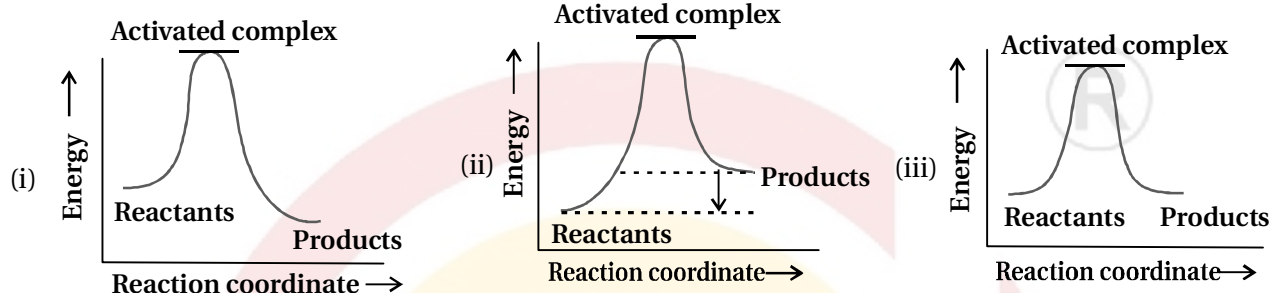Section A

● **Choose correct answer from the given options.** [Each carries 1 Mark] **[5]**

1. Which of the following graphs represents exothermic reaction ?

(A) only (i) (B) only (ii) (C) only (iii) (D) (i) and (ii)

2. A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion ?

(A) 1.26×10^{15} s (B) 2.52×10^{14} s (C) 2.52×10^{28} s (D) infinite

3. If a substance with half life 3 days is taken at other place in 12 days. What amount of substance is left now....

(A) 1/4 (B) 1/8 (C) 1/16 (D) 1/32

4. For the non - stoichiometre reaction $2A + B \rightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial Concentration (A)	Initial Concentration (B)	Initial rate of formation of C (mol L^-S^-)
0.1 M	0.1 M	1.2×10^{-3}
0.1 M	0.2 M	1.2×10^{-3}
0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is :

(A) $\dfrac{dc}{dt} = k[A][B]^2$ (B) $\dfrac{dc}{dt} = k[A]$ (C) $\dfrac{dc}{dt} = k[A][B]$ (D) $\dfrac{dc}{dt} = k[A]^2[B]$

5. According to Arrhenius equation, the slope of $\log K \rightarrow \dfrac{1}{T}$ plot is ....

(A) $\dfrac{-E_a}{2.303}$ (B) $\dfrac{-E_a}{2.303R}$ (C) $\dfrac{-E_a}{2.303RT}$ (D) $\dfrac{E_a}{2.303RT}$

Section B

● **Write the answer of the following questions.** [Each carries 2 Marks] **[12]**

1. Explain : What is instantaneous rate ? How it is determine ?

2. What is rate law ? Give a relation between rate of reaction and concentration of reactants.

3. The conversion of molecules 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 ?

4. Explain pseudo first order by giving example.

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5. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

6. 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.

Section C

● **Write the answer of the following questions. [Each carries 3 Marks]** **[12]**

7. What is Activation Energy (E_a) ? Explain graph of reaction of activation energy and write about its probability.

8. What is first order reaction ? Determine the integrated rate equation for first order reaction R → P.

9. 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 4×10^{10} s^{-1}. Calculate k at 318 K and E_a.

10. 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.

Section D

● **Write the answer of the following questions. [Each carries 4 Marks]** **[12]**

11. Derive the formula of first order reaction for, (i) Rate constant K, (ii) Half life period (graph is not required)

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

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

Calculate the rate constant.

13. 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 $L^{-1}\,s^{-1}$	5.7×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

What is the order of the reaction with respect to A and B ?
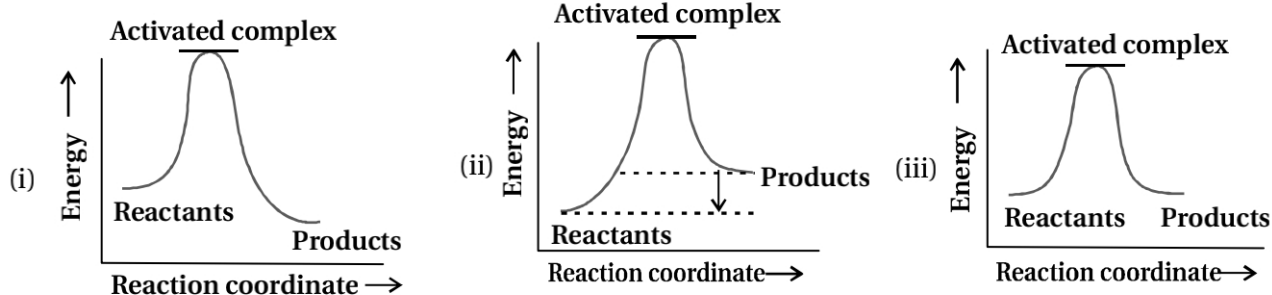
Wish You - All The Best

