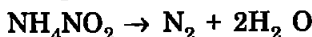


LESSON AT A GLANCE

- **Chemical kinetics:** It deals with the study of reaction rates and their mechanism.
- **Rate of a chemical reaction:** It is defined as the change in concentration of any of the reactants or products with time at any particular moment of time. Its unit is mole L⁻¹ S⁻¹.
- **Instantaneous rate:** It is the rate of a reaction at a given instant of time, i.e. $\frac{\Delta x}{\Delta t}$ (average rate) becomes $\frac{dx}{dt}$ when Δt approaches zero.
- **Rate law:** Expression based on experimental fact, which describes the reaction rate in terms of molar concentration of reacting species.
- **Rate constant (K):** The rate of reaction when the concentration of each of reacting species is unity. It is also known as velocity constant or specific reaction rate of the reaction.
- **Molecularity:** Total number of atoms, ions or molecules of the reactants involved in the reaction is termed as its molecularity. It is always in whole number. It cannot be zero and never be more than three.
- **Order of a reaction:** The sum of the exponents (powers) of the concentration terms in the experimental rate law of reaction, is termed as order of the reaction. It can be zero, 1, 2, 3 or any in fractional value.
- **Zero order reaction:** Reactions in which the rate of reaction does not change with the concentration of reaction, i.e. $r = K[A]^0 = K$.
- **First order reaction:** A reaction in which the rate of reaction is directly proportional to the concentration of reacting substance, i.e. $r = K[A]$.

- **Molecularity of a Reaction:** The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.
- **Elementary Reaction:** Reaction taking place in one step is called elementary reaction.
- **Unimolecular Reaction:** The reaction can be unimolecular when one reacting species is involved.

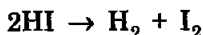
For example, decomposition of ammonium nitrate.



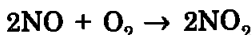
- **Bimolecular Reaction:** When the molecularity of the reaction is 2 it is called bimolecular.

For example, dissociation of HI:

The balanced equation is



- **Trimolecular Reaction:** These reactions involve simultaneous collision between three reacting species. For example:



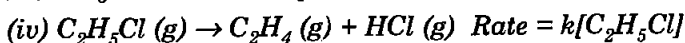
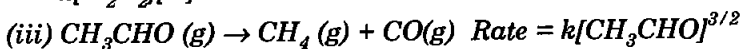
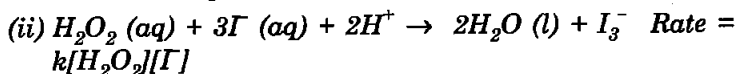
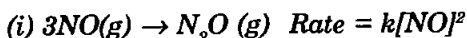
Here molecularity = 3

- **Complex Reaction:** When a sequence of elementary reactions gives us the products, the reactions are called complex reactions.

For complex reaction, order is given by the slowest step and generally, molecularity of the slowest step is same as the order of the overall reaction.

TEXTBOOK QUESTIONS SOLVED

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



Ans. (i) From rate law: Rate = $k[\text{NO}]^2$

$$\text{Order} = 2$$

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

(ii) From rate law: Rate = $k [\text{H}_2\text{O}_2] [\text{I}^-]$

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

$$\text{Dimensions of } k: k = \frac{\text{Rate}}{[\text{H}_2\text{O}_2] [\text{I}^-]} = \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^2} = \text{L mol}^{-1}\text{s}^{-1}$$

(iii) From rate law: Rate = $k [\text{CH}_3\text{CHO}]^{3/2}$

$$\text{Order} = \frac{3}{2}$$

$$\text{Dimensions of } k = \frac{\text{Rate}}{[\text{CH}_3\text{CHO}]^{3/2}} = \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^{3/2}}$$

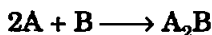
$$= \text{L}^{1/2}\text{mol}^{-1/2}\text{s}^{-1}$$

(iv) From rate law: Rate = $k [\text{C}_2\text{H}_5\text{Cl}]$

$$\text{Order} = 1$$

$$\text{Dimensions of } k = \frac{\text{Rate}}{[\text{C}_2\text{H}_5\text{Cl}]} = \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})} = \text{s}^{-1}$$

4.2 For the reaction:



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

Ans. Rate law: Rate = $k [\text{A}] [\text{B}]^2$

$$\text{Given } k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

Initial Rate

$$\text{Initial concentration: } [\text{A}] = 0.1 \text{ mol L}^{-1}; [\text{B}] = 0.2 \text{ mol L}^{-1}$$

$$\therefore \text{Initial rate} = (2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}) (0.1 \text{ mol L}^{-1})$$

$$(0.2 \text{ mol L}^{-1})^2$$

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

Rate when $[\text{A}] = 0.06 \text{ mol L}^{-1}$

$$\text{Decrease in concentration of A} = (0.1 - 0.06) \text{ mol L}^{-1}$$

$$= 0.04 \text{ mol L}^{-1}.$$

From the reaction $2A + B \longrightarrow A_2B$

2 mol A react with 1 mol B

\therefore 0.04 mol A react with $\frac{0.04}{2} = 0.02$ mol of B.

