

Chemical Kinetics

(Some Important Problem of NCERT)

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

(a) $3\text{NO}(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g}) + \text{NO}_2(\text{g})$:	Rate = $k[\text{NO}]^2$
(b) $\text{H}_2\text{O}_2(\text{aq}) + 3\text{I}^-(\text{aq}) + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{I}_3^-$:	Rate = $k[\text{H}_2\text{O}_2][\text{I}^-]$
(c) $\text{CH}_3\text{CHO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$:	Rate = $k[\text{CH}_3\text{CHO}]^{3/2}$
(d) $\text{CHCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{g}) + \text{HCl}(\text{g})$:	Rate = $k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$
(e) $\text{C}_2\text{H}_5\text{Cl}(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g}) + \text{HCl}(\text{g})$:	Rate = $k[\text{C}_2\text{H}_5\text{Cl}]$

Ans.

(a) order w.r.t. $\text{NO}(\text{g}) = 2$
 overall order of reaction = 2

(b) order w.r.t. $\text{H}_2\text{O}_2 = 1$
 order w.r.t. $\text{I}^- = 1$
 order w.r.t. $\text{H}^+ = 0$
 overall order = $1 + 1 = 2$

(c) order w.r.t. $\text{CH}_3\text{CHO}(\text{g}) = 3/2$
 overall order = $3/2$ or **1.5**

(d) order w.r.t. $\text{CHCl}_3(\text{g}) = 1$
 overall order = $1 + 0.5 = 1.5$

(e) order w.r.t. $\text{C}_2\text{H}_5\text{Cl}(\text{g}) = 1$
 overall order = **1**.

Q. 2. For the reaction: $2\text{A} + \text{B} + \text{C} \rightarrow \text{A}_2\text{B} + \text{C}$; the rate = $k[\text{A}][\text{B}]^2$ with $k = 2.0 \times 10^{-6} \text{ M}^{-2} \text{ s}^{-1}$. Calculate the initial rate of the reaction when $[\text{A}] = 0.1 \text{ M}$, $[\text{B}] = 0.2 \text{ M}$ and $[\text{C}] = 0.8 \text{ M}$. If the rate of reverse reaction is negligible then calculate the rate of reaction after $[\text{A}]$ is reduced to 0.06 M .

Ans.

(i) Initial rate of the reaction = $k[\text{A}][\text{B}]^2$ (given)
 $= 2.0 \times 10^{-6} \times 0.1 \times (0.2)^2$
 $= 8 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$

(ii) $[\text{A}] = 0.06 \text{ mol L}^{-1}$
 $[\text{B}] = 0.2 - \frac{1}{2} \times 0.04$

$$= 0.2 - 0.02 = 0.18 \text{ mol L}^{-1} \quad [\text{ 2 moles of A react with 1 mol of B so 0.04 mol of A will react with 0.02 mol of B}]$$

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

$$= 2 \times 10^{-6} \times 0.06 \times (0.18)^2$$

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

Q. 3. The rate for the decomposition of NH_3 on platinum surface is zero order. What are the rate of production of N_2 and H_2 if $k = 2.5 \times 10^{-4} \text{ Ms}^{-1}$.

Ans. $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$

$$K = 2.5 \times 10^{-4} \text{ m s}^{-1}$$

$$d / dt [\text{N}_2] = 1 / 3 d / dt [\text{H}_2] = K = 2.5 \times 10^{-4} \text{ m s}^{-1}$$

$$d / dt [\text{N}_2] = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{and } d / dt [\text{H}_2] = 3 \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

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

$$\text{Rate} = k [\text{CH}_3\text{OCH}_3]^{3/2}$$

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

$$\mathbf{\text{rate} = k [p \text{CH}_3\text{OCH}_3]^{3/2}}$$

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

Ans. $\text{Rate} = K [\text{CH}_3\text{OCH}_3]^{3/2}$; The units of rate are **bar s⁻¹**.

$$\text{bar s}^{-1} = k [\text{bar}]^{3/2} \quad [\text{ pressure is measured in bar}]$$

$$\text{or } k = \text{bar s}^{-1} / (\text{bar})^{3/2} \text{ or } \text{bar}^{-1/2} \text{ s}^{-1}$$

Thus unit of k is **bar^{-1/2} s⁻¹**.

