NCERT Solutions for Class 12 Chemistry Part 1 Chapter 4

Chemical Kinetics Class 12

Chapter 4 Chemical Kinetics Exercise Solutions

In text : Solutions of Questions on Page Number : **98**

Q1 :

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 $= -\dfrac{\Delta[R]}{\Delta t}$

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

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

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

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

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

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

Q2 :

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 $= -\dfrac{1}{2}\dfrac{\Delta[A]}{\Delta t}$

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

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

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

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

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

Q3 :

For a reaction, A + B Ã¢â ’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 $= \frac{1}{2} + 2$

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

$= 2.5$

Q4 :

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.

Q5 :

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 1storder 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)

Q6 :

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 1storder reaction,

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

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

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

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

$$= 0.01155 \text{ min}^{-1}$$
$$= 1.155 \text{ min}^{-1}$$

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

Q7 :

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

Q8 :

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

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:

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

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

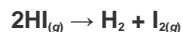$$\Rightarrow E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2}{10}$$

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

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

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

Q9 :

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:

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

$T = 581 \text{ K}$

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

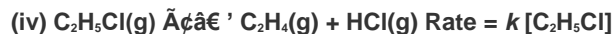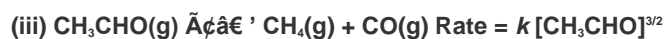Now, the fraction of molecules of reactants having energy equal to or greater than activation energy is given as:
$x = e^{-E_a/RT} \Rightarrow \ln x = -E$

Exercise : Solutions of Questions on Page Number : **117**
Q1 :

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

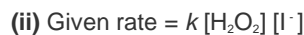**(i) 3 NO(g) Ã¢â€™ N_2O(g) Rate = $k[NO]^2$**

(ii) H_2O_2 (aq) + 3 I⁻ (aq) + 2 H⁺Ã¢â€™ 2 H_2O (l) + I_3^- Rate = $k[H_2O_2][I^-]$

(iii) CH_3CHO(g) Ã¢â€™ CH_4(g) + CO(g) Rate = $k [CH_3CHO]^{3/2}$

(iv) C_2H_5Cl(g) Ã¢â€™ 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 $k = \dfrac{Rate}{[NO]^2}$

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

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

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

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

Therefore, order of the reaction = 2

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

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

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

(iii) Given rate = $k [CH_3CHO]^{3/2}$
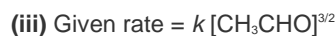
Therefore, order of reaction = $\dfrac{3}{2}$

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

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

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

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

(iv) Given rate = k [C_2H_5Cl]

Therefore, order of the reaction = 1

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

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

$$= s^{-1}$$

Q2 :

For the reaction:

$2A + B \rightarrow A_2B$

the rate = k[A][B]^2 with k= 2.0 x 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 L^{-1}, the concentration of A reacted = (0.1 - 0.06) mol L^{-1} = 0.04 mol L^{-1}

Therefore, concentration of B reacted $= \dfrac{1}{2} \times 0.04\ mol\ L^{-1}$ = 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
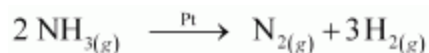
$= 3.89$ mol $L^{-1}s^{-1}$

Q3 :

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.

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

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 $L^{-1}s^{-1}$

Q4 :

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}

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

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

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

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

Q5 :

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

Answer :

The factors that affect the rate of a reaction areas follows.

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

(ii) Temperature

(iii) Presence of a catalyst

Q6 :

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 :

Letthe 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. $[A] = \frac{1}{2}a$, then the rate of the reaction would be

$$R' = k(\frac{1}{2}a)^2$$

$$= \frac{1}{4}ka^2$$

$$= \frac{1}{4}R$$

....

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

Q7 :

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

Q8 :

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, $= \dfrac{-d[Ester]}{dt}$

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

$$= \dfrac{0.14}{30}$$

= 4.67 × 10^{-3}mol L^{-1}s^{-1}

(ii) For a pseudo first order reaction,

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

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

= 1.911 × 10^{-2}s^{-1}

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

= 1.957 × 10^{-2}s^{-1}

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

= 2.075 × 10^{-2}s^{-1}

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

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

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

Q9 :

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

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

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

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

Therefore, the rate of reaction will increase 9 times.

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

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

Therefore, the rate of reaction will increase 8 times.

Q10 :

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?

Answer :

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

Therefore,

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

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

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

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

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

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

$$\Rightarrow 2.821 = 2^x$$

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

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

= 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.

