

CHAPTER 3 CHEMICAL KINETICS

INTEXT QUESTIONS

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Question 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.

Solution :

$$\text{Average rate of reaction } r_{\text{av}} = \frac{-\Delta R}{\Delta t} = \frac{\Delta [P]}{\Delta t}$$

$$= \frac{(0.03 - 0.02) \text{ M}}{25 \times 60 \text{ sec}}$$

$$= \frac{0.01 \text{ M}}{25 \times 60 \text{ s}} = 6.66 \text{ M s}^{-1}$$

$$= 6.67 \times 10^{-6} \text{ M s}^{-1}$$

Question 2. In a reaction, $2A \rightarrow \text{Products}$, the 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?

Solution :

$$\text{Average rate} = -\frac{1}{2} \frac{\Delta [A]}{\Delta t}$$

$$= -\frac{1}{2} \frac{[A]_2 - [A]_1}{t_2 - t_1}$$

$$= -\frac{1}{2} \frac{0.4 - 0.5}{10}$$

$$= -\frac{1}{2} \frac{-0.1}{10}$$

$$= 0.005 \text{ mol L}^{-1} \text{ min}^{-1}$$

$$= 5 \times 10^{-3} \text{ M min}^{-1}$$

$$= 0.005 \text{ mol L}^{-1} \text{ min}^{-1}$$

$$= 5 \times 10^{-3} \text{ M min}^{-1}$$

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

Solution :

The order of the reaction $r = k [A]^{1/2} [B]^2$

$$= 1/2 + 2$$

$$= 2.5$$

Question 4. 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?

Solution :

The reaction $X \rightarrow Y$ follows second order kinetics.

Therefore, the rate equation for this reaction will be:

$$\text{Rate} = k[X]^{2(1)}$$

Let $[X] = a \text{ mol L}^{-1}$, then equation (1) can be written as:

$$\text{Rate}_1 = k \cdot (a)^2$$

$$= ka^2$$

If the concentration of X is increased to three times, then $[X] = 3a \text{ mol L}^{-1}$

Now, the rate equation will be:

$$\text{Rate} = k (3a)^2$$

$$= 9(ka^2)$$

Hence, the rate of formation will increase by 9 times.

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

Solution :

From the question, we can write down the following information:

Initial amount = 5 g

Final concentration = 3 g

Rate constant = $1.15 \times 10^{-3} \text{ s}^{-1}$

We know that for a 1st order reaction,

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

$$= \frac{2.303}{1.15 \times 10^{-3}} \log \frac{5}{3}$$

$$= \frac{2.303}{1.15 \times 10^{-3}} \times 0.2219$$

$$= 444.38 \text{ s}$$

$$= 444 \text{ s (approx)}$$

Question 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.

Solution :

We know that for a 1st order reaction,

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

It is given that $t_{1/2} = 60$ min

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

$$= 0.693 / 60$$

$$= 0.01155 \text{ min}^{-1}$$

$$= 1.155 \text{ min}^{-1}$$

Or

$$k = 1.925 \times 10^{-2} \text{ s}^{-1}$$

INTEXT QUESTIONS

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

Solution

:

The rate constant of a reaction is nearly doubled with a 10° rise in temperature. However, the exact dependence of the rate of a chemical reaction on temperature is given by Arrhenius equation,

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

Where,

A is the Arrhenius factor or the frequency factor

T is the temperature

R is the gas constant

E_a is the activation energy

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

Solution

It is given that $T_1 = 298$ K

$$\therefore T_2 = (298 + 10) \text{ K}$$

$$= 308 \text{ K}$$

We also know that the rate of the reaction doubles when temperature is increased by 10° .

Therefore, let us take the value of $k_1 = k$ and that of $k_2 = 2k$

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

Now, substituting these values in the equation:

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

We get:

$$\log \frac{2k}{k} = \frac{E_a}{2.303 \times 8.314} \left[\frac{10}{298 \times 308} \right]$$

$$\Rightarrow \log 2 = \frac{E_a}{2.303 \times 8.314} \left[\frac{10}{298 \times 308} \right]$$

$$\Rightarrow E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2}{10}$$

$$= 52897.78 \text{ J mol}^{-1}$$

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

Question 9. The activation energy for the reaction $2\text{HI}_{(g)} \rightarrow \text{H}_2 + \text{I}_{2(g)}$ is $209.5 \text{ kJ mol}^{-1}$ at 581K . Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Solution

In the given case:

$$E_a = 209.5 \text{ kJ mol}^{-1} = 209500 \text{ J mol}^{-1}$$

$$T = 581 \text{ K}$$

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

Now, the fraction of molecules of reactants having energy equal to or greater than activation energy is given as:

$$x = e^{-E_a / RT}$$

$$\Rightarrow \ln x = -E_a / RT$$

$$\Rightarrow \log x = -E_a / 2.303RT$$

$$\Rightarrow \log x = -209500 \text{ J mol}^{-1} / 2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 581$$

$$= -18.8323$$

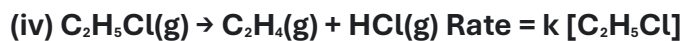
$$\text{Now, } x = \text{Antilog}(-18.8323)$$

$$= 1.471 \times 10^{-19}$$

EXERCISES

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



Solution

:

(i) Given rate = $k [\text{NO}]^2$

Therefore, order of the reaction = 2

Dimension of $k = \text{Rate} / [\text{NO}]^2$

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

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

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

(ii) Given rate = $k [\text{H}_2\text{O}_2] [\text{I}^-]$

Therefore, order of the reaction = 2

Dimension of

$$k = \text{Rate} / [\text{H}_2\text{O}_2][\text{I}^-]$$

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

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

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

Therefore, order of reaction = 3 / 2

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

$$= \text{mol L}^{-1} \text{s}^{-1} / (\text{mol L}^{-1})^{3/2}$$

$$= \text{mol L}^{-1} \text{s}^{-1} / \text{mol}^{3/2} \text{L}^{-3/2}$$

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

(iv) Given rate = $k [\text{C}_2\text{H}_5\text{Cl}]$

Therefore, order of the reaction = 1

Dimension of $k = \text{Rate} / [\text{C}_2\text{H}_5\text{Cl}]$

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

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

Question 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} .

Solution

:

The initial rate of the reaction is

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

$$= (2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}) (0.1 \text{ mol L}^{-1}) (0.2 \text{ mol L}^{-1})^2$$

$$= 8.0 \times 10^{-9} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

When $[\text{A}]$ is reduced from 0.1 mol L^{-1} to 0.06 mol L^{-1} , the concentration of A reacted = $(0.1 - 0.06) \text{ mol L}^{-1} = 0.04 \text{ mol L}^{-1}$

Therefore, concentration of B reacted $1/2 \times 0.04 \text{ mol L}^{-1} = 0.02 \text{ mol L}^{-1}$

Then, concentration of B available, $[\text{B}] = (0.2 - 0.02) \text{ mol L}^{-1}$

$$= 0.18 \text{ mol L}^{-1}$$

After $[\text{A}]$ is reduced to 0.06 mol L^{-1} , the rate of the reaction is given by,

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

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

$$= 3.89 \text{ mol L}^{-1} \text{ s}^{-1}$$

Question 3. The decomposition of NH₃ on platinum surface is zero order reaction. What are the rates of production of N₂ and H₂ if k = 2.5 × 10⁻⁴ mol⁻¹ L s⁻¹?

Solution

The decomposition of NH₃ on platinum surface is represented by the following equation.



Therefore,

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

However, it is given that the reaction is of zero order.

Therefore,

$$\begin{aligned} -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} &= \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = k \\ &= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

Therefore, the rate of production of N₂ is

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

And, the rate of production of H₂ is

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

$$= 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Question 4. The decomposition of dimethyl ether leads to the formation of CH₄, H₂ 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.,

$$\text{rate} = k (P_{\text{CH}_3\text{OCH}_3})^{3/2}$$

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

Solution :

If pressure is measured in bar and time in minutes, then

Unit of rate = bar min⁻¹

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

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

Therefore, unit of rate constants(k) = bar min⁻¹ / bar^{3/2}

$$= \text{bar}^{-1/2} \text{ min}^{-1}$$

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

Solution :

The factors that affect the rate of a reaction are as follows.

(i) Concentration of reactants (pressure in case of gases)

(ii) Temperature

(iii) Presence of a catalyst

Question 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?

Solution :

Let the concentration of the reactant be [A] = a

Rate of reaction, R = k [A]²

$$= ka^2$$

(i) If the concentration of the reactant is doubled, i.e. $[A] = 2a$, then the rate of the reaction would be

$$R = k(2a)^2$$

$$= 4ka^2$$

$$= 4R$$

Therefore, the rate of the reaction would increase by 4 times.

(ii) If the concentration of the reactant is reduced to half, i.e. $[A] = 1/2 a$, then the rate of the reaction would be

$$R = k(1/2a)^2$$

$$= 1/4 Ka^2$$

$$= 1/4 R$$

Therefore, the rate of the reaction would be reduced to

Question 7. What change would happen in the rate constant of a reaction when there is a change in its temperature? How can this temperature effect on rate constant be represented quantitatively?

Solution

:

When a temperature of 10° rises for a chemical reaction then the rate constant increases and becomes near to double of its original value.

The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation,

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

Where,

k = rate constant,

A = Frequency factor / Arrhenius factor,

R = gas constant

T = temperature

E_a = activation energy for the reaction.

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

t/s	0	30	60	90
[Ester]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.