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

Ans. Variation factors that affect the rate of a reaction are

- (i) concentration of reactants
- (ii) Physical state of reactants
- (iii) Nature of reactants
- (iv) Temperature
- (v) Pressure
- (vi) Catalyst.

Q. 6 A reaction is second order with respect to a reaction. How is the rate of reaction affected if the concentration of the reactant is

- (i) doubled (ii) reduced to 1/2?

Ans. Since the reaction is of second order w.r.t. a reactant, so its rate equation is
rate = $k [\text{reactant}]^2$

If concentration of reactant is doubled, the rate will become 4 times ($2^2 = 4$)

If concentration reactant is reduced to 1 / 2, the rate will become 1 / 4 times [$(1 / 2)^2 = 1 / 4$].

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

Ans. Generally the rate of a reaction increases with increase in temperature. We can represent the effect of temperature on rate constant with the help of the following equation.

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

It is an empirical equation called **Arrhenius equation**. In this equation

A = Arrhenius factor

k = rate constant

E_a = activation energy

R = gas constant

T = Absolute temperature.

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

t / s	0	30	60	90
[Ester] / M	0.55	0.31	0.17	0.085

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

(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

Ans. (i) Average rate between time 30 s to 60 s = $0.31 - 0.17 / 30 = 0.14 / 30 = 4.67 \times 10^{-3} \text{ s}^{-1}$.

(ii) For a pseudo first order reaction, the reaction rate w.r.t. ester should be 1 when $[\text{H}_2\text{O}]$ is constant.

Thus $k [\text{H}_2\text{O}] = 2.303 / t \log a / (a - x)$ [For first order reaction]

$$\text{At } t = 30 \text{ min, } k = 2.303 / 30 \log 0.55 / 0.31$$

$$= 2.303 / 30 [1.7404 = 1.4914]$$

$$\text{or } k = 2.303 \ 0.249 / 30 = \mathbf{1.91 \ 10^{-2} \ \text{min}^{-1}}$$

$$\text{at } t = 60 \text{ min, } k = 2.303 / 60 \log 0.55 / 0.17$$

$$= 2.303 / 60 [1.7404 = 1.2304]$$

$$= 2.303 \ 0.51 / 60 = \mathbf{1.95 \ 10^{-2} \ \text{min}^{-1}}$$

Since the value of k [H_2O] is constant so it is a *pseudo first order reaction*.

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

(i) Write differential rate equation.

(ii) How is the rate affected when the concentration of B is tripled?

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

Ans. (i) $\text{rate} = k [\text{A}] [\text{B}]^2$

(ii) $\text{rate} = k [\text{A}] [3\text{B}]^2$ or $k [\text{A}] [\text{B}]^2 \cdot 9$ rate become 9 times.

(iii) $\text{rate} = k [2\text{A}] [2\text{B}]^2 = \mathbf{8 \ k [\text{A}] [\text{B}]^2}$ rate becomes 8 times.

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

A / M	0.20	0.20	0.40
B / M	0.30	0.10	0.05
$r_0 / \text{M s}^{-1}$	$5.07 \cdot 10^{-5}$	$5.07 \cdot 10^{-5}$	$7.6 \cdot 10^{-5}$

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

Ans. Let the rate equation be

$$\text{rate} = k [\text{A}]^x [\text{B}]^y.$$

From run 1 and run 2, we have

$$5.07 \cdot 10^{-5} = k [0.20]^x [0.30]^y \quad \dots \text{ (i)}$$

$$\text{and } 5.07 \cdot 10^{-5} = k [0.20]^x [0.10]^y \quad \dots \text{ (ii)}$$

