Question 4.1:

For the reaction R → 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.

Answer

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

$$= -\frac{[R]_2 - [R]_1}{t_2 - t_1}$$

$$= -\frac{0.02 - 0.03}{25}\ M\ min^{-1}$$

$$= -\frac{-0.01}{25} M\ min^{-1}$$

$$= 4 \times 10^{-4}\ M\ min^{-1}$$

$$= \frac{4 \times 10^{-4}}{60}\ M\ s^{-1}$$

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

Question 4.2:

In a reaction, 2A → 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?

Answer

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 mol L^{-1} min^{-1}

= 5 × 10^{-3} M min^{-1}

Question 4.3:

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

Answer

The order of the reaction $= \frac{1}{2} + 2$

$$= 2\frac{1}{2}$$

= 2.5

Question 4.4:

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?

Answer

The reaction X → Y follows second order kinetics.

Therefore, the rate equation for this reaction will be:

Rate = $k[X]^2$ (1)

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

$Rate_1 = k.(a)^2$

$= ka^2$

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

Now, the rate equation will be:

Rate = $k\ (3a)^2$

= $9(ka^2)$

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

Question 4.5:

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

Answer

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

Initial amount = 5 g

Final concentration = 3 g

Rate constant = 1.15 10^{-3} 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 s

= 444 s (approx)

Question 4.6:

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.

Answer

We know that for a 1st order reaction,

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

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

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

$$= \frac{0.693}{60}$$

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

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

$$\text{Or } k = 1.925 \times 10^{-4} \text{ s}^{-1}$$

Question 4.7:

What will be the effect of temperature on rate constant?

Answer

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,

$$k = \text{Ae}^{-Ea/RT}$$

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 4.8:

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

Answer

It is given that T_1 = 298 K

$\therefore T_2$ = (298 + 10) K

= 308 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, $R = 8.314\ J\ K^{-1}\ mol^{-1}$

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:

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

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

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

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

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

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Question 4.9:

The activation energy for the reaction

$2HI_{(g)} \rightarrow H_2 + I_{2(g)}$

is 209.5 kJ mol^{-1} at 581K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Answer

In the given case:

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

$T = 581\ K$

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

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

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

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

$$\Rightarrow \log x = -\frac{E_a}{2.303\ RT}$$

$$\Rightarrow \log x = \frac{209500\,\text{J mol}^{-1}}{2.303 \times 8.314\,\text{JK}^{-1}\,\text{mol}^{-1} \times 581} = 18.8323$$

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

Question 4.1:

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

(i) $3\ NO(g) \rightarrow N_2O\ (g)$ Rate = $k[NO]^2$

(ii) $H_2O_2\ (aq) + 3\ I^-\ (aq) + 2\ H^+ \rightarrow 2\ H_2O\ (l) + I_3^-$ Rate = $k[H_2O_2][I^-]$

(iii) $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$ Rate = $k\ [CH_3CHO]^{3/2}$

(iv) $C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$ Rate = $k\ [C_2H_5Cl]$

Answer

(i) Given rate = $k\,[NO]^2$

Therefore, order of the reaction = 2

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

$$= \frac{\text{mol L}^{-1}\ \text{s}^{-1}}{\left(\text{mol L}^{-1}\right)^2}$$

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

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

(ii) Given rate = $k\,[H_2O_2]\,[I^-]$

Therefore, order of the reaction = 2

Dimension of $k = \dfrac{\text{Rate}}{[H_2O_2][I^-]}$

$$= \frac{\text{mol L}^{-1}\ \text{s}^{-1}}{\left(\text{mol L}^{-1}\right)\left(\text{mol L}^{-1}\right)}$$

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

(iii) Given rate = $k\,[CH_3CHO]^{3/2}$

Therefore, order of reaction = $\dfrac{3}{2}$

Dimension of $k = \dfrac{\text{Rate}}{[CH_3CHO]^{\frac{3}{2}}}$

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

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

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

(iv) Given rate = $k\,[C_2H_5Cl]$

Therefore, order of the reaction = 1

Dimension of $k = \frac{\text{Rate}}{[C_2H_5Cl]}$

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

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

Question 4.2:

For the reaction:

$2A + B \rightarrow A_2B$

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

Answer

The initial rate of the reaction is

Rate = k [A][B]^2

= (2.0×10^{-6} mol^{-2} L^2 s^{-1}) (0.1 mol L^{-1}) (0.2 mol L^{-1})^2

= 8.0×10^{-9} mol^{-2} L^2 s^{-1}

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

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

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

= 0.18 mol L^{-1}

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

Rate = k [A][B]^2

= (2.0×10^{-6} mol^{-2} L^2 s^{-1}) (0.06 mol L^{-1}) (0.18 mol L^{-1})^2

= 3.89 mol L^{-1} s^{-1}

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

Answer

The decomposition of NH_3 on platinum surface is represented by the following equation.

$$2\,NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$$

Therefore,

$$\text{Rate} = -\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt}$$

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

Therefore,

$$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = k$$

$$= 2.5\times10^{-4}\ \text{mol}\ L^{-1}\ s^{-1}$$

Therefore, the rate of production of N_2 is

$$\frac{d[N_2]}{dt} = 2.5\times10^{-4}\ \text{mol}\,L^{-1}s^{-1}$$

And, the rate of production of H_2 is

$$\frac{d[H_2]}{dt} = 3\times2.5\times10^{-4}\ \text{mol}\,L^{-1}s^{-1}$$

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

Question 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

Rate = $k\,[CH_3OCH_3]^{3/2}$

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

$$\text{Rate} = k\left(p_{CH_3OCH_3}\right)^{3/2}$$

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

Answer

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

Unit of rate = bar min^{-1}

$$\text{Rate} = k\left(p_{CH_3OCH_3}\right)^{3/2}$$

$$\Rightarrow k = \frac{\text{Rate}}{\left(p_{CH_3OCH_3}\right)^{3/2}}$$

Therefore, unit of rate constants $(k) = \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}}$

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

Question 4.5:

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

Answer

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 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?

Answer

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] = 2*a*, then the rate of the reaction would be

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

= $4ka^2$

= 4 R

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

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

$$R'' = k\left(\frac{1}{2}a\right)^2$$
$$= \frac{1}{4}ka$$
$$= \frac{1}{4}R$$

Therefore, the rate of the reaction would be reduced to $\frac{1}{4}^{th}$.

Question 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?

Answer

The rate constant is nearly doubled with a rise in temperature by 10° for a chemical reaction.

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

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

where, *k* is the rate constant,

A is the Arrhenius factor or the frequency factor,

R is the gas constant,

T is the temperature, and

E_a is the energy of activation for the reaction

Question 4.8:

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.

Answer

(i) Average rate of reaction between the time interval, 30 to 60 seconds, $= \frac{d[\text{Ester}]}{dt}$

$= \frac{0.31 - 0.17}{60 - 30}$

$= \frac{0.14}{30}$

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

(ii) For a pseudo first order reaction,

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

For t = 30 s, $k_1 = \frac{2.303}{30} \log \frac{0.55}{0.31}$

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

For t = 60 s, $k_2 = \frac{2.303}{60} \log \frac{0.55}{0.17}$

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

For t = 90 s, $k_3 = \frac{2.303}{90} \log \frac{0.55}{0.085}$

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

Then, average rate constant, $k = \frac{k_1 + k_2 + k_3}{3}$

$$= \frac{\left(1.911 \times 10^{-2}\right) + \left(1.957 \times 10^{-2}\right) + \left(2.075 \times 10^{-2}\right)}{3}$$

$$= 1.98 \times 10^{-2} \text{ s}^{-1}$$

Question 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?

Answer

(i) The differential rate equation will be

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

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

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

Therefore, the rate of reaction will increase 9 times.

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

$$-\frac{d[\mathrm{R}]}{dt} = k[\mathrm{A}][\mathrm{B}]^2$$
$$= k[2\mathrm{A}][2\mathrm{B}]^2$$
$$= 8 \cdot k[\mathrm{A}][\mathrm{B}]^2$$

Therefore, the rate of reaction will increase 8 times.