Solution

:

(i) Average rate of reaction between the time interval, 30 to 60 seconds, d[ester] / dt

$$= (0.31 - 0.17) / (60 - 30)$$

$$= 0.14 / 30$$

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

(ii) For a pseudo first order reaction,

$$k = 2.303 / t \log [R]^0 / [R]$$

For t = 30 s, k₁

$$= 1.911 \times 10^{-2} \text{ s}^{-1}$$

For t = 60 s, k₁ = 2.303 / 30 log 0.55 / 0.31

$$= 1.957 \times 10^{-2} \text{ s}^{-1}$$

For t = 90 s, k₃ = 2.303 / 90 log 0.55 / 0.085

$$= 2.075 \times 10^{-2} \text{ s}^{-1}$$

$$= 2.075 \times 10^{-2} \text{ s}^{-1}$$

Then, average rate constant, $k = k_1 + k_2 + k_3 / 3$

$$= 1.911 \times 10^{-2} + 1.957 \times 10^{-2} + 2.075 \times 10^{-2/3}$$

$$= 1.981 \times 10^{-2} \text{ s}^{-1}$$

Question 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?

Solution

(i) The differential rate equation will be

(i) The differential rate equation will be

$$-\frac{d[R]}{dt} = k[A][B]^2$$

(ii) If the concentration of B is increased three times, then

$$\begin{aligned} -\frac{d[R]}{dt} &= k[A][3B]^2 \\ &= 9 \cdot k[A][B]^2 \end{aligned}$$

Therefore, the rate of reaction will increase 9 times.

(iii) When the concentrations of both A and B are doubled,

$$\begin{aligned} -\frac{d[R]}{dt} &= k[A][B]^2 \\ &= k[2A][2B]^2 \\ &= 8 \cdot k[A][B]^2 \end{aligned}$$

Therefore, the rate of reaction will increase 8 times.

Question 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 the reaction with respect to A and B?

Solution

Let the order of the reaction with respect to A be x and with respect to B be y .

Therefore,

$$r_0 = k[A]^x [B]^y$$

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

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

$$1.43 \times 10^{-4} = k[0.40]^x [0.05]^y \quad \text{(iii)}$$

Dividing equation (i) by (ii), we obtain

$$\frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{k[0.20]^x [0.30]^y}{k[0.20]^x [0.10]^y}$$

$$\Rightarrow 1 = \frac{[0.30]^y}{[0.10]^y}$$

$$\Rightarrow \left(\frac{0.30}{0.10}\right)^0 = \left(\frac{0.30}{0.10}\right)^y$$

$$\Rightarrow y = 0$$

Dividing equation (iii) by (ii), we obtain

$$\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{k[0.40]^x [0.05]^y}{k[0.20]^x [0.30]^y}$$

$$\Rightarrow \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{[0.40]^x}{[0.20]^x} \quad \left[\begin{array}{l} \text{Since } y = 0, \\ [0.05]^y = [0.30]^y = 1 \end{array} \right]$$

$$\Rightarrow 2.821 = 2^x$$

$$\Rightarrow \log 2.821 = x \log 2 \quad \text{(Taking log on both sides)}$$

$$\Rightarrow x = \frac{\log 2.821}{\log 2}$$

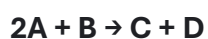
Dividing equation (iii) by (ii), we obtain

$$= 1.496$$

$$= 1.5 \text{ (approximately)}$$

Hence, the order of the reaction with respect to A is 1.5 and with respect to B is zero.

Question 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.

Solution

Let the order of the reaction with respect to A be x and with respect to B be y.

Therefore, rate of the reaction is given by,

Let the order of the reaction with respect to A be x and with respect to B be y .

Therefore, rate of the reaction is given by,

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

According to the question,

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

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

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

$$2.40 \times 10^{-2} = k[0.4]^x [0.1]^y \quad (\text{iv})$$

Dividing equation (iv) by (i), we obtain

$$\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k[0.4]^x [0.1]^y}{k[0.1]^x [0.1]^y}$$

$$\Rightarrow 4 = \frac{[0.4]^x}{[0.1]^x}$$

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

$$\Rightarrow (4)^1 = 4^x$$

$$\Rightarrow x = 1$$

Dividing equation (ii) by (i), we obtain

Dividing equation (iv) by (i), we obtain

Let the order of the reaction with respect to A be x and with respect to B be y .