From (i) and (ii), we get $1 = (0.30 / 0.10)^y$

$$\text{or } \mathbf{1 = 3^y \text{ or } y = 0}$$

Again from run 2 and run 3, we have

$$5.07 \cdot 10^{-5} = k [0.20]^x [0.10]^y \quad \dots \text{ (iii)}$$

$$\text{and } 14.6 \cdot 10^{-5} = k [0.40]^x [0.10]^y \quad \dots \text{ (iv)}$$

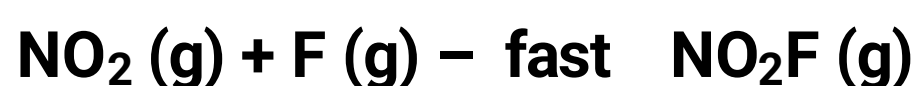
From (iii) and (iv), we get

$$14.6 \cdot 10^{-5} / 5.07 \cdot 10^{-5} = (.40)^x / (.20)^x \text{ or } \mathbf{2.87 = 2^x}$$

or $x = 1.5$

Thus order of reaction w.r.t. A is 1.5 and w.r.t. B is zero. The overall order is 1.5

Q. 11 Reaction between NO_2 and F_2 to give NO_2F takes place by the following mechanism:



Write the rate expression for the reaction.

Ans. The rate of a reaction is determined by slowest step, therefore **rate = $k[\text{NO}_2][\text{F}_2]$** .

Q. 12 The following results have been obtained during the kinetic studies of the reaction: **$2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$**

Experiment	[A] / M	[B] / M	Initial rate of formation of D / M 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. Let the rate be given by

$$\text{rate} = k[\text{A}]^x [\text{B}]^y$$

From experiment 1 and 4, we get

$$6.0 \times 10^{-3} = k[0.1]^x [0.1]^y \quad \dots \text{(i)}$$

$$2.4 \times 10^{-2} = k[0.4]^x [0.1]^y \quad \dots \text{(ii)}$$

From (i) and (ii), we get

$$2.4 \times 10^{-2} / 6.0 \times 10^{-3} = (0.4 / 0.1)^x$$

or **$4 = 4^x$ or $x = 1$**

From experiment 2 and 3, we get

$$7.2 \times 10^{-2} = k[0.3]^x [0.2]^y \quad \dots \text{(iii)}$$

$$2.88 \times 10^{-1} = k[0.3]^x [0.4]^y \quad \dots \text{(iv)}$$

From (iii) and (iv), we get

$$2.88 \times 10^{-1} / 7.2 \times 10^{-2} = (0.4 / 0.2)^y$$

or **$4 = 2^y$ or $y = 2$**

Thus, **rate = $k[\text{A}][\text{B}]^2$** [This the rate law]

Substituting the values of experiment 1 in this law,

$$k = 6.0 \times 10^{-3} / 1 \times 10^{-3} = \mathbf{6 \text{ mol}^{-2} \text{L}^2 \text{min}^{-1}}$$

Q. 13 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] / M	[B] / M	Initial rate / M 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.

Experiment	[A] / M	[B] / M	Initial rate/M min ⁻¹
1	0.1	0.1	2 × 10 ⁻²
2	0.2	0.2	4 × 10 ⁻²
3	0.4	0.4	8 × 10 ⁻²
4	0.1	0.2	2 × 10 ⁻²

Q. 14 Calculate the half life of a first order reaction from their rate constants given below:

(a) 200 s⁻¹ (b) 2 min⁻¹ (c) 4 year⁻¹

Ans. For a first order reaction $t_{1/2} = 0.693 / k$

(a) $t_{1/2} = 0.693 / 200$ or 3.464 × 10⁻³ s

(b) $t_{1/2} = 0.693 / 2$ or 3.4645 min

(c) $t_{1/2} = 0.693 / 4$ or 0.173 year.