Concentration of unreacted B

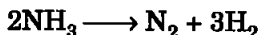
$$= [B] = (0.2 - 0.02) = 0.18 \text{ mol L}^{-1}$$

Putting the concentration of A and B in the rate law

$$\begin{aligned} \text{Rate} &= k[A][B]^2 \\ &= (2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1})(0.06 \text{ mol L}^{-1})(0.18 \text{ mol L}^{-1})^2 \\ &= 3.89 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}. \end{aligned}$$

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

Ans. For the reaction



$$\text{Rate} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} \quad \dots(1)$$

Also for zero order reaction

$$\text{Rate} = k \quad \dots(2)$$

From equations (1) and (2)

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = k \quad \dots(3)$$

$$\text{Rate of production of } \text{N}_2 = \frac{d[\text{N}_2]}{dt} = k$$

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

$$\therefore \text{Rate of production of } \text{N}_2 = k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

From equation (3)

Rate of production of H_2

$$\begin{aligned} &= \frac{d[\text{H}_2]}{dt} = 3k = 3 \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \\ &= 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}. \end{aligned}$$

4.4 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, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.,

$$\text{Rate} = k (p_{\text{CH}_3\text{COCH}_3})^{\frac{3}{2}}$$

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

Ans. Given: Unit of pressure = bar

Unit of time = minute

\therefore Unit of rate = bar min⁻¹

$$\text{Rate law: Rate} = k (p_{\text{CH}_3\text{COCH}_3})^{\frac{3}{2}}$$

$$k = \frac{\text{Rate}}{(p_{\text{CH}_3\text{COCH}_3})^{\frac{3}{2}}} = \frac{\text{bar min}^{-1}}{\text{bar}^{\frac{3}{2}}} = \text{bar}^{-\frac{1}{2}} \text{ min}^{-1}$$

4.5 Mention the factors that affect the rate of a chemical reaction.

Ans. Factors affecting the rate of a chemical reaction:

- 1. Concentration:** In general the rate of a reaction increases when concentration of reactants is increased.
- 2. Temperature:** Most of the chemical reactions are accelerated by increase in temperature.
- 3. Catalyst:** Rate of a reaction increases in presence of a catalyst.
- 4. Nature of reactants:** Reactions involving ionic reactants are fast as compared to those involving covalent reactants.
- 5. Surface area of the reactants:** In case of solid reactants, the rate of reaction increases with the surface area of the particles of the reactants.
- 6. Light:** In case of photochemical reactions, the rate of reaction increases with increasing the intensity of light.

4.6 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. Since the reaction is second order with respect to a reactant say A. The rate law is:

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

Let the concentration of A be x mol L⁻¹

$$\therefore \text{Rate} = r_1 = k x^2$$

(i) When the concentration of A is doubled,

$$[A] = 2x \text{ and Rate} = r_2 = k(2x)^2 = 4kx^2 = 4r_1$$

Thus, rate is increased to 4 times to the original rate.

(ii) When the concentration of A is reduced to half,

$$[A] = \frac{1}{2}x \text{ and Rate} = r_3 = k\left(\frac{1}{2}x\right)^2 = \frac{1}{4}kx^2.$$

Thus, the rate is decreased to one-fourth of the original rate.

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

Ans. Rate constant of a reaction generally increases with rise in temperature. Quantitatively the relation between the two is given by the Arrhenius equation.

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

where k = rate constant of the reaction at temperature T (on Kelvin scale) A = frequency factor E_a = energy of activation.

4.8 In a pseudo first order hydrolysis of ester in water, the following results were obtained:

t/s	0	30	60	90
$[Ester]/\text{mol L}^{-1}$	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 = $-\frac{C_2 - C_1}{t_2 - t_1}$

From the data when $t = t_1 = 30$ s, $C_1 = 0.31$ mol L⁻¹ and when $t = t_2 = 60$ s; $C_2 = 0.17$ mol L⁻¹

$$\begin{aligned} \therefore \text{Average rate} &= -\frac{(0.17 - 0.31) \text{ mol L}^{-1}}{(60 - 30) \text{ s}} = \frac{0.14 \text{ mol L}^{-1}}{30 \text{ s}} \\ &= 4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}. \end{aligned}$$

(ii) Since the reaction is pseudo first order, the integrated rate law is

$$k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

$$C_0 = 0.55 \text{ mol L}^{-1} \text{ when } t = 0$$

(a) When $t = 30 \text{ s}$, $C_t = 0.31 \text{ mol L}^{-1}$

$$k_1 = \frac{2.303}{30 \text{ s}} \log \frac{0.55}{0.31} = 1.91 \times 10^{-2} \text{ s}^{-1}$$

(b) When $t = 60 \text{ s}$, $C_t = 0.17 \text{ mol L}^{-1}$

$$k_2 = \frac{2.303}{60 \text{ s}} \log \frac{0.55}{0.17} = 1.96 \times 10^{-2} \text{ s}^{-1}$$

(c) When $t = 90 \text{ s}$; $C_t = 0.085 \text{ mol L}^{-1}$

$$\therefore k_3 = \frac{2.303}{90 \text{ s}} \log \frac{0.55}{0.085} = 2.07 \times 10^{-2} \text{ s}^{-1}$$

$$\begin{aligned} \text{Average value of } k &= \left(\frac{1.91 + 1.96 + 2.07}{3} \right) \times 10^{-2} \text{ s}^{-1} \\ &= 1.98 \times 10^{-2} \text{ s}^{-1}. \end{aligned}$$

4.9 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 the concentrations of both A and B are doubled?