Therefore, rate of the reaction is given by,

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

According to the question,

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

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

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

$$2.40 \times 10^{-2} = k[0.4]^x [0.1]^y \quad (\text{iv})$$

Dividing equation (iv) by (i), we obtain

$$\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k[0.4]^x [0.1]^y}{k[0.1]^x [0.1]^y}$$

$$\Rightarrow 4 = \frac{[0.4]^x}{[0.1]^x}$$

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

$$\Rightarrow (4)^1 = 4^x$$

$$\Rightarrow x = 1$$

Dividing equation (ii) by (i), we obtain

Dividing equation (iii) by (ii), we obtain

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \frac{k[0.3]^x [0.4]^y}{k[0.3]^x [0.2]^y}$$

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

$$\Rightarrow 4 = 2^y$$

$$\Rightarrow 2^2 = 2^y$$

$$\Rightarrow y = 2$$

Therefore, the rate law is

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

\Rightarrow

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

From experiment I, we obtain

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

From experiment II, we obtain

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

From experiment III, we obtain

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

From experiment IV, we obtain

$$k = \frac{2.40 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.4 \text{ mol L}^{-1})(0.1 \text{ mol L}^{-1})^2}$$
$$= 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

Therefore, rate constant, $k = 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$

Question 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}

Solution

The given reaction is of the first order with respect to A and of zero order with respect to B.

Therefore, the rate of the reaction is given by,

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

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

From experiment I, we obtain

$$2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} = k (0.1 \text{ mol L}^{-1})$$

$$\Rightarrow k = 0.2 \text{ min}^{-1}$$

From experiment II, we obtain

$$4.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} = 0.2 \text{ min}^{-1} [A]$$

$$\Rightarrow [A] = 0.2 \text{ mol L}^{-1}$$

From experiment III, we obtain

$$\text{Rate} = 0.2 \text{ min}^{-1} \times 0.4 \text{ mol L}^{-1}$$

$$= 0.08 \text{ mol L}^{-1} \text{ min}^{-1}$$

From experiment IV, we obtain

$$2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} = 0.2 \text{ min}^{-1} [A]$$

$$\Rightarrow [A] = 0.1 \text{ mol L}^{-1}$$

Question 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

Solution

:

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

$$= 0.693 / 200 \text{ s}^{-1}$$

$$= 3.47 \times 10^{-3} \text{ s (approximately)}$$

$$\text{(ii) Half life, } t_{1/2} = 0.693 / k$$

$$= 0.693 / 2 \text{ min}^{-1}$$

$$= 0.35 \text{ min (approximately)}$$

$$\text{(iii) Half life, } t_{1/2} = 0.693 / k$$

$$= 0.693 / 4 \text{ years}^{-1}$$

$$= 0.173 \text{ years (approximately)}$$

Question 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.

Solution

$$\text{Here, } k = 0.693 / t_{1/2}$$

$$= 0.693 / 5730 \text{ years}^{-1}$$

It is known that,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$
$$= \frac{2.303}{\frac{0.693}{5730}} \log \frac{100}{80}$$

$$= 1845 \text{ years (approximately)}$$

Hence, the age of the sample is 1845 years.

Question 15. The experimental data for decomposition of N_2O_5

$[\text{2N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2]$ in gas phase at 318K 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 3	1.36 6	1.14 4	0.93	0.78	0.64	0.53	0.43	0.35

(i) Plot $[\text{N}_2\text{O}_5]$ against t.

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

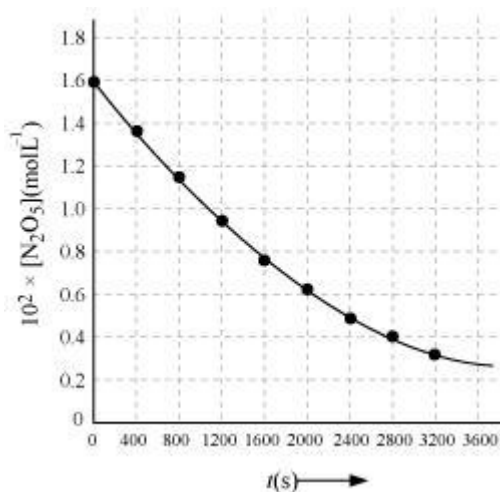
(iii) Draw a graph between $\log [\text{N}_2\text{O}_5]$ and t.

(iv) What is the rate law?

(v) Calculate the rate constant.

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

Solution

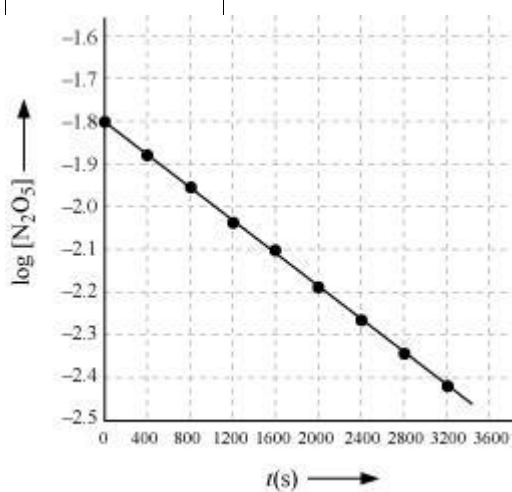


(ii) Time corresponding to the concentration, $1630 \times 10^2 / 2 \text{ mol L}^{-1} = 81.5 \text{ mol L}^{-1}$ is the half life. From the graph, the half life is obtained as 1450 s.