$\boxed{\text{Section A}}$

● **Choose correct answer from the given options. [Each carries 1 Mark]** [5]

1. Which of the following graphs represents exothermic reaction ?

(i) Activated complex / Energy / Reactants / Products / Reaction coordinate →

(ii) Activated complex / Energy / Products / Reactants / Reaction coordinate →

(iii) Activated complex / Energy / Reactants   Products / Reaction coordinate →

   (A) only (i)   (B) only (ii)   (C) only (iii)   (D) (i) and (ii)

Ans. **(A)** only (i)

➡ As per figure energy of reactant = H_R

   Energy of product = H_P

   So, (energy of reactant H_P) < (energy of reactant H_r)

   ∴ $\Delta H = H_P - Hr = (-)$ ve

➡ In this reaction the energy is released as the product formed. So graph (i) is exothermic reaction graph.

➡ Graph (ii) is endothermic reaction and in graph (iii) heat change will not take place.

2. A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion ?

   (A) 1.26×10^{15} s   (B) 2.52×10^{14} s   (C) 2.52×10^{28} s   (D) infinite

Ans. **(D)** infinite

➡ Whole of the substance never reacts because in every half life. 50% of the substance reacts. Hence, time taken for 100% completion of a reaction is infinite.

   $t_{1/2} = 1.26 \times 10^4 \text{s}$

   $\therefore k = \dfrac{0.693}{t^{\frac{1}{v}}} = \dfrac{0.693}{1.26 \times 10^4}$

➡ The final concentration when the reaction is completed 100% = $[R]_t$ = zero

   So $t_{100\%} = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]_t}$

   $= \dfrac{2.303}{k} \log \dfrac{[R]_0}{\text{zero}}$

   $= \dfrac{2.303}{k} \log \ (\text{infinite})$

   $\approx \dfrac{2.303}{k} \times 10^{\infty} = \infty$

➡ If any reaction $t_{1/2}$ = exact value, then it will take infinite time for 100% completion. So option (D)

is correct.

3. If a substance with half life 3 days is taken at other place in 12 days. What amount of substance is left now....

   (A) 1/4   (B) 1/8   (C) 1/16   (D) 1/32

Ans. (C) 1/16

4. For the non - stoichiometre reaction $2A + B \rightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial Concentration (A)	Initial Concentration (B)	Initial rate of formation of C (mol L^-S^-)
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0.1 M	0.2 M	1.2×10^{-3}
0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is :

(A) $\dfrac{dc}{dt} = k[A][B]^2$ (B) $\dfrac{dc}{dt} = k[A]$ (C) $\dfrac{dc}{dt} = k[A][B]$ (D) $\dfrac{dc}{dt} = k[A]^2[B]$

Ans. (B) $\dfrac{dc}{dt} = k[A]$

➡ $2A + B \rightarrow C + D$

   Rate of Reaction $= \dfrac{-1}{2}\dfrac{d[A]}{dt} = -\dfrac{d[B]}{dt}$

   $= \dfrac{d[C]}{dt} = \dfrac{d[D]}{dt}$

➡ Let rate of Reaction $= k[A]^x[B]^y$

   or $\dfrac{d[C]}{dt} = k[A]^x[B]^y$

➡ Now from table,

   $1.2 \times 10^{-3} = k[0.1]^x[0.1]^y$ ......(i)

   $1.2 \times 10^{-3} = k[0.1]^x[0.2]^y$ ......(ii)

   $2.4 \times 10^{-3} = k[0.2]^x[0.1]^y$ ......(iii)

➡ Dividing equation (i) by (ii),

   $\dfrac{1.2 \times 10^{-3}}{1.2 \times 10^{-3}} = \dfrac{k[0.1]^x[0.1]^y}{k[0.1]^x[0.2]^y}$

   $\therefore \quad 1 = \left[\dfrac{1}{2}\right]^y \quad \therefore y = 0$

➡ Now, Dividing equation (i) by (iii)

   $\dfrac{1.2 \times 10^{-3}}{2.4 \times 10^{-3}} = \dfrac{k[0.1]^x[0.1]^y}{k[0.2]^x[0.1]^y}$

   $\therefore \quad \left[\dfrac{1}{2}\right]^1 = \left[\dfrac{1}{2}\right]^x \quad \therefore x = 1$

➡ Hence $\dfrac{d[C]}{dt} = k[A]^1[B]^0$.