Ans. Since the reaction is first order in A and second order in B

(i) Differential rate equation is

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

(ii) The new concentration of B = 3[B]

$$\therefore \text{New rate} = k[\text{A}] \{3[\text{B}]\}^2 = 9k [\text{A}] [\text{B}]^2$$

$$\therefore \text{New rate} = 9 \text{ times of the original rate}$$

(iii) New concentration of A = 2[A]

New concentration of B = 2[B]

$$\therefore \text{New rate} = k \{2[\text{A}]\} \{2[\text{B}]\}^2$$

$$= 2 \times 4k[\text{A}] [\text{B}]^2 = 8k [\text{A}] [\text{B}]^2$$

$$\therefore \text{New rate} = 8 \text{ times of the original rate.}$$

4.10 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:

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

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

Ans. Let the order of the reaction be x with respect to A and y with respect to B. Then the differential rate law is

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

From the given data

$$(r_0)_1 = 5.07 \times 10^{-5} = k (0.20)^x (0.30)^y \quad \dots(1)$$

$$(r_0)_2 = 5.07 \times 10^{-5} = k (0.20)^x (0.10)^y \quad \dots(2)$$

$$(r_0)_3 = 1.43 \times 10^{-4} = k (0.40)^x (0.05)^y \quad \dots(3)$$

From equations (1) and (2)

$$\frac{(r_0)_1}{(r_0)_2} = \frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{k (0.20)^x (0.30)^y}{k (0.20)^x (0.10)^y}$$

$$\text{or} \quad 1 = \left(\frac{0.30}{0.10} \right)^y = (3)^y$$

$$\therefore y = 0$$

Thus the reaction is zero order in B.

From equations (2) and (3)

$$\frac{(r_0)_3}{(r_0)_2} = \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{k (0.40)^x (0.05)^y}{k (0.20)^x (0.10)^y}$$

$$2.82 = \left(\frac{0.40}{0.20} \right)^x \left(\frac{0.05}{0.10} \right)^y = 2^x \left(\frac{1}{2} \right)^y$$

$$\text{Since} \quad y = 0$$

$$\therefore 2.82 = 2^x$$

Taking logarithm of both sides

$$\log 2.82 = x \log 2$$

$$\therefore x = \frac{\log 2.82}{\log 2} = \frac{0.4502}{0.3010} = 1.5$$

$$x = 1.5$$

\therefore Order with respect to A = 1.5 and the order with respect to B = 0.

4.11 The following results have been obtained during the kinetic studies of the reaction:



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. For the reaction



Let the rate law be

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

From the given data

$$(r_0)_1 = 6.0 \times 10^{-3} = k (0.1)^x (0.1)^y \quad \dots(1)$$

$$(r_0)_2 = 7.2 \times 10^{-2} = k (0.3)^x (0.2)^y \quad \dots(2)$$

$$(r_0)_3 = 2.88 \times 10^{-1} = k (0.3)^x (0.4)^y \quad \dots(3)$$

$$(r_0)_4 = 2.4 \times 10^{-2} = k (0.4)^x (0.1)^y \quad \dots(4)$$

From equations (1) and (4)

$$\frac{(r_0)_4}{(r_0)_1} = \frac{2.4 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k (0.4)^x (0.1)^y}{k (0.1)^x (0.1)^y}$$

$$4 = \left(\frac{0.4}{0.1} \right)^x = 4^x$$

$$\therefore x = 1.$$

Thus, the order with respect to A is 1.

From equations (2) and (3)

$$\frac{(r_0)_3}{(r_0)_2} = \frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \frac{k (0.3)^x (0.4)^y}{k (0.3)^x (0.2)^y}$$

$$4 = \left(\frac{0.4}{0.2} \right)^y = 2^y$$

$$\therefore y = 2$$

Thus, the order with respect to B = 2.

The rate law of the reaction is

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

Calculation of rate constant

From the rate law

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

From equation (1) (substituting the values of x and y)

$$k_1 = \frac{6.0 \times 10^{-3}}{(0.1) (0.1)^2} = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

From equation (2)

$$k_2 = \frac{7.2 \times 10^{-2}}{(0.3) (0.2)^2} = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

From equation (3)

$$k_3 = \frac{2.88 \times 10^{-1}}{(0.3) (0.4)^2} = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

From equation (4)

$$k_4 = \frac{2.4 \times 10^{-2}}{(0.4) (0.1)^2} = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

$$\therefore k = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}.$$

4.12 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. Since the given reaction is first order with respect to A and zero order with respect to B, the rate law is

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

From the data sets I and II, let the unknown concentration of A be $x \text{ mol L}^{-1}$

$$\frac{(r_0)_2}{(r_0)_1} = \frac{4.0 \times 10^{-2}}{2.0 \times 10^{-2}} = \frac{x}{0.1}$$

$$2 = \frac{x}{0.1}$$

$$x = 2 \times 0.1 = 0.2 \text{ mol L}^{-1}$$

From data sets I and III, let the unknown initial rate be $y \text{ mol L}^{-1} \text{ min}^{-1}$

$$\frac{(r_0)_3}{(r_0)_1} = \frac{y}{2.0 \times 10^{-2}} = \frac{k(0.4)}{k(0.1)} = 4$$

$$\therefore y = 4 \times 2.0 \times 10^{-2} = 8.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$$