Q. 15 The experimental data for decomposition of N₂O₅ [2N₂O₅ → 4NO₂ + O₂] in gas phase at 318 K are given below:

t / s	0	400	800	1200	1600	2000	2400	2800	3200
10 ² [N ₂ O ₅] / M	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(a) Plot [N₂O₅] against t

(b) Find the half life period for the reaction

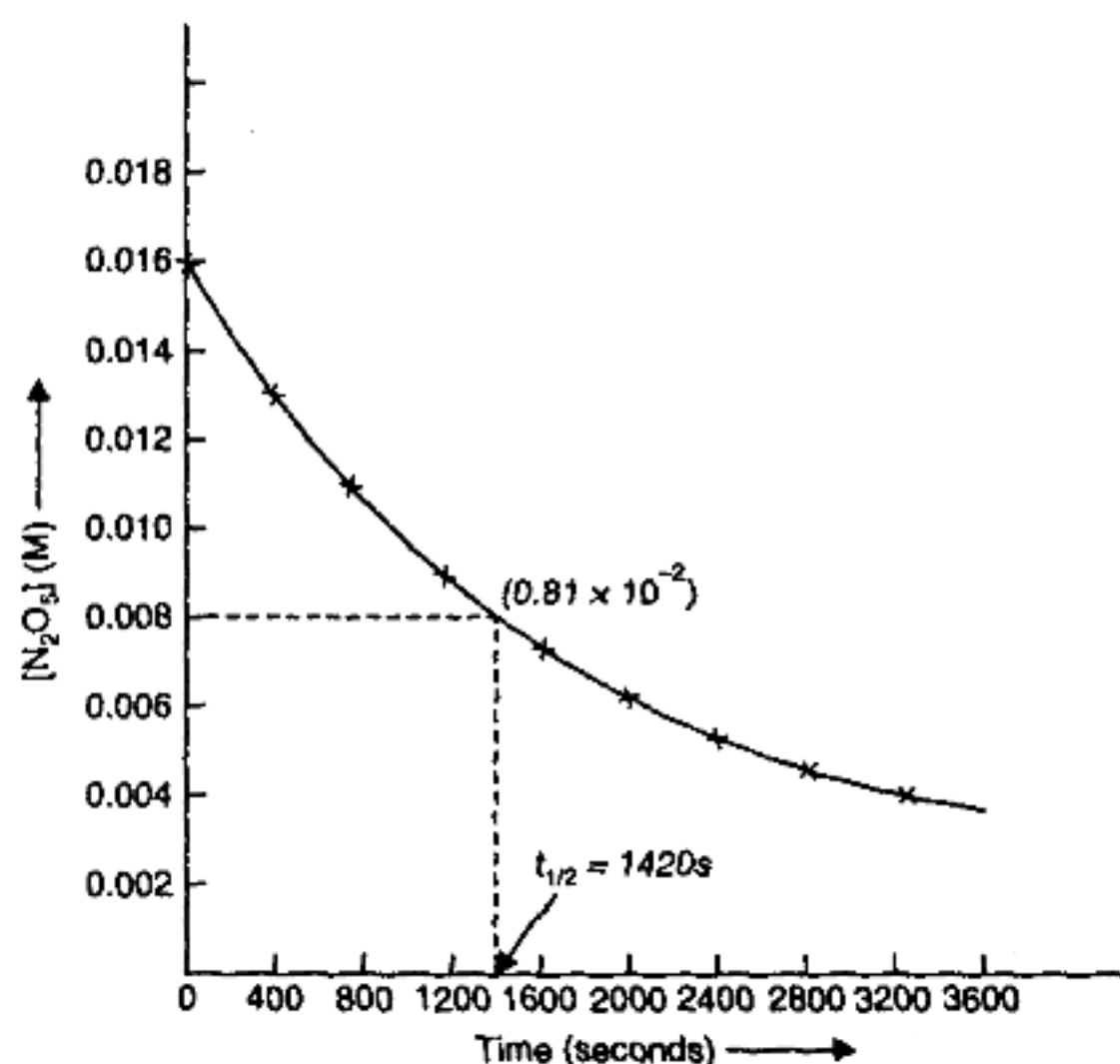
(c) Draw a graph between log [N₂O₅] and t

(d) What is rate law

(e) Calculate the rate constant

(f) Calculate the half life period from k and compare it with (b).