5. According to Arrhenius equation, the slope of $\log K \to \dfrac{1}{T}$ plot is ....

(A) $\dfrac{-E_a}{2.303}$ (B) $\dfrac{-E_a}{2.303R}$ (C) $\dfrac{-E_a}{2.303RT}$ (D) $\dfrac{E_a}{2.303RT}$

Ans. (B) $\dfrac{-E_a}{2.303R}$

<center>

Section B

</center>

● **Write the answer of the following questions. [Each carries 2 Marks]**   [12]

**1.** Explain : What is instantaneous rate ? How it is determine ?

➡ **Definition :** The rate of a particular moment of time, is called instantaneous rate. It is expressed by (r_{inst}).

➡ **Explanation :** Instantaneous rate is rate for smallest time. The smallest time interval say dt and during this time the change in concentration by decrease the concentration of reactants is d[R] then the Instantaneous rate is expressed by following. Instantaneous rate $= r_{inst} = -\dfrac{d[R]}{dt}$

➡ The average rate at the smallest time interval say dt (i.e. When Δt approaches zero), Hence, mathematically for an infinitesimally small dt instantaneous rate is given by

As $\Delta t \to 0$ or $r_{inst} = -\dfrac{d[R]}{dt} = \dfrac{d[P]}{dt}$ $\left[\textbf{Remember :} \text{ Average rate } r_{av} = -\dfrac{\Delta[R]}{\Delta t} = \dfrac{\Delta[P]}{\Delta t}\right]$

➡ **The procedure to determined instantaneous rate :** The instantaneous rate is determined graphically. It can be determined by drawing a tangent at time t on either of the curves for concentration of R & p vs time t and calculating its slope. Take the value of d[R] or d[p] & dt and calculate r_{inst} on the base of tangent of graph. **For more information, see figure of Q. No. 6.**
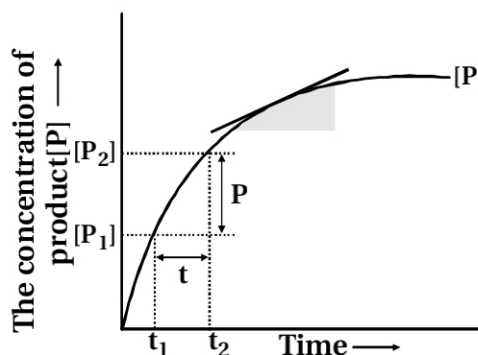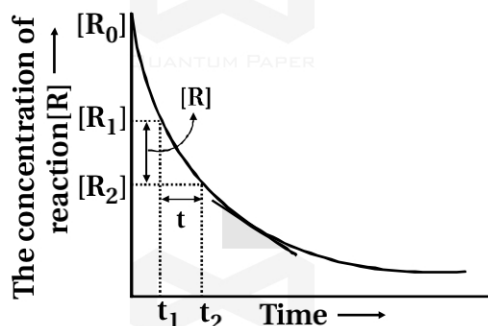
(i) [R] $\to$ t graph   (i) [R] $\to$ t graph

(ii) $r_{inst} = -\text{slope} = -\dfrac{d[R]}{dt}$ (ii) $r_{inst} = \text{slope} = \dfrac{d[P]}{dt}$

(iii) It is negative.   (iii) It is positive

2. What is rate law ? Give a relation between rate of reaction and concentration of reactants.

➡ Rate of reaction depends upon the experimental conditions such as concentration of reactants (pressure in case of gases), temperature and catalyst. The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products.

➡ The representation of rate of reaction in terms of concentration of the reactants is known as rate law. It is also called as rate equation or rate expression.

➡ The rate of a reaction decreases with the passage of time as the concentration of reactants decrease. Conversely rate generally increase when reactant concentrations increase.

∴ Rate of reaction ∝ Concentration of reactants

➡ So, rate of a reaction depends upon the concentration of reactants.

3. The conversion of molecules 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 ?

➡ Given reaction X → Y

Order of reaction = 2

∴ Rate $r_1 = -k\,[X]^2$

➡ Now, the concentration of X increase to three time then new concentration is = 3X mol L^{-1}.