Question 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/ 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?

Answer

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

Therefore,

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

$$5.07\times10^{-5} = k[0.20]^x [0.30]^y \qquad (i)$$

$$5.07\times10^{-5} = k[0.20]^x [0.10]^y \qquad (ii)$$

$$1.43\times10^{-4} = k[0.40]^x [0.05]^y \qquad (iii)$$

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

$$\frac{5.07\times10^{-5}}{5.07\times10^{-5}} = \frac{k[0.20]^x [0.30]^y}{k[0.20]^x [0.10]^y}$$

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

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

$$\Rightarrow y = 0$$

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

$$\frac{1.43\times10^{-4}}{5.07\times10^{-5}} = \frac{k[0.40]^x [0.05]^y}{k[0.20]^x [0.30]^y}$$

$$\Rightarrow \frac{1.43\times10^{-4}}{5.07\times10^{-5}} = \frac{[0.40]^x}{[0.20]^x} \qquad \left[\text{Since } y = 0, \; [0.05]^y = [0.30]^y = 1\right]$$

$$\Rightarrow 2.821 = 2^x$$

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

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

= 1.496

= 1.5 (approximately)

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

Question 4.11:

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

2A + B → C + D

Experiment	A/ mol L^{-1}	B/ mol L^{-1}	Initial rate of formation of D/mol L^{-1} min^{-1}
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

Answer

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,

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

According to the question,

$$6.0\times10^{-3} = k[0.1]^x[0.1]^y \qquad \text{(i)}$$

$$7.2\times10^{-2} = k[0.3]^x[0.2]^y \qquad \text{(ii)}$$

$$2.88\times10^{-1} = k[0.3]^x[0.4]^y \qquad \text{(iii)}$$

$$2.40\times10^{-2} = k[0.4]^x[0.1]^y \qquad \text{(iv)}$$

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

$$\frac{2.40\times10^{-2}}{6.0\times10^{-3}} = \frac{k[0.4]^x[0.1]^y}{k[0.1]^x[0.1]^y}$$

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

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

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

$$\Rightarrow x = 1$$

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

$$\frac{2.88\times10^{-1}}{7.2\times10^{-2}}=\frac{k[0.3]^x[0.4]^y}{k[0.3]^x[0.2]^y}$$

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

$$\Rightarrow 4=2^y$$

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

$$\Rightarrow y=2$$

Therefore, the rate law is

Rate = k [A] $[B]^2$

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

From experiment I, we obtain

$$k=\frac{6.0\times10^{-3}\ \text{mol L}^{-1}\ \text{min}^{-1}}{(0.1\ \text{mol L}^{-1})(0.1\ \text{mol L}^{-1})^2}$$

= 6.0 L^2 mol^{-2} min^{-1}

From experiment II, we obtain

$$k=\frac{7.2\times10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1}}{(0.3\,\text{mol L}^{-1})(0.2\,\text{mol L}^{-1})^2}$$

= 6.0 L^2 mol^{-2} min^{-1}

From experiment III, we obtain

$$k=\frac{2.88\times10^{-1}\ \text{mol L}^{-1}\ \text{min}^{-1}}{(0.3\,\text{mol L}^{-1})(0.4\,\text{mol L}^{-1})^2}$$

= 6.0 L^2 mol^{-2} min^{-1}

From experiment IV, we obtain

$$k=\frac{2.40\times10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1}}{(0.4\,\text{mol L}^{-1})(0.1\,\text{mol L}^{-1})^2}$$

= 6.0 L^2 mol^{-2} min^{-1}

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

Question 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}

Answer

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,

Rate = k $[A]^1$ $[B]^0$

$\Rightarrow$ Rate = k [A]

From experiment I, we obtain

2.0×10^{-2} mol L^{-1} min^{-1} = k (0.1 mol L^{-1})

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

From experiment II, we obtain

4.0×10^{-2} mol L^{-1} min^{-1} = 0.2 min^{-1} [A]

