2]}{dt}$$
$$= 2.5 \times 10^{-4}\,mol\,L^{-1}\,s^{-1}$$
$$\text{Rate of production of } N_2 = \frac{d\,[N_2]}{dt} = \mathbf{2.5 \times 10^{-4}\,mol\,L^{-1}\,s^{-1}}$$
$$\text{Rate of production of } H_2 = \frac{d\,[H_2]}{dt}$$
$$= 3 \times (2.5 \times 10^{-4}\,mol\,L^{-1}s^{-1}) = \mathbf{7.5 \times 10^{-4}\,mol\,L^{-1}\,s^{-1}}$$

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
$$\text{Rate} = k\,[CH_3OCH_3]^{3/2}.$$
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.*,
$$\text{Rate} = k[P_{CH_3OCH_3}]^{3/2}$$
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 $= bar\,min^{-1}$

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

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.
$$\text{Rate} = k\,[A]^2 = ka^2$$

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

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

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.

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

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

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

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 $r_0 = k[A]^m [B]^n$

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

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

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

Dividing (i) by (ii), $\dfrac{(r_0)_1}{(r_0)_2} = \dfrac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \dfrac{k(0.20)^m (0.30)^n}{k(0.20)^m (0.10)^n}$

        $1 = 3^n$ or $3^0 = 3^n \Rightarrow n = 0$

Dividing (iii) by (ii), $\dfrac{(r_0)_3}{(r_0)_2} = \dfrac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \dfrac{k(0.40)^m (0.05)^n}{k(0.20)^m (0.10)^n}$

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

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

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

Thus, order of reaction w.r.t. $A = \mathbf{1.5}$ and order of reaction w.r.t. $B = \mathbf{0}$.

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

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

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

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

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

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

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

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

or $\qquad \dfrac{1}{4} = \dfrac{(0.2)^n}{(0.4)^n} = \left(\dfrac{1}{2}\right)^n$

or $\qquad \left(\dfrac{1}{2}\right)^2 = \left(\dfrac{1}{2}\right)^n \qquad$ or $\qquad n = 2$

$\therefore \quad$ 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**

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

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

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}

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.
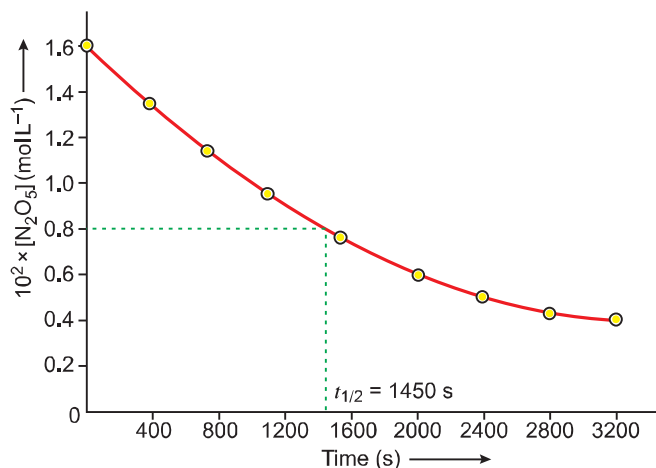
(*iv*) What is rate law?

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

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

Ans.

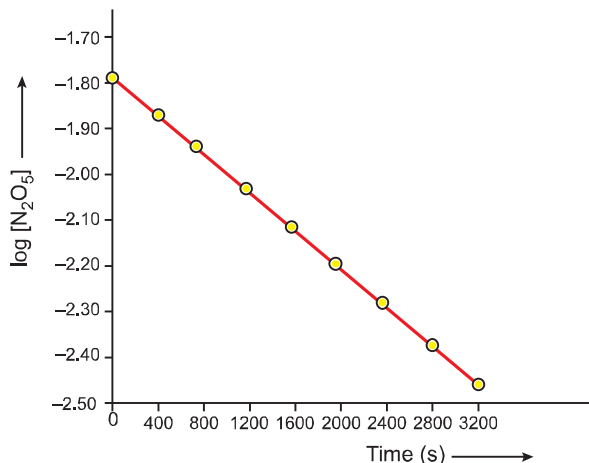| t (s)	0	400	800	1200	1600	2000	2400	2800	3200
$10^5 \times [N_2O_5]$/mol L^{-1}	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35
log $[N_2O_5]$	-1.79	-1.87	-1.94	-2.03	-2.11	-2.19	-2.28	-2.37	-2.46

(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 $= 0.815 \times 10^2$ M

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

(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 $k = \textbf{4.82} \times \textbf{10}^{-4} \textbf{ s}^{-1}$

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

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

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

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

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,

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

To calculate the amount left after 10 years:

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

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

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

or $\qquad\qquad \log [R] = -0.1071$

or $\qquad\qquad [R] = \text{Antilog } \overline{1}.8929 = \textbf{0.7814 μg}$

To calculate the amount left after 60 years:

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

or $\qquad\qquad \log [R] = -0.6425$

or $\qquad\qquad [R] = \text{Antilog } \overline{1}.3575 = \textbf{0.2278 μg}$

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, $[R] = [R]_0 - 0.9[R]_0 = 0.1[R]_0$

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

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

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

Ans. For a first order reaction

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

Chemical Kinetics

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

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

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

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

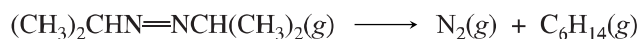$$t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{8.91 \times 10^{-3}}$$

$$t_{1/2} = \textbf{77.78 min}$$

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 $\qquad\qquad\quad P_0 \qquad\qquad\qquad 0 \qquad\quad 0$