➡ ∴ New rate $r_2 = k\,[3X]^2 = 9k\,[X]^2$

$$\therefore \frac{r_2}{r_1} = \frac{9\,k[X]^2}{k\,[X]^2} = 9$$

➡ So, new rate is nine times.

∴ So, it will effect nine times in the rate of formation of Y.

4. Explain pseudo first order by giving example.

➡ **Pseudo first order reaction :** The order of a reaction is sometimes altered by conditions. Consider a chemical reaction between two substances when one reactant is present in large excess and remain almost constant at the end of the reaction. This reaction are called pseudo first order reaction.

➡ **Example :** During the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the various constituents at the beginning ($t = 0$) and completion (t) of the reaction are given as under.

Reaction : $CH_3COOC_2H_5 + H_2O(l) \rightarrow CH_3COOH + C_2H_5OH$
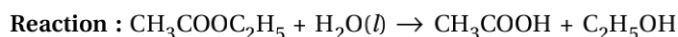
| $t = 0$ | 0.01 mole | 10 mole | 0 mole | 0 mole |
| $t = t$ | 0.0 mole | 9.99 mole | 0.01 mole | 0.01 mole |

➡ The concentration of water does not get altered much during the course of the reaction. So in the rate equation,

∴ Rate $= \dfrac{-d[R]}{dt} = k'\,[CH_3COOC_2H_5]\,[H_2O]$

the term $[H_2O]$ can be taken as constant. The equation, thus becomes Rate $= k\,[CH_3COOC_2H_5]$

where $k = k'\,[H_2O]$

∴ Rate $= k\,[CH_3COOC_2H_5]$

➡ And the reaction behave as first order reaction. Such reaction are called pseudo first order reaction.

5. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

➡ **(a) 90% reaction is complete so, calculation of t (90%) :**

Here, 90 % reaction is complete

∴ Remaining concentration is 10 %

If the initial concentration $= [R]_0$

So, concentration after completion of 90%

$$\text{Reaction} = \frac{[R]_0 \times 10}{100} = 0.1\,[R]_0 = [R]_{90}$$

$$\text{So, } t_{90} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_t} \qquad \Bigg| \qquad \frac{t_{99\%}}{t_{90\%}} = \frac{\log \frac{[R]_0}{[R]_t}}{\log \frac{[R]_0}{[R]_t}}$$

$$= \frac{2.303}{k} \log \frac{[R]_0}{0.1\,[R]_0} \qquad \Bigg| \qquad = \frac{\log 100}{\log 10} = 2$$

$$= \frac{2.303}{k} \log \frac{1}{0.1} \quad \left\{ \text{But } \frac{1}{0.1} = 10.0 \right\}$$

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

$$\therefore\ t_{90} = \frac{2.303}{k}\,(1) = \frac{2.303}{k}$$

➡ **(b) 99% reaction is complete, so, calculation of t (99%) :** 99 % reaction is complete so, 1% reactant is remaining so, If the initial concentration = $[R]_0$, So, the remaining concentration = $[R]_t$ (99)

$$[R]_t = 1\% \text{ of } [R]_0 = \frac{1}{100}\,[R]_0 = 0.01\,[R]_0$$

$$t_{(99\%)} = \frac{2.303}{k} \log \frac{[R]_0}{0.01\,[R]_0} = \frac{2.303}{k} \times 2$$

$$\therefore\ \frac{t_{99\%}}{t_{90\%}} = \left(\frac{2.303}{k} \right) \times 2 \times \left(\frac{k}{2.303} \right) = \frac{2}{1}$$

➡ So, if the first order reaction then time required for 99% completion is twice then time required for the completion of 90% of reaction.

6. 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.

➡ The half life of ^{14}C $t_{1/2}$ = 5730 year

After... time it is 80 ^{14}C.

➡ So if initially $^{14}C_0 = [R]_0$

so after t time $^{14}C = [R]_t = 80\%\,[R]_0 = 0.8\,[R_0]$

➡ All radioactive decay are first order reaction.

So, $t_{1/2} = \dfrac{0.693}{k}$ (But $t_{1/2}$ = 5730 years)

$$\therefore\ k = \frac{0.693}{5730} \text{ years}$$

➡ For, first order reaction,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]_t} = \frac{2.303 \times 5730}{0.693} \log \frac{[R]_0}{0.8\,[R]_0}$$

$$= \frac{2.303 \times 5730}{0.693} \log 1.25$$

$$= \frac{2.303 \times 5730}{0.693} \times 0.0969 = 1845.2 \text{ years}$$

● **Write the answer of the following questions. [Each carries 3 Marks]** [12]

7. What is Activation Energy (E_a) ? Explain graph of reaction of activation energy and write about its probability.

➡ The energy required to form the intermediate, called activated complex (C), is known as activation energy (E_a). **or**
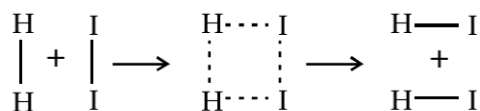
The minimum energy required to convert reactant to the product is called Activation Energy of reaction.