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

From experiment III, we obtain

Rate = 0.2 min^{-1} × 0.4 mol L^{-1}

= 0.08 mol L^{-1} min^{-1}

From experiment IV, we obtain

2.0×10^{-2} mol L^{-1} min^{-1} = 0.2 min^{-1} [A]

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

Question 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 $years^{-1}$

Answer

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

$= \frac{0.693}{200\ s^{-1}}$

= 3.47 s (approximately)

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

$= \frac{0.693}{2\ min^{-1}}$

= 0.35 min (approximately)

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

$= \frac{0.693}{4\ years^{-1}}$

= 0.173 years (approximately)

Question 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.

Answer

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

$= \frac{0.693}{5730}\ years^{-1}$

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 years (approximately)

Hence, the age of the sample is 1845 years.

Question 4.15:

The experimental data for decomposition of N_2O_5

$$\left[2N_2O_5 \longrightarrow 4NO_2 + O_2\right]$$

in gas phase at 318K are given below:

t(s)	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [N_2O_5]\,mol\,L^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(i) Plot $[N_2O_5]$ against *t*.

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

(iii) Draw a graph between log $[N_2O_5]$ and *t.*

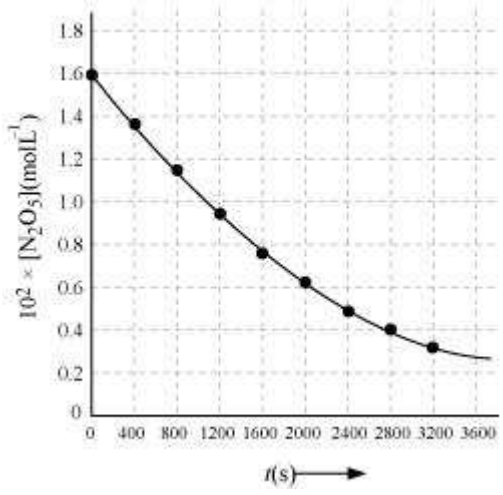
(iv) What is the rate law?

(v) Calculate the rate constant.

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

Answer

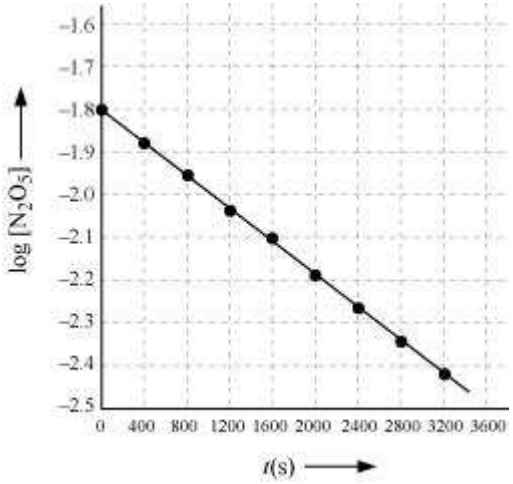
i.



(ii) Time corresponding to the concentration, $\frac{1.630\times10^{2}}{2}\,\text{mol L}^{-1} = 81.5\,\text{mol L}^{-1},$ is the half life. From the graph, the half life is obtained as 1450 s.

(iii)

t(s)	$10^2 \times [N_2O_5] / \text{mol L}^{-1}$	$\log[N_2O_5]$
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, $\log[N_2O_5]$ 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, $\log[N_2O_5]$ v/s *t*, we obtain

$$\text{Slope} = \frac{-2.46-(-1.79)}{3200-0}$$

$$= \frac{-0.67}{3200}$$

Again, slope of the line of the plot $\log[N_2O_5]$ v/s *t* is given by

$$-\frac{k}{2.303}.$$

Therefore, we obtain,

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

$$\Rightarrow k = 4.82\times10^{-4}\ s^{-1}$$

(vi) Half-life is given by,

$$t_{1/2} = \frac{0.639}{k}$$
$$= \frac{0.693}{4.82\times10^{-4}} s$$
$$= 1.438\times10^{3} s$$
$$= 1438 s$$

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

Question 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?