From data sets IV and I, let the unknown concentration of A be $z \text{ mol L}^{-1}$

$$\frac{(r_0)_4}{(r_0)_1} = \frac{2.0 \times 10^{-2}}{2.0 \times 10^{-2}} = \frac{k(z)}{k(0.1)}$$

$$1 = \frac{z}{0.1}$$

or

$$z = 0.1 \text{ mol L}^{-1}$$

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	0.2	4.0×10^{-2}
III	0.4	0.4	8.0×10^{-2}
IV	0.1	0.2	2.0×10^{-2}

4.13 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. For a first order reaction

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

(i) $k = 200 \text{ s}^{-1}$; $t_{1/2} = \frac{0.693}{200 \text{ s}^{-1}} = 3.46 \times 10^{-3} \text{ s}$

(ii) $k = 2 \text{ min}^{-1}$; $t_{1/2} = \frac{0.693}{2 \text{ min}^{-1}} = 3.46 \times 10^{-1} \text{ min}$

$$(iii) k = 4 \text{ years}^{-1}; t_{1/2} = \frac{0.693}{4 \text{ year}^{-1}} = 1.73 \times 10^{-1} \text{ year.}$$

4.14 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. Given $t_{1/2} = 5730$ years

$$\therefore k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ years}}$$

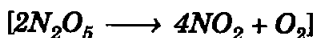
Let the initial concentration of C-14 (concentration in living tree) be 100.

The concentration observed in the artifact = 80.

From the integrated rate law of first order reaction

$$\begin{aligned} t &= \frac{2.303}{k} \log \frac{C_0}{C_t} = \frac{2.303 \times 5730}{0.693} \log \frac{100}{80} \text{ years} \\ &= \frac{2.303 \times 5730}{0.693} \log 1.25 \text{ years} \\ &= 1845 \text{ years.} \end{aligned}$$

4.15 The experimental data for decomposition of N_2O_5

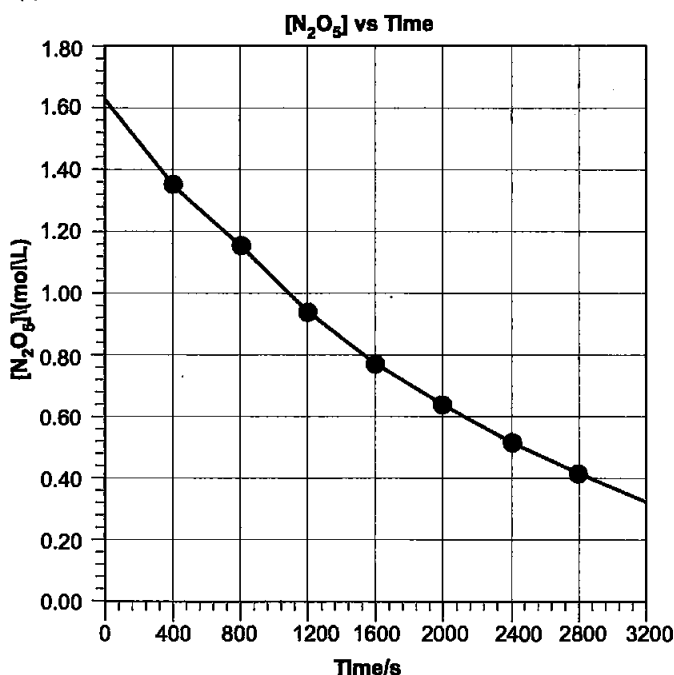


in gas phase at 318 K are given below:

t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [\text{N}_2\text{O}_5]/\text{mol L}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

- Plot $[\text{N}_2\text{O}_5]$ against t .
- Find the half-life period for the reaction.
- Draw a graph between $\log[\text{N}_2\text{O}_5]$ and t .
- What is the rate law?
- Calculate the rate constant.
- Calculate the half-life period from k and compare it with (ii).

Ans. (i)



(ii) **Half-life period**

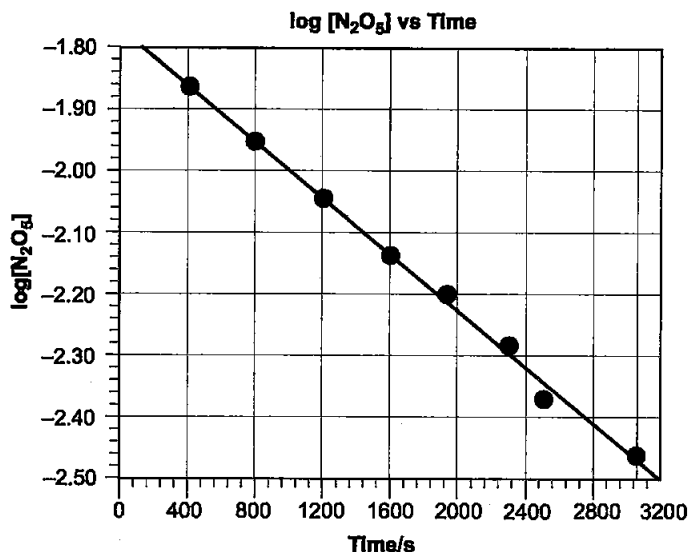
Initial concentration of N₂O₅ = $1.63 \times 10^{-2} \text{ mol L}^{-1}$

Half of initial concentration = $0.815 \times 10^{-2} \text{ mol L}^{-1}$

From the graph time corresponding to it = 1500 s.