➡ Explanation of activation energy with the help of graph. 2 mole HI is formed by the reaction of 1 mol H_2 with 1 mole I_2.
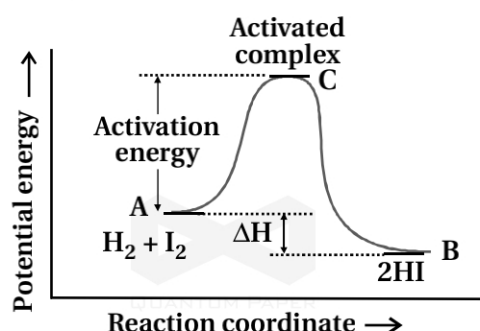
$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$
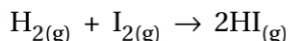
➡ According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate.

➡ It exists for a very short time and then breaks up to form two molecules of Hydrogen iodide.

$$\begin{matrix} H & & I \\ | & + & | \\ H & & I \end{matrix} \longrightarrow \begin{matrix} H\cdots I \\ \vdots \quad \vdots \\ H\cdots I \end{matrix} \longrightarrow \begin{matrix} H\!\!-\!\!I \\ + \\ H\!\!-\!\!I \end{matrix}$$

$H_2 + I_2 \ \infty\!\!\longrightarrow\ $ Intermediate (c) $\rightarrow$ 2HI

➡ The energy required to form this intermediate called activated complex (C), is known as activation energy (E_a).

$$\text{Activation Energy } (E_a) = \begin{pmatrix} \text{Potential energy of} \\ \text{intermediate complex (C)} \end{pmatrix} - \begin{pmatrix} \text{Potential energy} \\ \text{of reactants} \end{pmatrix}$$

➡ **The probability of reaction and E_a :**

(i) The collision of molecules with more kinetic energy than E_a result into product.

(ii) The collision of molecules with less kinetic energy than E_a do not form product.

(iii) $E_a \geq$ energy of collide-molecule than product will form.

(iv) According to Arrhenius energy of activation and rate of reaction is related as

$$k = A\, e^{-\frac{E_a}{RT}} \text{ and } \ln k = \ln A - \frac{E_a}{RT}$$

8. What is first order reaction ? Determine the integrated rate equation for first order reaction R $\rightarrow$ P.

➡ **First order reaction :** The rate of the reaction is proportional to the first power of the concentration of the reactant R is called first order reaction.

The rate of first order reaction $\propto [R]^1$

Where, reaction $R \rightarrow P$ is first order reaction.

➡ The differential rate expression of first order reaction is as under

$$\text{Rate} = -\frac{d[R]}{dt} = k[R] \qquad \qquad ...(i)$$

$$\therefore \frac{d[R]}{[R]} = -k\,dt \quad ...(ii)$$

➡ Integrating this equation both side,

$$\ln [R] = -kt + I \qquad \qquad ...(iii)$$

Here, I = Constant of integration

➡ When, $t = 0$, $[R] = [R]_0$. Where $[R]_0$ is the initial concentration of the reactant. Put this value in eq. (iii)

$$\ln [R]_0 = -k \times (0) + I$$

$$\therefore \ln [R]_0 = I \qquad \qquad ...(iv)$$

➡ If we put $I = \ln [R]_0$ in equation (iii), we get

$$\ln [R] = -kt + \ln [R]_0 \quad ...(VA)$$

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

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

$$\therefore k = \frac{1}{t} \times \ln \frac{[R]_0}{[R]} \qquad \qquad ...(VB)$$

➡ Equation V(A) and V(B) both are integrated rate equation of first order reaction.

➡ The equation (VA) and (VB) can written in the form

$$\log [R] = -\frac{kt}{2.303} + \log [R]_0 \qquad \qquad ...(VIA)$$

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

Note : Equation VA and VIA are straight line equations. So, if we plot $\ln [R] \rightarrow t$ and $\log [R] \rightarrow t$ we get a straight line with slope $= -k$ and intercept equal to $\ln [R]_0$ and $\log [R]_0$.