(iii)

t(s)	$10^2 \times [\text{N}_2\text{O}_5] \text{ mol L}^{-1}$	$\text{Log}[\text{N}_2\text{O}_5]$
0	1.63	- 1.79
400	1.36	- 1.87

800	1.14	- 1.94
1200	0.93	- 2.03
1600	0.78	- 2.11
2000	0.64	- 2.19
2400	0.53	- 2.28
2800	0.43	- 2.37
3200	0.35	- 2.46



(iv) The given reaction is of the first order as the plot, $\text{Log}[N_2O_5]$ v/s t , is a straight line. Therefore, the rate law of the reaction is

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

(v) From the plot, $\text{Log}[N_2O_5]$ v/s t , we obtain

$$-k / 2.303$$

Again, slope of the line of the plot $\text{Log}[N_2O_5]$ v/s t is given by

$$-k / 2.303. = -0.67 / 3200$$

Therefore, we obtain,

$$-k / 2.303 = -0.67 / 3200$$

$$\Rightarrow k = 4.82 \times 10^{-4} \text{ s}^{-1}$$

(vi) Half-life is given by,

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

$$= 0.693 / 4.82 \times 10^{-4} \text{ s}$$

$$= 1.438 \times 10^3$$

This value, 1438 s, is very close to the value that was obtained from the graph.

Question 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?

Solution

:

It is known that,

It is known that,

$$\begin{aligned} t &= \frac{2.303}{k} \log \frac{[R]_0}{[R]} \\ &= \frac{2.303}{60 \text{ s}^{-1}} \log \frac{1}{1/16} \\ &= \frac{2.303}{60 \text{ s}^{-1}} \log 16 \\ &= 4.6 \times 10^{-2} \text{ s (approximately)} \end{aligned}$$

Hence, the required time is $4.6 \times 10^{-2} \text{ s}$.

Question 17. During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. 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.

Solution :

$$\text{Here, } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} \text{ y}^{-1}$$

It is known that,

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

$$\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$

$$\Rightarrow 10 = \frac{2.303}{0.693} (-\log [R])$$

$$\Rightarrow \log [R] = -\frac{10 \times 0.693}{2.303 \times 28.1}$$

$$\Rightarrow [R] = \text{antilog} (-0.1071)$$

$$= \text{antilog} (\bar{1}.8929)$$

$$= 0.7814 \mu\text{g}$$

Therefore, 0.7814 μg of ^{90}Sr will remain after 10 years.

Again,

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

$$\Rightarrow 60 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$

$$\Rightarrow \log [R] = -\frac{60 \times 0.693}{2.303 \times 28.1}$$

$$\Rightarrow [R] = \text{antilog} (-0.6425)$$

$$= \text{antilog} (\bar{1}.3575)$$

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

Therefore, 0.2278 μg of ^{90}Sr will remain after 60 years.

Question 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.

Solution

:

For a first order reaction, the time required for 99% completion is

$$t_1 = 2.303/k \text{ Log } 100/100-99$$

$$= 2.303/k \text{ Log } 100$$

$$= 2 \times 2.303/k$$

For a first order reaction, the time required for 90% completion is

$$t_2 = 2.303/k \text{ Log } 100 / 100-90$$

$$= 2.303/k \text{ Log } 10$$

$$= 2.303/k$$

Therefore, $t_1 = 2t_2$

Hence, the time required for 99% completion of a first order reaction is twice the time required for the completion of 90% of the reaction.

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

Solution

:

For a first order reaction,

$$t = 2.303/k \text{ Log } [R]^0 / [R]$$

$$k = 2.303/40\text{min} \text{ Log } 100 / 100-30$$

$$= 2.303/40\text{min} \text{ Log } 10 / 7$$

$$= 8.918 \times 10^{-3} \text{ min}^{-1}$$

Therefore, $t_{1/2}$ of the decomposition reaction is

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

$$= 0.693 / 8.918 \times 10^{-3} \text{ min}$$

$$= 77.7 \text{ min (approximately)}$$

= 77.7 min (approximately)

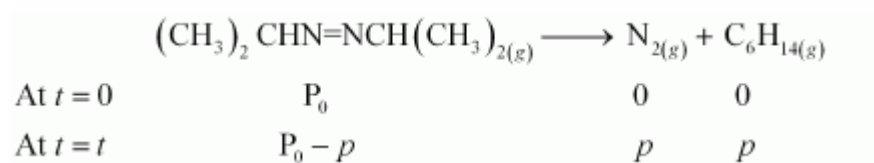
Question 20. For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

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

Calculate the rate constant.

Solution

The decomposition of azoisopropane to hexane and nitrogen at 543 K is represented by the following equation.