Answer

It is known that,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$
$$= \frac{2.303}{60\ s^{-1}} \log \frac{1}{1/16}$$
$$= \frac{2.303}{60\ s^{-1}} \log 16$$
$$= 4.6\times10^{-2}\ s\ (\text{approximately})$$

Hence, the required time is 4.6 × 10^{-2} s.

Question 4.17:

During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1µg 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.

Answer

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

Here,

It is known that,

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

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

$$\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}}\left(-\log[R]\right)$$

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

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

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

$$= 0.7814\mu g$$

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

Again,

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

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

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

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

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

$$= 0.2278\mu g$$

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

Question 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.

Answer

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

$$t_1 = \frac{2.303}{k}\log\frac{100}{100-99}$$
$$= \frac{2.303}{k}\log 100$$
$$= 2\times\frac{2.303}{k}$$

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

$$t_2 = \frac{2.303}{k}\log\frac{100}{100-90}$$
$$= \frac{2.303}{k}\log 10$$
$$= \frac{2.303}{k}$$

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 4.19:

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

Answer

For a first order reaction,

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

$$k = \frac{2.303}{40\ \mathrm{min}}\log\frac{100}{100-30}$$
$$= \frac{2.303}{40\ \mathrm{min}}\log\frac{10}{7}$$
$$= 8.918\times10^{-3}\ \mathrm{min}^{-1}$$

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

$$t_{1/2} = \frac{0.693}{k}$$
$$= \frac{0.693}{8.918\times10^{-3}}\ \mathrm{min}$$

= 77.7 min (approximately)

Question 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.

Answer

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

$$(CH_3)_2CHN{=}NCH(CH_3)_{2(g)} \longrightarrow N_{2(g)} + C_6H_{14(g)}$$

At $t = 0$	P_0	0	0
At $t = t$	$P_0 - p$	p	p

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, $P_o - p = P_o - (P_t - P_o)$

$= 2P_0 - P_t$

For a first order reaction,

$$k = \frac{2.303}{t}\log\frac{P_0}{P_0 - p}$$

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

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

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

When t = 720 s, $k = \frac{2.303}{720\ s}\log\frac{35.0}{2\times35.0-63.0}$

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

Hence, the average value of rate constant is

$$k = \frac{\left(2.175\times10^{-3}\right)+\left(2.235\times10^{-3}\right)}{2}s^{-1}$$

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

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Question 4.21:

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

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

Experiment	Time/s^{-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.

Answer

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

	$SO_2Cl_{2(g)}$	$\longrightarrow$	$SO_{2(g)}$	+	$Cl_{2(g)}$
At $t=0$	P_0		0		0
At $t=t$	P_0-p		p		p

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, $P_o - p = P_o - (P_t - P_o)$

$= 2\,P_0 - P_t$

For a first order reaction,

$$k = \frac{2.303}{t}\log\frac{P_0}{P_0 - p}$$

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

When t = 100 s, $k = \frac{2.303}{100\ \text{s}}\log\frac{0.5}{2\times 0.5 - 0.6}$

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

When P_t = 0.65 atm,

$P_0 + p = 0.65$

$\Rightarrow p = 0.65 - P_0$

$= 0.65 - 0.5$

$= 0.15$ atm

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

$p_{SOCl_2} = P_0 - p$

$= 0.5 - 0.15$

$= 0.35$ atm

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

Rate = $k(p_{SOCl_2})$

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

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

Question 4.22:

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

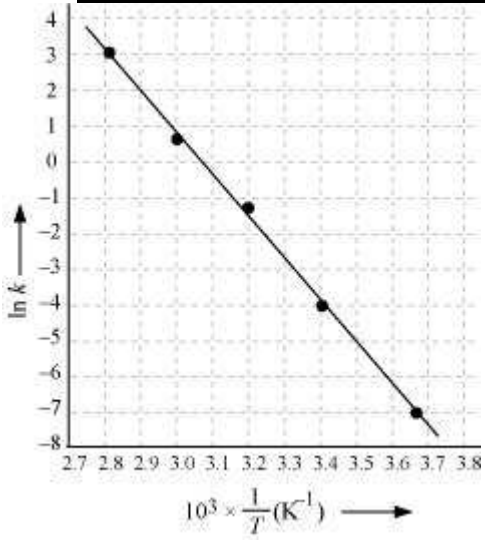
Draw a graph between ln k and $1/T$ and calculate the values of A and E_a.