➡ Taking antilog of equation (VA) at both side, we get

$$[R] = [R]_0\, e^{-kt} \qquad \qquad ...(vii)$$

9. 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 4×10^{10} s^{-1}. Calculate k at 318 K and E_a.

➡ **The time t_1, temperature T_1 for 10% completion of first order reaction :**

$T_1 = 298$ K, time $= t_1$

If initial concentration $= [R]_0$ mol L^{-1}

The reaction is complete 10%, so 90% reactant will be remain.

$\therefore [R]_t = 0.9\,[R]_0$ mol L^{-1}

$$\therefore \; \log k_{298} = \frac{2.303}{t_1} \log \frac{[R]_0}{0.9\,[R]_0} = \frac{2.303}{t_1} \log \frac{1}{0.9}$$

$$\therefore \; t_1 = \frac{2.303}{\log k_{298}} \times 0.04575$$

$$\therefore \; t_1 = \frac{0.1054}{\log k_{298}} \qquad\qquad \ldots(1)$$

➡ Inintial concentration = $[R]_0$ mol L^{-1}, T_2 = 308 K.

The 25 % reaction is completed in t time.

∴ The concentration after completion of 75 % reaction = 75 % of $[R]_0$

$$\therefore \; [R]_t = 0.75\,[R]_0 \text{ mol } L^{-1}$$

$$k_{308} = \frac{2.303}{t_2} \times \log \frac{[R]_0}{0.75\,[R]_0}$$

$$= \frac{2.303}{t_2} \times \log 1.3333 = \frac{2.303 \times 0.1249}{t_2}$$

$$\therefore \; t_2 = \frac{0.2878}{\log k_{308}} \qquad\qquad \ldots(2)$$

But $t_1 = t_2$

$$\therefore \; \frac{0.1059}{k_{(298)}} = \frac{0.2878}{k_{(308)}}$$

$$\therefore \; \frac{k_{(308)}}{k_{(298)}} = \frac{0.2878}{0.1059} = 2.717 \qquad\qquad \ldots(3)$$

➡ **Calculation of E_a :**

$A = 4 \times 10^{10}$ s^{-1} so, at 318 K temperature k = (?) E_a (?)

$$\therefore \; \frac{\log k_2}{\log k_1} = \frac{E_a}{2.303 \times 8.314} \left(\frac{308 - 298}{308 \times 298} \right)$$

$$\therefore \; \log 2.717 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{308 \times 298}$$

$$\therefore \; 0.4324 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{308 \times 298}$$

$$\therefore \; E_a = 75990.0 \text{ J mol}^{-1}$$

$$= 75.99 \text{ kJ mol}^{-1} \approx 76.0 \text{ kJ mol}^{-1}$$

➡ **Calculation of k at 318 K temperature :**

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

$$= \log 4 \times 10^{10} - \frac{75990 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 318 \text{ K}}$$

$$= 10.6021 - 12.4803$$

$$= -1.8782 = \overline{2} \cdot 1218$$

$$\therefore \; k = \text{Antilog } \overline{2} \cdot 1218 = 1.3237 \times 10^{-2} \text{ s}^{-1}$$

$$\therefore \; k = 0.013267 \text{ s}^{-1} \approx 0.013 \text{ s}^{-1}$$

10. 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.

➡ Nuclear explosion is a first order reaction.

1 μg ^{90}Sr is observed in new born baby.

∴ $[R]_0 = 1$ μg

Time t_1 = After 10 years, so, $[R]_{t_1} = x$ $[R]_{t_1} = x$ μg

and time t_2 = After 60 years, so, $[R]_{t_2} = y$ μg

➡ constant of explosion reaction = k. If the reaction is of first order.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1 \text{ year}} = 2.4662 \times 10^{-2} \text{ years}$$

➡ After 10 years, the calculation of remaining ^{90}Sr :

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]_t} \qquad \text{Where, } t = 10$$

$$\therefore \quad 10 = \frac{2.303}{2.4662 \times 10^{-2}} \frac{\log 1 \text{ μg}}{x \text{ μg}}$$

$$\therefore \log \frac{1}{x} = \frac{10 \times 0.024662}{2.303} = 0.1070$$

$$\therefore \frac{1}{x} = \text{Anti log } 0.1070$$

$$\therefore \frac{1}{x} = 1.2794$$

$$\therefore x = 0.7816 \text{ μg } ^{90}Sr \text{ will be remaining.}$$

➡ **Suppose $^{90}S = y$ μg after $t = 60$ year,**

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

$$\therefore 60 = \frac{2.303}{0.024662} \log \frac{1}{y}$$

$$\therefore \frac{60 \times 0.024662}{2.303} = \log 1 - \log y$$

$$\therefore \quad 0.6425 = 0 - \log y = -\log y$$

$$\therefore \quad \log y = -0.6425$$

$$\therefore \quad y = \text{Antilog } (-0.6425)$$

$$= 0.228 \text{ μg } ^{90}Sr \text{ will remain}$$

Section D

● Write the answer of the following questions. [Each carries 4 Marks]   [12]