(iii)

t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [\text{N}_2\text{O}_5]/\text{mol L}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35
$\log[\text{N}_2\text{O}_5]$	-1.79	-1.87	-1.94	-2.03	-2.11	-2.19	-2.28	-2.37	-2.46



Plot of log [N₂O₅] vs time.

(iv) **Rate law**

Since the graph between log [N₂O₅] and t is a straight line with a negative slope, the reaction is first order and the rate law as

$$\text{Rate} = k [\text{N}_2\text{O}_5]$$

(v) Slope of the above plot = $-\frac{k}{2.303}$

when $t = 0$ s, $\log[\text{N}_2\text{O}_5] = -1.79$

when $t = 3200$ s, $\log [\text{N}_2\text{O}_5] = -2.46$

$$\text{slope} = \frac{\Delta \log[\text{N}_2\text{O}_5]}{\Delta t} = \frac{-2.46 - (-1.79)}{3200 - 0} = -\frac{0.67}{3200}$$

Thus $-\frac{k}{2.303} = -\frac{0.67}{3200}$

or $k = \frac{2.303 \times 0.67}{3200} = 4.82 \times 10^{-4} \text{ s}^{-1}$

(vi) **Half-life period from k**

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.82 \times 10^{-4} \text{ s}^{-1}} = 1438 \text{ s.}$$

4.16 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. Given $k = 60 \text{ s}^{-1}$

Let the initial concentration C_0 be $a \text{ mol L}^{-1}$

Given that the concentration left C_t is $\frac{a}{16}$

Let the time required for it be t ,

$$\begin{aligned} \text{Then} \quad t &= \frac{2.303}{k} \log \frac{C_0}{C_t} \\ &= \frac{2.303}{60 \text{ s}^{-1}} \log \frac{a}{a/16} \\ &= \frac{2.303}{60 \text{ s}^{-1}} \log 16 = \frac{2.303 \times 1.2041}{60} \text{ s} \\ &= 0.0462 \text{ s.} \end{aligned}$$

Alternately

Since concentration is reduced to $\frac{1}{16} = \frac{1}{2^4}$ the time required is 4 times of the half-life period.

$$\therefore t = \frac{4 \times 0.693}{k} = \frac{4 \times 0.693}{60 \text{ s}^{-1}} = 0.0462 \text{ s.}$$

4.17 During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 year. If $1 \mu\text{g}$ 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. Given $t_{1/2} = ^{90}\text{Sr} = 28.1 \text{ year}$.

Since radioactive decay follows the first order kinetics

$$\text{Decay constant} = k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} \text{ year}^{-1}$$

(i) Amount of ^{90}Sr left after 10 years

$$k = \frac{0.693}{28.1} \text{ year}^{-1}, t = 10 \text{ year}, C_0 = 1 \mu\text{g}, C_t = ?$$

$$k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

$$\frac{0.693}{28.1} \text{ year}^{-1} = \frac{2.303}{10 \text{ year}} \log \frac{1}{C_t}$$

$$-\log C_t = \frac{0.693}{28.1} \times \frac{10}{2.303} = 0.1071$$

$$\log C_t = -0.1071$$

$$C_t = \text{antilog } \bar{1}.8929$$

$$C_t = 0.7815 \mu\text{g}$$

(ii) Amount of ^{90}Sr left after 60 years

$$t = 60 \text{ year}, C_0 = 1 \mu\text{g}, c_t = ?$$

$$k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

$$\frac{0.693}{28.1} \text{ year}^{-1} = \frac{2.303}{60} \log \frac{1}{C_t}$$

$$-\log C_t = \frac{0.693}{28.1} \times \frac{60}{2.303} = 0.6425$$

$$\log C_t = -0.6425$$

$$C_t = \text{antilog } \bar{1}.3575$$

$$C_t = 0.2278 \mu\text{g}.$$

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

Ans. For first order reaction

$$t = \frac{2.303}{k} \log \frac{C_0}{C_t}$$

For 99% completion of reaction

$$t = t_{0.99}, C_0 = 1, C_t = (1 - 0.99) = 0.01 = 10^{-2}$$

$$t_{0.99} = \frac{2.303}{k} \log \frac{1}{10^{-2}} = \frac{2.303}{k} \log 10^2 = \frac{2.303}{k} \times 2$$

For 90% completion of reaction

$$t = t_{0.90}, C_0 = 1, C_t = (1 - 0.9) = 0.1 = 10^{-1}$$

$$\therefore t_{0.90} = \frac{2.303}{k} \log \frac{1}{10^{-1}} = \frac{2.303}{k} \log 10 = \frac{2.303}{k}$$

Comparing $t_{0.99}$ and $t_{0.90}$ (required expression)

$$t_{0.99} = 2 \times t_{0.90}.$$

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

Ans. $t = 40 \text{ min } C_0 = 1 ; C_t = 1 - 0.30 = 0.70$

$$k = \frac{2.303}{t} \log \frac{C_0}{C_t} = \frac{2.303}{40} \log \frac{1}{0.70} = \frac{2.303}{40} \times 0.1549$$

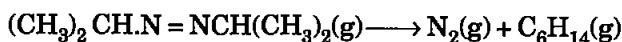
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693 \times 40}{2.303 \times 0.1549} = 77.70 \text{ min.}$$

4.20 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.