After time, t , total pressure, $P_t = (P_0 - p) + p + p$

$$\Rightarrow P_t = (P_0 + p)$$

$$\Rightarrow p = P_t - P_0$$

therefore, $P_0 - p = P_0 - P_t + P_0$

$$= 2P_0 - P_t$$

For a first order reaction,

$$k = 2.303/t \log P_0 / P_0 - p$$

$$= 2.303/t \log P_0 / 2P_0 - P_t$$

When $t = 360$ s, $k = 2.303 / 360\text{s} \log 35.0 / 2 \times 35.0 - 54.0$

$$= 2.175 \times 10^{-3} \text{ s}^{-1}$$

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

$$= 2.235 \times 10^{-3} \text{ s}^{-1}$$

Hence, the average value of rate constant is

$$k = (2.175 \times 10^{-3} + 2.235 \times 10^{-3}) / 2 \text{ s}^{-1}$$

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

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

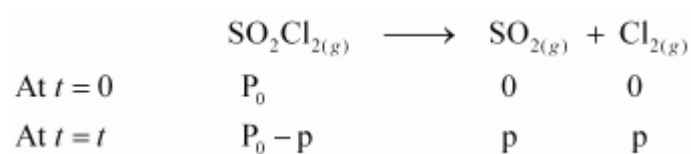


Experiment	Time/s ⁻¹	Total pressure/atm
1	0	0.5
2	100	0.6

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

Solution

The thermal decomposition of SO_2Cl_2 at a constant volume is represented by the following equation.



After time, t , total pressure, $P_t = (P_0 - p) + p + p$

$$\Rightarrow P_t = (P_0 + p)$$

$$\Rightarrow p = P_t - P_0$$

therefore, $P_0 - p = P_0 - P_t + P_0$

$$= 2 P_0 - P_t$$

For a first order reaction,

$$k = 2.303/t \log P_0 / P_0 - p$$

$$= 2.303/t \log P_0 / 2 P_0 - P_t$$

When $t = 100$ s,

$$k = 2.303 / 100s \log 0.5 / 2 \times 0.5 - 0.6$$

$$= 2.231 \times 10^{-3} s^{-1}$$

When $P_t = 0.65$ atm,

$$P_0 + p = 0.65$$

$$\Rightarrow p = 0.65 - P_0$$

$$= 0.65 - 0.5$$

$$= 0.15 \text{ atm}$$

Therefore, when the total pressure is 0.65 atm, pressure of SOCl_2 is

$$p_{\text{SOCl}_2} = P_0 - p$$

$$= 0.5 - 0.15$$

$$= 0.35 \text{ atm}$$

Therefore, the rate of equation, when total pressure is 0.65 atm, is given by,

$$\text{Rate} = k(p_{\text{SOCl}_2})$$

$$= (2.23 \times 10^{-3} s^{-1}) (0.35 \text{ atm})$$

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

Question 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

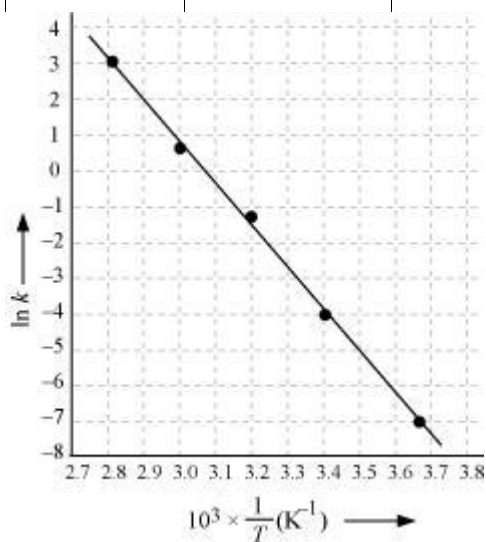
Draw a graph between $\ln k$ and $1/T$ and calculate the values of A and E_a .

Predict the rate constant at 30° and $50^\circ C$.

Solution :

From the given data, we obtain

T/°C	0	20	40	60	80
T/K	273	293	313	333	353
$1/T / k^{-1}$	3.66×10^{-3}	3.41×10^{-3}	3.19×10^{-3}	3.0×10^{-3}	2.83×10^{-3}
$10^5 \times k / S^{-1}$	0.0787	1.70	25.7	178	2140
$\ln k$	-7.147	-4.075	-1.359	-0.577	3.063



Slope of the line,

$$\frac{y_2 - y_1}{x_2 - x_1} = -12.301 \text{ K}$$

According to Arrhenius equation,

$$\text{Slope} = -\frac{E_a}{R}$$

$$\Rightarrow E_a = -\text{Slope} \times R$$

$$= -(-12.301 \text{ K}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= 102.27 \text{ kJ mol}^{-1}$$

Again,

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

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

When $T = 273 \text{ K}$,

$$\ln k = -7.147$$

$$\begin{aligned} \text{Then, } \ln A &= -7.147 + \frac{102.27 \times 10^3}{8.314 \times 273} \\ &= 37.911 \end{aligned}$$