11. Derive the formula of first order reaction for, (i) Rate constant K, (ii) Half life period (graph is not required)

➡ **First order reaction :** The rate of the reaction is proportional to the first power of the concentration of the reactant R is called first order reaction.

The rate of first order reaction $\propto [R]^1$

Where, reaction R → P is first order reaction.

➡ The differential rate expression of first order reaction is as under

$$\text{Rate} = -\frac{d[R]}{dt} = k\,[R] \qquad \text{...(i)}$$

$$\therefore \frac{d[R]}{[R]} = -k\,dt \quad \text{...(ii)}$$

➡ Integrating this equation both side,

$$\ln\,[R] = -kt + I \qquad \text{...(iii)}$$

Here, I = Constant of integration

➡ When, $t = 0$, $[R] = [R]_0$. Where $[R]_0$ is the initial concentration of the reactant. Put this value in eq. (iii)

$$\ln\,[R]_0 = -k \times (0) + I$$

$$\therefore \ln\,[R]_0 = I \qquad \text{...(iv)}$$

➡ If we put $I = \ln\,[R]_0$ in equation (iii), we get

$$\ln\,[R] = -kt + \ln\,[R]_0 \quad \text{...(VA)}$$

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

$$\therefore kt = \ln\,\frac{[R]_0}{[R]}$$

$$\therefore k = \frac{1}{t} \times \ln\,\frac{[R]_0}{[R]} \qquad \text{...(VB)}$$

➡ Equation V(A) and V(B) both are integrated rate equation of first order reaction.

➡ The equation (VA) and (VB) can written in the form

$$\log\,[R] = -\frac{kt}{2.303} + \log\,[R]_0 \qquad \text{...(VIA)}$$

$$k = \frac{2.303}{t}\,\log\,\frac{[R]_0}{[R]} \qquad \text{...(VIB)}$$

Note : Equation VA and VIA are straight line equations. So, if we plot ln [R] → t and log [R] → t we get a straight line with slope = $-k$ and intercept equal to ln $[R]_0$ and log $[R]_0$.

➡ Taking antilog of equation (VA) at both side, we get

$$[R] = [R]_0\,e^{-kt} \qquad \text{...(vii)}$$

➡ For a first order reaction, rate constant (k) is given by following equation

$$k = \frac{2.303}{t}\,\log\,\frac{[R]_0}{[R]} \qquad \text{...(b)}$$

➡ In this equation $t = t_{1/2}$ = half life time.

At initial $t = 0$ time, the concentration of Reactant = $[R]_0$

After $t_{1/2}$ time, the concentration of Reactant = [R]

$$= \frac{1}{2}\,(\text{initial case}) = \frac{1}{2}\,[R]_0$$

➡ Put $t = t_{1/2}$ and $[R] = \frac{[R]_0}{2}$ in equation (b),

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

$$\therefore k = \frac{2.303}{t_{1/2}} \log 2.0$$

$$\therefore k = \frac{2.303}{t_{1/2}} \times 0.3010$$
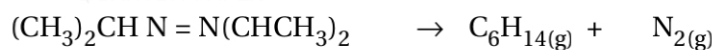
$$\therefore k = \frac{0.693}{t_{1/2}} \quad \text{and}$$

$$t_{1/2} = \frac{0.693}{k} = \text{half life of first order reaction}$$

➥ **Derivation :** It can be seen that for a first order reaction.

➥ Half life period is constant.

➥ It is independent of initial concentrations of the reacting species.

➥ The half life $t_{1/2}$ of a first order equation is really calculated from the rate constant & vice versa.

➥ For zero order reaction $t_{1/2} \propto [R]_0$ and for first order reaction $t_{1/2}$ is independent of $[R]_0$.

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

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

Calculate the rate constant.