Ans. For the reaction



$$t = 0 \qquad p_0 \qquad 0 \qquad 0$$

$$t = t \qquad p_0 - p \qquad p \qquad p$$

Total pressure at time $t = p_t = p_0 - p + p + p = p_0 + p$

Since concentration of a gaseous substance is directly proportional to its partial pressure

$$C_0 \propto p_0$$

$$C_t \propto p_0 - p$$

From the calculations shown above

$$p_t = p_0 + p$$

$$p = p_t - p_0$$

and

$$p_0 - p = p_0 - (p_t - p_0) = (2p_0 - p_t)$$

\therefore

$$C_t \propto 2p_0 - p_t$$

$$k = \frac{2.303}{t} \log \left(\frac{p_0}{2p_0 - p_t} \right)$$

From the given data

t/s	0	360	720
$p/\text{mm Hg}$	35.0	54.0	63.0

$$p_0 = 35.0 \text{ mm Hg.}$$

When $t = 360$ s, $2p_0 - p_t = 2 \times 35.0 - 54.0 = 16.0$

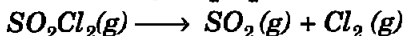
$$\begin{aligned} k_1 &= \frac{2.303}{360 \text{ s}} \log \frac{35}{16} = \frac{2.303}{360} \log 2.1875 \\ &= \frac{2.303 \times 0.3400}{360} \text{ s}^{-1} \\ &= 2.175 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

When $t = 720$ s, $2p_0 - p_t = 2 \times 35.0 - 63 = 7.0$

$$\begin{aligned} k_2 &= \frac{2.303}{720 \text{ s}} \log \frac{35.0}{7.0} = \frac{2.303}{720} \log 5 \\ &= \frac{2.303 \times 0.6990}{720} \\ &= 2.236 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Average } k &= \left(\frac{2.175 + 2.236}{2} \right) \times 10^{-3} \text{ s}^{-1} \\ &= 2.20 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

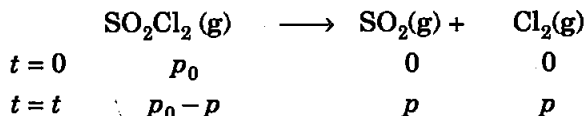
4.21 The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.



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

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

Ans.



when $t = t$, $p_{\text{total}} = p_0 - p + p + p = (p_0 + p)$

Thus, this reaction is similar to the previous question

$$C_0 \propto p_0$$

$$C_t \propto 2p_0 - p_t$$

Since $p_0 = 0.5$ atm and $p_t = 0.6$ atm

$$C_0 \propto 0.5 \text{ atm}$$

$$C_t \propto 2 \times 0.5 - 0.6 \propto 0.4 \text{ atm}$$

$$\begin{aligned} k &= \frac{2.303}{t} \log \frac{C_0}{C_t} \\ &= \frac{2.303}{100 \text{ s}} \log \frac{0.5}{0.4} = \frac{2.303}{100 \text{ s}} \log 1.25 \\ &= \frac{2.303 \times 0.0969}{100} = 2.2316 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

When $p_t = 0.65$ atm

$$C_t = 2p_0 - p_t = 2 \times 0.5 - 0.65 = 0.35 \text{ atm}$$

Since the reaction is of first order

$$\begin{aligned} \text{Rate} &= k p_{\text{SO}_2\text{Cl}_2} = (2.2316 \times 10^{-3} \text{ s}^{-1}) (0.35 \text{ atm}) \\ &= 7.8 \times 10^{-4} \text{ atm s}^{-1}. \end{aligned}$$

4.22 The rate constant for the decomposition of N_2O_5 at various temperatures is given below:

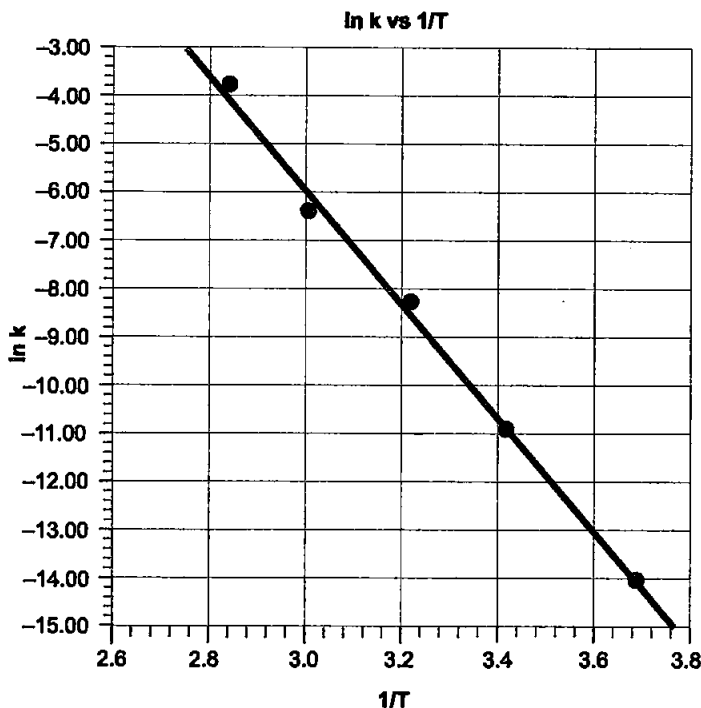
$T/^\circ\text{C}$	0	20	40	60	80
$10^5 \times k/\text{s}^{-1}$	0.0787	1.70	25.7	178	2140

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. From the given data.