Q11 :

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

2A + B Ã¢â' 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,

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

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

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

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

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 (iii) by (ii), we obtain

Therefore, the rate law is

Rate = k [A] [B]^2

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

From experiment I, we obtain

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

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

From experiment II, weobtain

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

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

From experiment III, we obtain

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

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

From experiment IV, we obtain

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

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

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

Q12 :

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

⇒ Rate = k [A]

From experiment I, we obtain

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

⇒ k= 0.2 min^{-1}

From experiment II, we obtain

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

⇒ [A] = 0.2 mol L^{-1}

From experiment III, we obtain

Rate = 0.2 min^{-1} x 0.4 mol L^{-1}

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

From experiment IV, we obtain

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

⇒ [A] = 0.1 mol L^{-1}

Q13 :

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

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

= 3.47 ×10^{-3} s (approximately)

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

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

= 0.35 min (approximately)

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

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

= 0.173 years (approximately)

Q14 :

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

$$= \dfrac{0.693}{5730} \text{ years}^{-1}$$
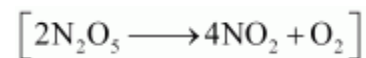
It is known that,

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

$$= \dfrac{2.303}{\dfrac{0.693}{5730}} \log \dfrac{100}{80}$$

= 1845 years (approximately)

Hence, the age of the sample is 1845 years.

Q15 :

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:

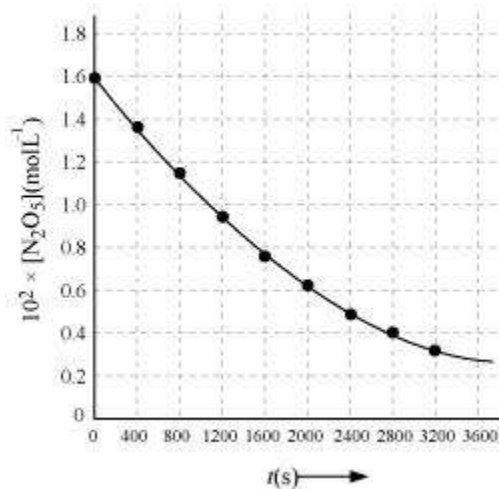| $t(s)$	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [N_2O_5] \text{mol L}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(i) Plot [N_2O_5] against _t._

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

(iii) Draw a graph between log [N₂O₅] and _t._

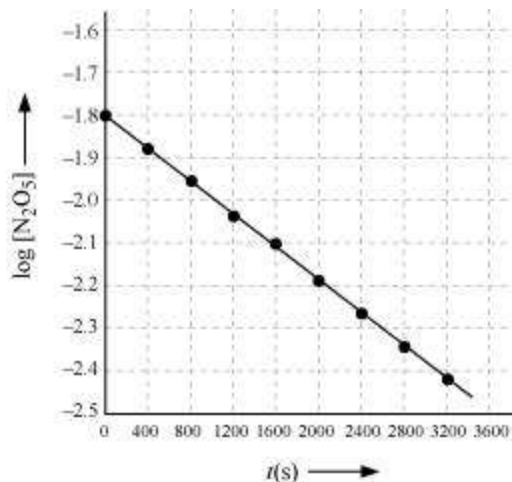**(iv) What is the rate law?**

(v)

Answer :

(ii) Time corresponding to the concentration, $\dfrac{1.630 \times 10^2}{2}\,\text{mol L}^{-1} = 81.5\,\text{mol L}^{-1}$, is the half life. From the graph, the half life is obtained as 1450 s.

(iii)

t(s)	$10^2 \times \left[N_2O_5\right]/\,mol\,L^{-1}$	$\log\left[N_2O_5\right]$
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,

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

Q16 :

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,

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

$$= \frac{2.303}{60 \text{ s}^{-1}} \log \frac{1}{1/16}$$

$$= \frac{2.303}{60 \text{ s}^{-1}} \log 16$$

$$= 4.6 \times 10^{-2} \text{ s (approximately)}$$

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

Q17 :

During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1ÃŽÂ¼g 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 :

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

It is known that,

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

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

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

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

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

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

$$= 0.7814\mu g$$

Therefore, 0.7814 ÃŽÂ¼g of ^{90}Sr will remain after 10 years.

Again,

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

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

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

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

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

$$= 0.2278\,\mu g$$

Therefore, 0.2278 ÃŽÂ¼g of ^{90}Sr will remain after 60 years.

Q18 :

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.

Q19 :

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

Answer :

For a first order reaction,

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

$$k = \frac{2.303}{40 \text{ min}} \log \frac{100}{100-30}$$

$$= \frac{2.303}{40 \text{ min}} \log \frac{10}{7}$$

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

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

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

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

= 77.7 min (approximately)

Q20 :

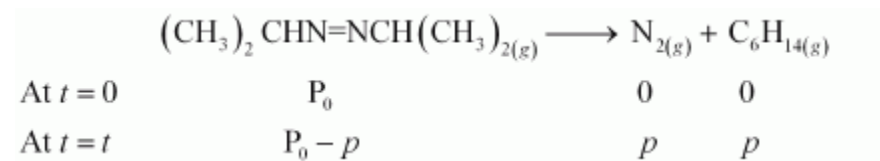**For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.**

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.

$$(CH_3)_2 CHN=NCH(CH_3)_{2(g)} \longrightarrow N_{2(g)} + C_6H_{14(g)}$$

At $t = 0$ P_0 0   0

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

www.ncrtsolutions.in

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,

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

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

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

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

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

Hence, the average value of rate constant is

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

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

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

Q21 :