Ans. (a) Plot of $[N_2O_5]$ vs time is:



(b) Time taken for the concentration of N_2O_5 to change from $1.63 \times 10^{-2} \text{ mol L}^{-1}$ to half the value, (From the graph) $t_{1/2} = 1420 \text{ s}$

(c) Plot of $\log(N_2O_5)$ vs time is:

(d) $\text{rate} = k [N_2O_5]$

(e) Since straight line is obtained by plotting $[N_2O_5]$ against time, so it is a first order reaction.

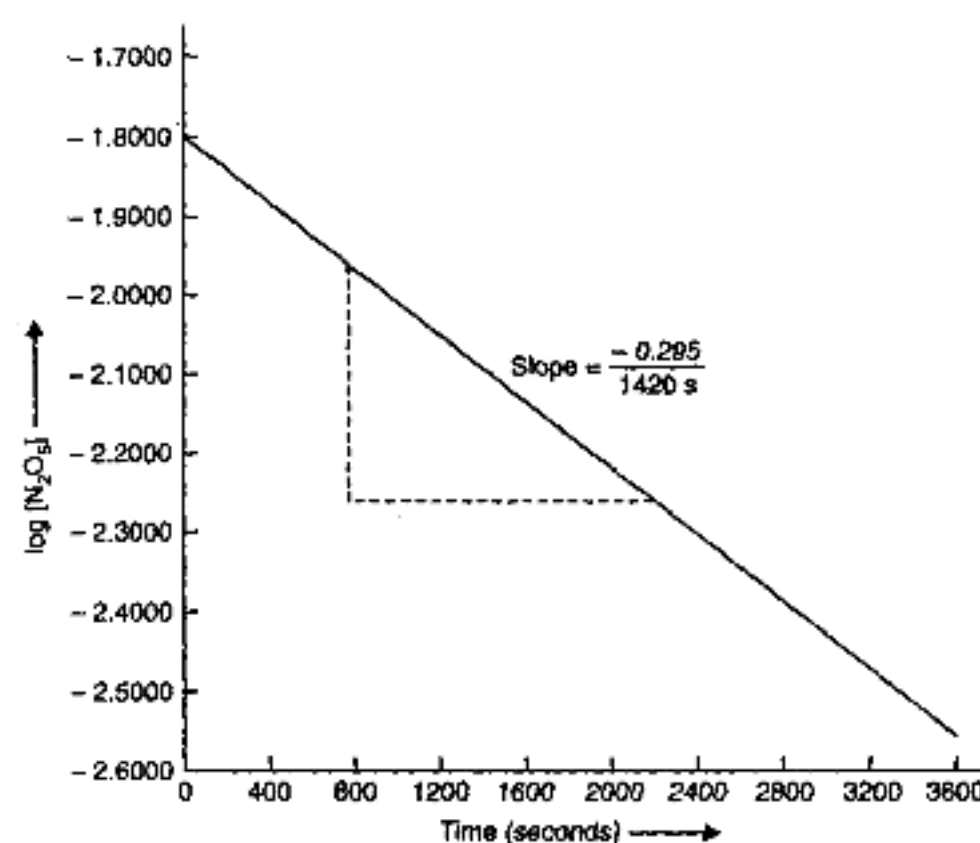
Slope = $-k / 2.303 = -0.295 / 1420 \text{ s}$

or $k = 0.295 \times 2.303 / 1420 \text{ s} = 4.853 \times 10^{-4} \text{ s}^{-1}$

(f) Half life, $t_{1/2} = 0.693 / k$

$t_{1/2} = 0.693 / 4.853 \times 10^{-4} = 1482 \text{ s}$

It is quite close to $t_{1/2}$ calculated from graph (i.e. 1420 s).



(For first order reaction)

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 $1 / 16^{\text{th}}$ value?

Ans. Using the relation

$k = 2.303 / t \log a / (a - x)$ (For 1st order reaction)

we get $60 \text{ s}^{-1} = 2.303 / t \log a / 1 / 16$

or $60 \text{ s}^{-1} = 2.303 / t \log 16 = 2.303 / t \log 2^4$

or $t = 2.303 / 60 \times 4 \times 0.3010 = 4.62 \times 10^{-2} \text{ s}$.