$T/^\circ\text{C}$	T/K	$1/T$	k/s^{-1}	$\ln k$
0	273	3.66×10^{-3}	0.787×10^{-5}	-14.055
20	293	3.41×10^{-3}	1.7×10^{-5}	-10.982
40	313	3.20×10^{-3}	25.7×10^{-5}	-8.266
60	333	3.00×10^{-3}	178×10^{-5}	-6.331
80	353	2.83×10^{-3}	2140×10^{-5}	-3.844



From the graph

when $t = 30\text{ }^\circ\text{C}$, $T = 303\text{ K}$, $\frac{1}{T} = 0.0033$ and

$$\ln k = -9.6652$$

$$k \text{ at } 30\text{ }^\circ\text{C} = 6.34 \times 10^{-5}$$

when $t = 50\text{ }^\circ\text{C}$, $T = 323\text{ K}$; $\frac{1}{T} = 0.00310$ and

$$\ln k = -7.2421$$

$$k \text{ at } 50\text{ }^\circ\text{C} = 7.16 \times 10^{-4}$$

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

Ans. According to Arrhenius equation

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

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

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

$$= 179900 \text{ J mol}^{-1}, R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

Putting the values in the equation

$$\log 2.418 \times 10^{-5} \text{ s}^{-1}$$

$$= \log A - \frac{179900 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 546 \text{ K}}$$

$$- 4.6165 \text{ s}^{-1} = \log A - 17.2082$$

$$\log A = 17.2082 - 4.6165 = 12.5917$$

$$A = 3.91 \times 10^{12} \text{ s}^{-1}.$$

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

Ans. From the units of k , the reaction is of first order and its integrated rate law is

$$k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

Given: $k = 2.0 \times 10^{-2} \text{ s}^{-1}$, $t = 100 \text{ s}$, $C_0 = 1.0 \text{ mol L}^{-1}$

Putting these values

$$2.0 \times 10^{-2} \text{ s}^{-1} = \frac{2.303}{100 \text{ s}} \log \left(\frac{1 \text{ mol L}^{-1}}{C_t} \right)$$

$$\log \left(\frac{1 \text{ mol L}^{-1}}{C_t} \right) = \frac{2.0 \times 10^{-2} \text{ s}^{-1} \times 100 \text{ s}}{2.303} = 0.8684$$

$$\frac{1 \text{ mol L}^{-1}}{C_t} = \text{antilog } 0.8684 = 7.3858$$

$$C_t = \frac{1}{7.3858} \text{ mol L}^{-1} = 0.1354 \text{ mol L}^{-1}.$$

4.25 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. The reaction is of 1st order and $t_{1/2} = 3.00$ hour

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

The fraction that remains after 8 hours = $\frac{C_t}{C_0}$

$$k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

$$0.231 \text{ hr}^{-1} = \frac{2.303}{8 \text{ hr}} \log \frac{C_0}{C_t}$$

$$\log \frac{C_0}{C_t} = \frac{0.231 \text{ hr}^{-1} \times 8 \text{ hr}}{2.303} = 0.8024$$

$$\log \frac{C_t}{C_0} = -0.8024$$

$$\frac{C_t}{C_0} = \text{antilog}(-0.8024) = 0.158$$

\therefore Fraction that remains unreacted = 0.158.

4.26 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. The decomposition of hydrocarbons follows the equation

$$k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000 \text{ K}/T} \quad \dots (1)$$

According to Arrhenius equation ... (2)

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

Comparing equations (1) and (2)

$$\frac{E_a}{RT} = \frac{28000 \text{ K}}{T}$$

$$\begin{aligned} E_a &= \frac{28000 \text{ K}}{T} \times RT = 28000 \text{ K} \times R \\ &= 28000 \text{ K} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 232.79 \text{ kJ mol}^{-1}. \end{aligned}$$

4.27 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. The rate constant for first order decomposition of H_2O_2 is given by the relation

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

According to Arrhenius equation $k = A.e^{-E_a/RT}$

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

Comparing the two equations

$$\frac{E_a}{2.303 RT} = \frac{1.24 \times 10^4 \text{ K}}{T}$$

$$E_a = 2.303 \times R \times 1.24 \times 10^4 \text{ K}$$

$$= 2.303 \times (8.134 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1.24 \times 10^4 \text{ K})$$

$$= 237.42 \text{ kJ mol}^{-1}.$$

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

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{256 \times 60 \text{ s}} = 4.51 \times 10^{-5} \text{ s}^{-1}$$

Substituting this value in the given relation

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

$$- 4.3458 = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\text{or } \frac{1.25 \times 10^4 \text{ K}}{T} = 14.34 + 4.3458 = 18.6858$$

$$\text{or } T = \frac{1.25 \times 10^4 \text{ K}}{18.6858} = 668.96 \text{ K} = 669 \text{ K}.$$

4.28 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 60 kJ mol^{-1} . At what temperature would k be $1.5 \times 10^4 \text{ s}^{-1}$?