Therefore, $A = 2.91 \times 10^6$

When $T = 30 + 273 \text{ K} = 303 \text{ K}$,

$$\frac{1}{T} = 0.0033 \text{ K} = 3.3 \times 10^{-3} \text{ K}$$

Then, at $\frac{1}{T} = 3.3 \times 10^{-3} \text{ K}$,

$$\ln k = -2.8$$

Therefore, $k = 6.08 \times 10^{-2} \text{ s}^{-1}$

Again when $T = 50 + 273 \text{ K} = 323 \text{ K}$,

$$1/T = 3.1 \times 10^{-3} \text{ K}$$

$$\ln k = -0.5$$

Therefore, $k = 0.607 \text{ s}^{-1}$

Question 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.

Solution :

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

$$T = 546 \text{ K}$$

$$E_a = 179.9 \text{ kJ mol}^{-1} = 179.9 \times 10^3 \text{ J mol}^{-1}$$

According to the Arrhenius equation,

$$\begin{aligned}
 k &= Ae^{-E_a/RT} \\
 \Rightarrow \ln k &= \ln A - \frac{E_a}{RT} \\
 \Rightarrow \log k &= \log A - \frac{E_a}{2.303 RT} \\
 \Rightarrow \log A &= \log k + \frac{E_a}{2.303 RT} \\
 &= \log(2.418 \times 10^{-5} \text{ s}^{-1}) + \frac{179.9 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 546 \text{ K}}
 \end{aligned}$$

$$= (0.3835 - 5) + 17.2082$$

$$= 12.5917$$

Therefore, $A = \text{antilog}(12.5917)$

$$= 3.9 \times 10^{12} \text{ s}^{-1} \text{ (approximately)}$$

Question 24. Consider a certain reaction $A \rightarrow \text{Products}$ 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} .

Solution :

$$k = 2.0 \times 10^{-2} \text{ s}^{-1}$$

$$T = 100 \text{ s}$$

$$[A]_0 = 1.0 \text{ mol L}^{-1}$$

Since the unit of k is s^{-1} , the given reaction is a first order reaction.

$$\text{Therefore, } k = 2.303/t \text{ Log } [A]^0 / [A]$$

$$\Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} = 2.303/100\text{s} \text{ Log } 1.0 / [A]$$

$$\Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} = 2.303/100\text{s} (- \text{Log } [A])$$

$$\Rightarrow - \text{Log } [A] = - (2.0 \times 10^{-2} \times 100) / 2.303$$

$$\Rightarrow [A] = \text{antilog } [- (2.0 \times 10^{-2} \times 100) / 2.303]$$

$$= 0.135 \text{ mol L}^{-1} \text{ (approximately)}$$

Hence, the remaining concentration of A is 0.135 mol L^{-1} .

Question 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?

Solution : For a first order reaction,

$$k = 2.303/t \text{ Log } [R]^0 / [R]$$

It is given that, $t_{1/2} = 3.00$ hours

$$\text{Therefore, } k = 0.693 / t_{1/2}$$

$$= 0.693 / 3 \text{ h}^{-1}$$

$$= 0.231 \text{ h}^{-1}$$

$$\text{Then, } 0.231 \text{ h}^{-1} = 2.303 / 8\text{h} \text{ Log } [R]^0 / [R]$$

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

$$\Rightarrow \frac{[R]_0}{[R]} = \text{antilog}(0.8024)$$

$$\Rightarrow \frac{[R]_0}{[R]} = 6.3445$$

$$\Rightarrow \frac{[R]}{[R]_0} = 0.1576 \text{ (approx)}$$

$$= 0.158$$

Hence, the fraction of sample of sucrose that remains after 8 hours is 0.158.

Question 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 .

Solution

The given equation is

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

Arrhenius equation is given by,

$$k = Ae^{-E_a/RT} \text{ (ii)}$$

From equation (i) and (ii), we obtain

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

$$\Rightarrow E_a = R \times 28000 \text{ K}$$

$$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 28000 \text{ K}$$

$$= 232792 \text{ J mol}^{-1}$$

$$= 232.792 \text{ kJ mol}^{-1}$$

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

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

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

Solution

Arrhenius equation is given by,

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

$$\Rightarrow \ln k = \ln A - E_a/RT$$

$$\Rightarrow \ln k = \log A - E_a/RT$$

$$\Rightarrow \log k = \log A - E_a/2.303RT \quad (i)$$

The given equation is

$$\log k = 14.34 - 1.25 \times 10^4 K/T \quad (ii)$$

From equation (i) and (ii), we obtain

$$E_a/2.303RT = 1.25 \times 10^4 K/T$$

$$= 1.25 \times 10^4 K \times 2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 239339.3 \text{ J mol}^{-1} \text{ (approximately)}$$