Q. 17 The rates of most reaction double when their temperature is raised from 298 K to 308 K. Calculate their activation energy.

Ans. Using the relation,

$$\log k_2 / k_1 = E_a / R \quad 2.303 [1 / T_1 - 1 / T_2], \text{ we get}$$

$$\log 2 = E_a / 8.314 \quad 2.303 [1 / 298 - 1 / 308] \quad [k_2 / k_1 = 2]$$

$$\text{or} \quad \log 2 = E_a / 19.15 \quad 10 / 2.98 \quad 308$$

$$\text{or} \quad E_a = 0.3010 \quad 19.15 \quad 298 \quad 308 / 10 \text{ J mol}^{-1}$$

$$= 529052 / 10 \text{ J mol}^{-1} = \mathbf{52.905 \text{ kJ mol}^{-1}}$$

Q. 18 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 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° and 50°C .

Ans. Prepare the table for $1 / T$ and $\log k$, from given values.

T (K)	273	293	313	333	353
1 / T	0.003663	0.003413	0.003195	0.003003	0.002833
$\log k$	- 6.1040	- 4.7696	- 3.5900	- 2.7496	- 1.6996

Now draw the plot of $\log k$ vs $1 / T$, we get

From the graph, we get

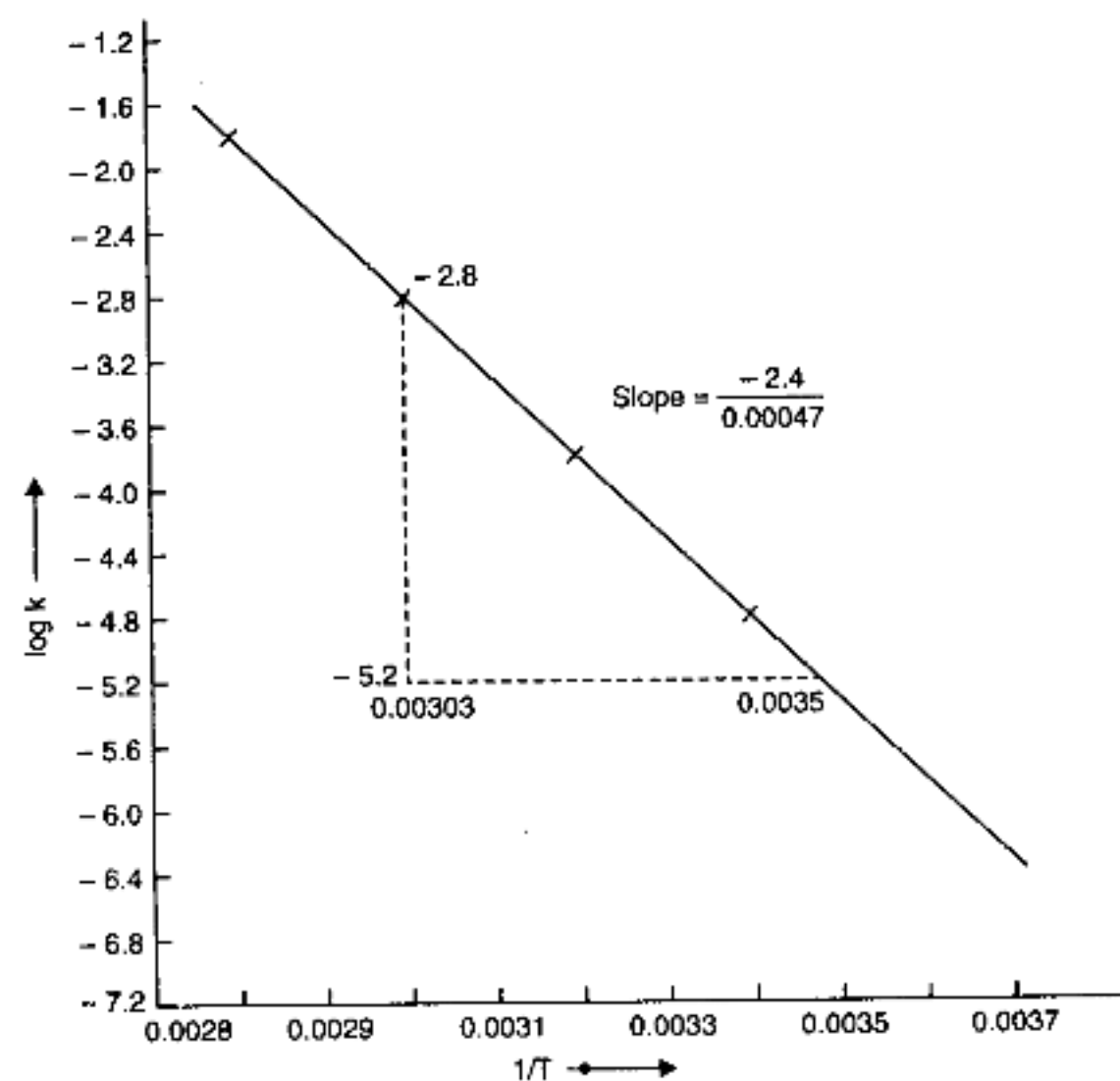
$$\text{Slope} = - 2.4 / 0.00047 = - E_a / 2.303 R$$