Ans. According to Arrhenius equation

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

$$\text{or } \frac{1}{T_1} - \frac{1}{T_2} = \frac{2.303 R}{E_a} \times \log \frac{k_2}{k_1}$$

Given: $k_1 = 4.50 \times 10^3 \text{ s}^{-1}$, $T_1 = (10 + 273) = 283 \text{ K}$

$k_2 = 1.5 \times 10^4 \text{ s}^{-1}$; $E_a = 60 \text{ kJ mol}^{-1} = 60000 \text{ J mol}^{-1}$

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Substituting these values

$$\frac{1}{283 \text{ K}} - \frac{1}{T_2} = \frac{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{60000 \text{ J mol}^{-1}} \times \log \frac{1.5 \times 10^4}{4.50 \times 10^3}$$

$$= \frac{2.303 \times 8.314}{60000} \text{ K}^{-1} \times \log 3.33$$

$$= \frac{2.303 \times 8.314 \times 0.5228}{60000} = 1.6684 \times 10^{-4} \text{ K}^{-1}$$

$$\begin{aligned} \text{or } \frac{1}{T_2} &= \frac{1}{283 \text{ K}} - 1.6684 \times 10^{-4} \text{ K}^{-1} \\ &= (3.5336 \times 10^{-3} - 1.6684 \times 10^{-4}) \text{ K}^{-1} \\ &= 0.003367 \text{ K}^{-1} \end{aligned}$$

$$T_2 = \frac{1}{0.003367} = 297 \text{ K} = 297 - 273 = 24 \text{ }^\circ\text{C}.$$

4.29 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. Calculation of E_a

For a first order reaction

$$k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

(i) At 298 K, $k = k_{298 \text{ K}}$, $t = t_1$ and since the reaction is 10% complete, $C_t = (100 - 10) = 90\%$ of C_0 i.e., $0.9 C_0$. Thus

$$\begin{aligned} k_{298 \text{ K}} &= \frac{2.303}{t_1} \log \frac{C_0}{0.9 C_0} = \frac{2.303}{t_2} \log \frac{1}{0.9} \\ &= \frac{2.303}{t_1} \times 0.0458 \end{aligned}$$

$$\text{or } t_1 = \frac{2.303 \times 0.0458}{k_{298 \text{ K}}}$$

(ii) At 308 K; $k = k_{308 \text{ K}}$, $t = t_2$ and since the reaction is 25% complete, $C_t = (100 - 25) = 75\%$ of C_0 i.e. $0.75 C_0$.

Thus,

$$\begin{aligned} k_{308 \text{ K}} &= \frac{2.303}{t_2} \log \frac{C_0}{0.75 C_0} = \frac{2.303}{t_2} \log \frac{1}{0.75} \\ &= \frac{2.303}{t_2} \times 0.1249 \end{aligned}$$

$$\text{or } t_2 = \frac{2.303}{k_{308 \text{ K}}} \times 0.1249$$

Since $t_1 = t_2$, therefore,

$$\frac{2.303 \times 0.0458}{k_{298 \text{ K}}} = \frac{2.303 \times 0.1249}{k_{308 \text{ K}}}$$

$$\frac{k_{308 \text{ K}}}{k_{298 \text{ K}}} = \frac{0.1249}{0.0458} = 2.7271 \text{ and}$$

$$\log \frac{k_{308 \text{ K}}}{k_{298 \text{ K}}} = \log 2.7271 = 0.4357$$

According to Arrhenius equation

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

$$k_1 = k_{298 \text{ K}}, k_2 = k_{308 \text{ K}}, T_1 = 298 \text{ K}, T_2 = 308 \text{ K}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Putting these values in Arrhenius equation

$$\log \frac{k_{308 \text{ K}}}{k_{298 \text{ K}}} = \frac{E_a}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left[\frac{(308 - 298) \text{ K}}{298 \text{ K} \times 308 \text{ K}} \right]$$

$$0.4357 = \frac{E_a}{19.147 \text{ J K}^{-1} \text{ mol}^{-1}} \left[\frac{10}{298 \times 308 \text{ K}} \right]$$

$$E_a = \frac{0.4357 \times 19.1471 \times 298 \times 308}{10} \text{ J mol}^{-1}$$

$$= 76569.8 \text{ J mol}^{-1} = 76.57 \text{ kJ mol}^{-1}$$

Calculation of k at 318 K

According to Arrhenius equation

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

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

$$\text{Given: } T = 318 \text{ K}, E_a \text{ (calculated)} = 76569.8 \text{ J mol}^{-1}$$

$$A = 4 \times 10^{10} \text{ s}^{-1}, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\therefore \log k$$

$$= \log 4 \times 10^{10} - \frac{76569.8 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 318 \text{ K}}$$

$$= 10.6021 - 12.5755 = -1.9734$$

$$\log k = \bar{2}.0266$$

$$k = 0.01063 = 1.063 \times 10^{-2} \text{ s}^{-1}.$$

4.30 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.

Ans. Since the rate quadruples when temperature changes from 298 K to 313 K

$$k_2 = 4k_1$$

$$T_1 = 293 \text{ K and } T_2 = 313 \text{ K}$$

According to logarithmic form of Arrhenius equation

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

Putting the values

$$\begin{aligned} \log \frac{4k_1}{k_1} &= \frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left[\frac{(313 - 293) \text{ K}}{293 \text{ K} \times 313 \text{ K}} \right] \\ &= \frac{E_a \times 20}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 293 \text{ K} \times 313 \text{ K}} \end{aligned}$$

$$\therefore \log 4 = 0.6021$$

$$\begin{aligned} \therefore E_a &= \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20} \text{ J mol}^{-1} \\ &= 52863.3 \text{ J mol}^{-1} \\ &= 52.86 \text{ kJ mol}^{-1} \end{aligned}$$

□□□