➥ **(a) Calculation of rate constant after 360 second :**

$$\text{azoisopropane} \xrightarrow[\text{decomposition}]{543\ K} \text{Hexane}_{(g)} + \text{Nitrogen}_{(g)}$$

$$(CH_3)_2CH\ N = N(CHCH_3)_2 \quad \rightarrow \quad C_6H_{14(g)} + \quad N_{2(g)}$$

$t = 0$ Pressure at:	35 mm Hg	zero	zero
Difference :	$-x$ mm	$+x$ mm	$+x$ mm
Pressure after 360 s	$(35 - x)$	$+x$	$+x$
mm Hg :	$35 - 19 = 16$	19	19

$$\left[\begin{array}{l} \text{Total pressure after 360 second} = 54.0\ \text{mm Hg} \quad \text{and} \\ (35 - x) + x + x = \text{total pressure} = 54.0\ \text{mm Hg} \\ \quad \therefore x = 19\ \text{mm Hg} \end{array}\right]$$

➥ So, For azoisopropene,

$[R]_0 = $ inital concentration = initial pressure

$\quad = 35$ mm $= p_i$

$[R]_t = $ final concentration after 360 second

$\quad = 16$ mm $= p_t$

⮕ Reaction is of first order.

$$\therefore\ k = \frac{2.303}{t}\ \log\frac{p_i}{p_t}$$

$$\therefore\ k = \frac{2.303}{t}\ \log\left(\frac{35}{16}\right)$$

$$\therefore\ k = \frac{2.303}{360\ s}\ 0.3399 = 2.1747 \times 10^{-3}\ s^{-1}$$

⮕ **(b) Calculation of k after 720 s :**

At, $t = 0$ time, the initial pressure $= p_i$

$$= 35.0\ mm = [R]_0$$

Total pressure at $t = 720$ time $= 63\ mm$

If at equilibium $(35 - y) + y + y = (35 + y)$

$$= 63\ mm\ and\ y = (63 - 35) = 28\ mm$$

$$\therefore\ [R]_t = p_t = 1\ (35 - 28) = 7\ mm$$

$$\therefore\ k = \frac{2.303}{720\ s}\ \log\left(\frac{35}{7}\right) = \frac{2.303}{720} \times 0.6990$$

$$= 0.0024\ s^{-1}$$

⮕ Average $k = \dfrac{(2.1747 \times 10^{-3}) + (2.4 \times 10^{-3})}{2}$

$$= 2.21 \times 10^{-3}\ s^{-1}$$

13. 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}	5.7×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

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

⮕

Reaction :	A	+B	→ Product	r_0 mol L^{-1}s^{-1}
Initial conc.(i)	0.20	0.3		5.07×10^{-5}
(mol L^{-1}) (ii)	0.20	0.1		5.07×10^{-5}
(iii)	0.40	0.05		1.43×10^{-4}

Suppose with respect to A order of reaction $= x$ and with respect to B order is y,

Rate of reaction $= k\ [A]^x\ [B]^y$

$r_1 = k\ (0.20)^x\ (0.3)^y = 5.07 \times 10^{-5}$

and $r_2 = k\ (0.20)^x\ (0.1)^y = 5.07 \times 10^{-5}$

$r_3 = k\ (0.40)^x\ (0.05)^y = 1.43 \times 10^{-4}$

⮕ **Calculation of y :**

So, $\dfrac{r_1}{r_2} = \dfrac{k(0.20)^x\ (0.3)^y}{k(0.20)^x\ (0.1)^y} = \dfrac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}}$

$\therefore \dfrac{r_1}{r_2} = (3)^y = 1$

$\therefore 3^y = 1 \qquad$ So $y = 0$

Because $3^0 = 1$

➡ **Calculation of x :**

In equation (i) and (iii) the value of y is substituted as zero

$\qquad r_1 = k(0.20)^x (0.3)^y$

$\qquad\qquad = k(0.2)^x (0.3)°$

$\therefore r_1 = k(0.2)^x$

$\qquad\qquad = 5.07 \times 10^{-5}$

$\qquad r_{iii} = k(0.4)^x (0.05)°$

$\therefore 1.43 \cdot 10^{-4} = k(0.4)^x$

$\therefore r_{iii} = 1.43 \times 10^{-4} = k(0.4)^x$

$\therefore \dfrac{r_{(iii)}}{r_{(i)}} = \dfrac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \dfrac{k(0.4)^x}{k(0.2)^x}$

$\therefore 2.8205 = \left(\dfrac{0.4}{0.2}\right)^x = 2^x$

So, $\log 2.8205 = x \log 2$

$\therefore 0.4503 = x \times 0.3010$

$\therefore x = \dfrac{0.4503}{0.3010} = 1.5$

➡ So, the order of reaction with respect to x is 1.5.