$$\text{Activation energy, } E_a = 2.4 \quad 2.303 \quad R / 0.00047$$

$$= 2.4 \quad 2.303 \quad 8.314 \text{ mol}^{-1} / 0.00047$$

$$= 97772 \text{ J mol}^{-1}$$

$$= 97.772 \text{ kJ mol}^{-1}.$$



Computation of k values

T	1 / T	Value of log k (from graph)	Value of k
303	0.003300	- 4.2	6.31×10^{-5}
323	0.003096	- 3.16	6.92×10^{-4}
343	0.002915	- 2.20	6.31×10^{-3}

Q. 19 The half life for radioactive decay of ^{14}C is 5730 y. An archaeological artefact contained wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

Ans. $t_{1/2} = 5730 \text{ y}$

$$= 0.693 / 5730 \text{ y}$$

we have, $k = 2.303 / t \log a / a - x$ (For first order reaction)

Substituting the given values, we get

$$\frac{0.693}{5730\text{y}} = \frac{2.303}{t} \log \frac{100}{80}$$

or
$$\frac{0.693}{5730\text{y}} = \frac{2.303}{t} \log \frac{5}{4}$$

or
$$\frac{0.693}{5730\text{y}} = \frac{2.303}{t} (0.6990 - 0.6020)$$

$$= \frac{2.303}{t} \cdot (0.0970)$$

$$t = \frac{2.303 \cdot 0.0970 \cdot 5730}{0.693} = 1847 \text{ years.}$$

Q. 20 During nuclear explosion, one of the products is ^{90}Sr with half - life of 28.1 y. If 1 g 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. Radioactive decay is a first order reaction

$$k = 2.303 / t \log C_0 / C$$

where C_0 is the initial concentration and C is the concentration after time ' t '

Given
$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1 \text{ y}}$$

$C_0 = 1 \text{ g}$ $t = 10 \text{ years.}$

$C = ?$

Substituting the given values, we get

$$\frac{0.693}{28.1} = \frac{2.303}{10} \log \frac{1}{C}$$

or $\log \frac{1}{C} = \frac{0.693 \cdot 10}{28.1 \cdot 2.303} = \frac{6.93}{64.6}$ or 0.107

or $\frac{1}{C} = \text{anti log } 0.107 = 1.279$

or $C = \frac{1}{1.279}$ or $0.7842 \mu\text{g}$.

Similarly after 60 years the amount left (C) can be calculated.

$$\frac{0.693}{28.1} = \frac{2.303}{10} \log \frac{1}{C}$$

or $\log \frac{1}{C} = \frac{0.693 \cdot 10}{28.1 \cdot 2.303} = \frac{41.58}{64.6} = 0.65$

or $\frac{1}{C} = \text{anti log } (0.65) = 4.467$

or $C = \frac{1}{4.467}$ or $0.224 \mu\text{g}$.