$$= 239.34 \text{ kJ mol}^{-1}$$

Also, when $t_{1/2} = 256$ minutes,

$$k = 0.693 / t^{1/2}$$

$$= 0.693 / 256$$

$$= 2.707 \times 10^{-3} \text{ min}^{-1}$$

$$= 4.51 \times 10^{-5} \text{ s}^{-1}$$

$$= 2.707 \times 10^{-3} \text{ min}^{-1}$$

$$= 4.51 \times 10^{-5} \text{ s}^{-1}$$

It is also given that, $\log k = 14.34 - 1.25 \times 10^4 \text{ K}/T$

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

$$\Rightarrow \log(0.654 - 05) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\Rightarrow \frac{1.25 \times 10^4 \text{ K}}{T} = 18.686$$

$$\Rightarrow T = \frac{1.25 \times 10^4 \text{ K}}{18.686}$$

$$= 668.95 \text{ K}$$

$$= 669 \text{ K (approximately)}$$

Question 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 $1.5 \times 10^4 \text{ s}^{-1}$?

Solution

:

From Arrhenius equation, we obtain

$$\log k_2/k_1 = E_a / 2.303 R (T_2 - T_1) / T_1 T_2$$

$$\text{Also, } k_1 = 4.5 \times 10^3 \text{ s}^{-1}$$

$$T_1 = 273 + 10 = 283 \text{ K}$$

$$k_2 = 1.5 \times 10^4 \text{ s}^{-1}$$

$$E_a = 60 \text{ kJ mol}^{-1} = 6.0 \times 10^4 \text{ J mol}^{-1}$$

Then,

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{6.0 \times 10^4 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{T_2 - 283}{283 T_2} \right)$$

$$\Rightarrow 0.5229 = 3133.627 \left(\frac{T_2 - 283}{283 T_2} \right)$$

$$\Rightarrow \frac{0.5229 \times 283 T_2}{3133.627} = T_2 - 283$$

$$\Rightarrow 0.0472 T_2 = T_2 - 283$$

$$\Rightarrow 0.9528 T_2 = 283$$

$$\Rightarrow T_2 = 297.019 \text{ K (approximately)}$$

$$= 297 \text{ K}$$

$$= 24^\circ\text{C}$$

Hence, k would be $1.5 \times 10^4 \text{ s}^{-1}$ at 24°C .

Question 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 .

Solution

:

For a first order reaction,

$$t = 2.303 / k \log a / a - x$$

$$\text{At } 298 \text{ K, } t = 2.303 / k \log 100 / 90$$

$$= 0.1054 / k$$

$$\text{At } 308 \text{ K, } t' = 2.303 / k' \log 100 / 75$$

$$= 2.2877 / k'$$

According to the question,

$$t = t'$$

$$\Rightarrow 0.1054 / k = 2.2877 / k'$$

$$\Rightarrow k' / k = 2.7296$$

From Arrhenius equation, we obtain

$$\begin{aligned}\log \frac{k'}{k} &= \frac{E_a}{2.303 R} \left(\frac{T' - T}{TT'} \right) \\ \log(2.7296) &= \frac{E_a}{2.303 \times 8.314} \left(\frac{308 - 298}{298 \times 308} \right) \\ E_a &= \frac{2.303 \times 8.314 \times 298 \times 308 \times \log(2.7296)}{308 - 298} \\ &= 76640.096 \text{ J mol}^{-1} \\ &= 76.64 \text{ kJ mol}^{-1}\end{aligned}$$

To calculate k at 318 K,

It is given that, $A = 4 \times 10^{10} \text{ s}^{-1}$, $T = 318 \text{ K}$

Again, from Arrhenius equation, we obtain

$$\begin{aligned}\log k &= \log A - \frac{E_a}{2.303 R T} \\ &= \log(4 \times 10^{10}) - \frac{76.64 \times 10^3}{2.303 \times 8.314 \times 318} \\ &= (0.6021 + 10) - 12.5876 \\ &= -1.9855\end{aligned}$$

Therefore, $k = \text{Antilog}(-1.9855)$

$$= 1.034 \times 10^{-2} \text{ s}^{-1}$$

Question 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.

Solution

:

From Arrhenius equation, we obtain

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

It is given that, $k_2 = 4k_1$

$$T_1 = 293 \text{ K}$$

$$T_2 = 313 \text{ K}$$

$$\text{Therefore, } \log \frac{4k_1}{k_1} = \frac{E_a}{2.303 \times 8.314} \left(\frac{313 - 293}{293 \times 313} \right)$$

$$\Rightarrow 0.6021 = \frac{20 \times E_a}{2.303 \times 8.314 \times 293 \times 313}$$

$$\Rightarrow E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20}$$

$$= 52863.33 \text{ J mol}^{-1}$$

$$= 52.86 \text{ kJ mol}^{-1}$$

Hence, the required energy of activation is $52.86 \text{ kJ mol}^{-1}$.