Predict the rate constant at 30º and 50ºC.

Answer

From the given data, we obtain

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



Slope of the line,

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

According to Arrhenius equation,

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

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

$$=-\left(-12.301\,\mathrm{K}\right)\times\left(8.314\ \mathrm{J\,K^{-1}mol^{-1}}\right)$$

$$=102.27\ \mathrm{kJ\,mol^{-1}}$$

Again,

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

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

When $T = 273\,K$,

$\ln k = -7.147$

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

$$= 37.911$$

$$\text{Therefore, } A = 2.91 \times 10^6$$

When $T = 30 + 273\,K = 303\,K$,

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

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

$\ln k = -2.8$

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

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

$$\frac{1}{T} = 0.0031\,K = 3.1 \times 10^{-3}\,K$$

Then, at $\frac{1}{T} = 3.1 \times 10^{-3}\,K$,

$\ln k = -0.5$

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

Question 4.23:

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

Answer

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

$T = 546$ K

E_a = 179.9 kJ mol^{-1} = 179.9 × 10^3 J mol^{-1}

According to the Arrhenius equation,

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

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

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

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

$$= \log\left(2.418\times10^{-5}\ s^{-1}\right) + \frac{179.9\times10^{3}\ J\ mol^{-1}}{2.303\times8.314\ Jk^{-1}\ mol^{-1}\times546\ K}$$

= (0.3835 − 5) + 17.2082

= 12.5917

Therefore, A = antilog (12.5917)

= 3.9 × 10^{12} s^{-1} (approximately)

Question 4.24:

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

Answer

k = 2.0 × 10^{-2} s^{-1}

T = 100 s

$[A]_o$ = 1.0 moL^{-1}

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

Therefore, $$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

$$\Rightarrow 2.0\times10^{-2}\ \text{s}^{-1} = \frac{2.303}{100\ \text{s}}\log\frac{1.0}{[\text{A}]}$$

$$\Rightarrow 2.0\times10^{-2}\ \text{s}^{-1} = \frac{2.303}{100\,\text{s}}\left(-\log[\text{A}]\right)$$

$$\Rightarrow -\log[\text{A}] = \frac{2.0\times10^{-2}\times100}{2.303}$$

$$\Rightarrow [\text{A}] = \text{anti}\log\left(-\frac{2.0\times10^{-2}\times100}{2.303}\right)$$

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

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

Question 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?

Answer

For a first order reaction,

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

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

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

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

= 0.231 h^{-1}

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

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

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

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

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

$$= 0.158$$

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

Question 4.26:

The decomposition of hydrocarbon follows the equation

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

Calculate E_a.

Answer

The given equation is

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

Arrhenius equation is given by,

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

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

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

$$\Rightarrow E_a = R \times 28000\ K$$

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

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

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

Question 4.27:

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

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

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

Answer

Arrhenius equation is given by,

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

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

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

$$\Rightarrow \log k = \log \mathrm{A} - \frac{E_a}{2.303\ RT} \qquad \text{(i)}$$

The given equation is

$$\log k = 14.34 - 1.25 \times 10^4\ \mathrm{K}/T \qquad \text{(ii)}$$

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

$$\frac{E_a}{2.303\ RT} = \frac{1.25 \times 10^4\ \mathrm{K}}{T}$$

$$\Rightarrow E_a = 1.25 \times 10^4 \mathrm{K} \times 2.303 \times R$$

= 1.25 × 10^4 K × 2.303 × 8.314 J K^{-1} mol^{-1}

= 239339.3 J mol⁻1 (approximately)