After time $t \qquad\qquad\qquad P_0 - p \qquad\qquad\quad p \qquad\quad p$

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

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

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

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

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

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

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

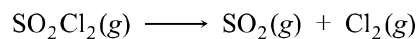Average value of $k = \dfrac{2.175 + 2.235}{2} \times 10^{-3} \text{ s}^{-1} = \textbf{2.20} \times \textbf{10}^{-3} \text{ s}^{-1}$

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

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

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

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

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

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

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

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

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

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 $\dfrac{1}{T}$, 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
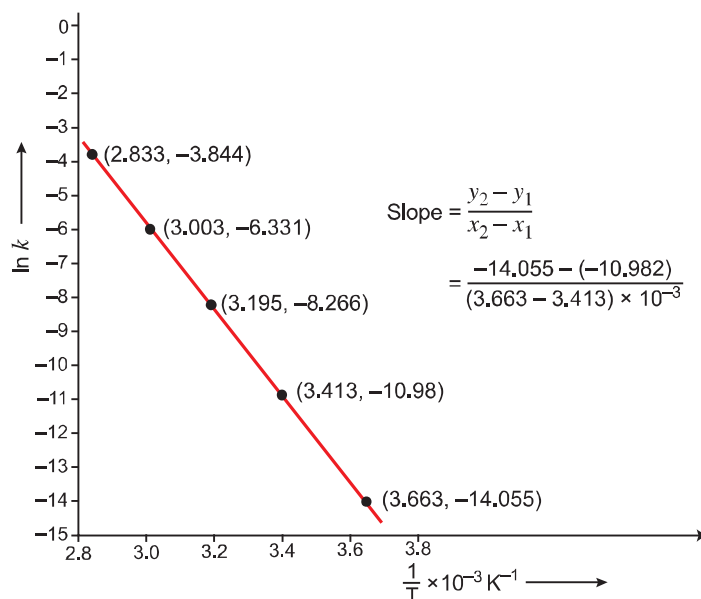
Graph of ln k vs 1/T

From the graph, we find that

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

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

We know that $\qquad$ ln $k = $ ln $A - \dfrac{E_a}{RT}$

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

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

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

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

Chemical Kinetics

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	6.13×10^{-5} s^{-1}
323	0.003096	− 6.3	1.84×10^{-3} s^{-1}

Q. 23. The rate constant for the decomposition of hydrocarbons is 2.418×10^{-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 $$\log A = \log k + \frac{E_a}{2.303\,RT}$$

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

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

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

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

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

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

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

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

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,

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

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

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

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

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

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

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

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

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

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

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, $\log k = 14.34 - \dfrac{1.25 \times 10^4}{T}$

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

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

or $\qquad E_a = 1.25 \times 10^4 \times 2.303 \times 8.314$

$$= 23.934 \times 10^4 \text{ J mol}^{-1}$$

$$E_a = \textbf{239.34 kJ mol}^{-1}$$

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

$$k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{256 \times 60} = 4.5 \times 10^{-5} \text{ s}^{-1}$$

Substituting the value of k in given equation, we get

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

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

or $\qquad \log 4.51 - 5 \log 10 = 14.34 - \dfrac{1.25 \times 10^4}{T}$

$$0.6542 - 5 = 14.34 - \dfrac{1.25 \times 10^4}{T} \qquad \text{or} \qquad \dfrac{1.25 \times 10^4}{T} = 18.6858$$

or $\qquad T = \dfrac{1.25 \times 10^4}{18.6858} = \textbf{669 K (approx.)}$

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

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,

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

$$\log \dfrac{1.5 \times 10^4}{4.5 \times 10^3} = \dfrac{60000 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left(\dfrac{T_2 - 283}{283 T_2} \right)$$

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

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

or $\qquad 0.9528 \, T_2 = 283$

or $\qquad T_2 = \dfrac{283}{0.9528} = 297 \text{ K} = 297 - 273°C = \textbf{24°C}$

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 $4 \times 10^{10} \text{ s}^{-1}$, calculate k at 318 K and E_a.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Multiple Choice Questions   [1 mark]

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

1. **In the reaction,**

$$\text{BrO}_3^-(aq) + 5\text{Br}^-(aq) + 6\text{H}^+ \longrightarrow 3\text{Br}_2(l) + 3\text{H}_2\text{O}(l)$$

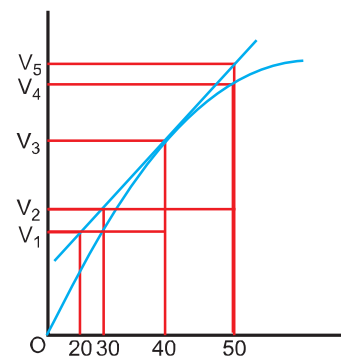**The rate of appearance of bromine is related to rate of disappearance of bromide ion as**

(a) $\dfrac{d[\text{Br}_2]}{dt} = \dfrac{-5}{3}\dfrac{d[\text{Br}^-]}{dt}$

(b) $\dfrac{d[\text{Br}_2]}{dt} = \dfrac{5}{3}\dfrac{d[\text{Br}^-]}{dt}$

(c) $\dfrac{d[\text{Br}_2]}{dt} = \dfrac{3}{5}\dfrac{d[\text{Br}^-]}{dt}$

(d) $\dfrac{d[\text{Br}_2]}{dt} = \dfrac{-3}{5}\dfrac{d[\text{Br}^-]}{dt}$

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,**

$$\text{H}_2(g) + \text{Br}_2(g) \longrightarrow 2\text{HBr}(g)$$

The experimental data suggests,

$$\text{Rate} = k[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}$$

The molecularity and order for the reaction is

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

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