= 239.34 kJ mol^{-1}

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

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

$$= \frac{0.693}{256}$$

= 2.707 × 10^{-3} min^{-1}

= 4.51 × 10^{-5} s^{-1}

It is also given that, log k = 14.34 − 1.25 × 10^4 K/T

$$\Rightarrow \log\left(4.51\times10^{-5}\right)=14.34-\frac{1.25\times10^{4}\ \text{K}}{T}$$

$$\Rightarrow \log\left(0.654-05\right)=14.34-\frac{1.25\times10^{4}\ \text{K}}{T}$$

$$\Rightarrow \frac{1.25\times10^{4}\ \text{K}}{T}=18.686$$

$$\Rightarrow T=\frac{1.25\times10^{4}\ \text{K}}{18.686}$$

= 668.95 K

= 669 K (approximately)

Question 4.28:

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

Answer

From Arrhenius equation, we obtain

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303\,\text{R}}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

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

$T_1 = 273 + 10 = 283$ K

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

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

Then,

$$\log\frac{1.5\times10^{4}}{4.5\times10^{3}}=\frac{6.0\times10^{4}\ \text{J mol}^{-1}}{2.303\times8.314\ \text{J K}^{-1}\text{mol}^{-1}}\left(\frac{T_2-283}{283T_2}\right)$$

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

$$\Rightarrow \frac{0.5229\times283\ T_2}{3133.627}=T_2-283$$

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

$$\Rightarrow 0.9528\ T_2=283$$

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

= 297 K

= 24°C

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

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Question 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 $4 \times 10^{10}\ s^{-1}$. Calculate k at 318 K and E_a.

Answer

For a first order reaction,

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

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

$$= \frac{0.1054}{k}$$

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

$$= \frac{2.2877}{k'}$$

According to the question,

$$t = t'$$

$$\Rightarrow \frac{0.1054}{k} = \frac{0.2877}{k'}$$

$$\Rightarrow \frac{k'}{k} = 2.7296$$

From Arrhenius equation, we obtain

$$\log\frac{k'}{k}=\frac{E_a}{2.303\,\mathrm{R}}\left(\frac{T'-T}{TT'}\right)$$

$$\log(2.7296)=\frac{E_a}{2.303\times 8.314}\left(\frac{308-298}{298\times 308}\right)$$

$$E_a=\frac{2.303\times 8.314\times 298\times 308\times \log(2.7296)}{308-298}$$

$$=76640.096\ \mathrm{J\,mol^{-1}}$$

$$=76.64\ \mathrm{kJ\,mol^{-1}}$$

To calculate *k* at 318 K,

It is given that, $A=4\times10^{10}\mathrm{s^{-1}},\ T=318\,\mathrm{K}$

Again, from Arrhenius equation, we obtain

$$\log k=\log A-\frac{E_a}{2.303\,\mathrm{R}\,T}$$

$$=\log\left(4\times10^{10}\right)-\frac{76.64\times10^3}{2.303\times8.314\times318}$$

$$=(0.6021+10)-12.5876$$

$$=-1.9855$$

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

$$=1.034\times10^{-2}\,\mathrm{s^{-1}}$$

Question 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.

Answer

From Arrhenius equation, we obtain

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303\,\mathrm{R}}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

It is given that, $k_2=4k_1$

$T_1=293\,\mathrm{K}$

$T_2=313\,\mathrm{K}$

$$\text{Therefore, }\log\frac{4k_1}{k_2}=\frac{E_a}{2.303\times8.314}\left(\frac{313-293}{293\times313}\right)$$

$$\Rightarrow 0.6021=\frac{20\times E_a}{2.303\times8.314\times293\times313}$$

$$\Rightarrow E_a=\frac{0.6021\times2.303\times8.314\times293\times313}{20}$$

$$=52863.33\ \mathrm{J\,mol^{-1}}$$

$$=52.86\ \mathrm{kJ\,mol^{-1}}$$

Hence, the required energy of activation is 52.86 kJmol^{-1}.