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

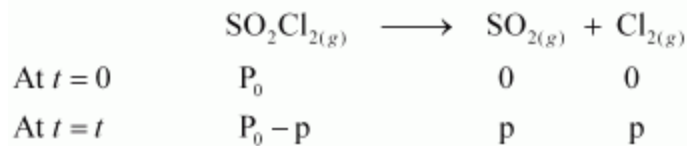$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

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.

www.ncrtsolutions.in

$$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$$

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

$= 2P_0 - P_t$

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

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

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 $= k(p_{SOCl_2})$

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

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

Q22 :

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

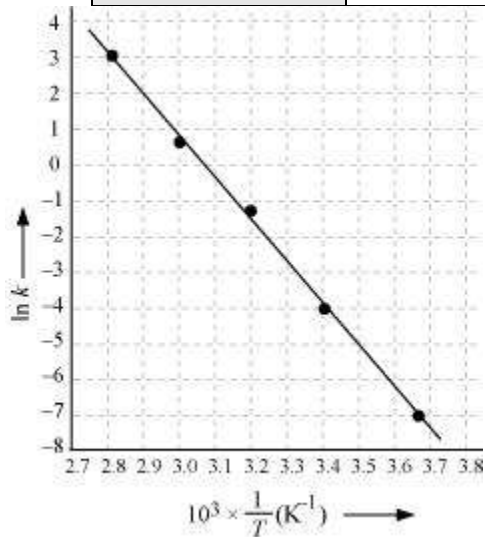**Draw a graph between ln k and $1/T$ and calculate the values of A and E_a.**

Predict the rate constant at 30 ° and 50 ºC.

Answer :

From the given data, we obtain

$T/°C$	0	20	40	60	80
T/K	273	293	313	333	353
$\dfrac{1}{T}/\ K^{-1}$	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,

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

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

$\ln k = -7.147$

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

$$= 37.911$$

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

$\ln k = -2.8$

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

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

Q23 :

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

Answer :

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

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

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

According to the Arrhenius equation,

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

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

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

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

$$= \log\left(2.418\times10^{-5} \, s^{-1}\right) + \frac{179.9\times10^3 \, J \, mol^{-1}}{2.303\times8.314 \, Jk^{-1} \, mol^{-1} \times 546 \, K}$$

= (0.3835 - 5) + 17.2082

= 12.5917

Therefore, A = antilog (12.5917)

= 3.9 × 10^{12}s^{-1}(approximately)

Q24 :

Consider a certain reaction A → Products with k = 2.0 x 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

$[A]_0$= 1.0 moL^{-1}

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

Therefore,

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

$$\Rightarrow 2.0 \times 10^{-2} \, s^{-1} = \frac{2.303}{100 \, s} \log \frac{1.0}{[A]}$$

$$\Rightarrow 2.0 \times 10^{-2} \, s^{-1} = \frac{2.303}{100 \, s} (-\log[A])$$

$$\Rightarrow -\log[A] = \frac{2.0 \times 10^{-2} \times 100}{2.303}$$

$$\Rightarrow [A] = \text{anti} \log \left(-\frac{2.0 \times 10^{-2} \times 100}{2.303} \right)$$

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

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

Q25 :

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,

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

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

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

Therefore,

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

= 0.231 h^{-1}

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

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

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

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

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

$$= 0.158$$

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

Q26 :

The decomposition of hydrocarbon follows the equation

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

Calculate E_a.

Answer :

The given equation is

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

Arrhenius equation is given by,

$k = A e^{-E_a/RT}$ (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}× 28000 K

= 232792 J mol^{-1}

= 232.792 kJ mol^{-1}

Q27 :

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

log k = 14.34 - 1.25 x 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,

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

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

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

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

The given equation is

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

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

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

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

= 1.25 × 10⁴K × 2.303 × 8.314 J K⁻¹mol⁻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 × 10⁻³min⁻¹

= 4.51 × 10⁻⁵s⁻¹

It is also given that, log k = 14.34 - 1.25 × 10⁴K/T

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

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

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

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

= 668.95 K

= 669 K (approximately)

Q28 :

The decomposition of A into product has value of k as 4.5 x 10³ s⁻¹ at 10°C and energy of activation 60 kJ mol⁻¹. At what temperature would k be 1.5 x 10⁴ s⁻¹?

Answer :

From Arrhenius equation, we obtain

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

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,

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

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

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

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

$$\Rightarrow 0.9528\ T_2=283$$

$$\Rightarrow T_2=297.019\ K\ (approximately)$$

= 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.

Q29 :

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, $\quad t = \frac{2.303}{k} \log \frac{100}{90}$

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

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

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

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

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

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

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

$$= 76640.096\ \text{J mol}^{-1}$$

$$= 76.64\ \text{kJ mol}^{-1}$$

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

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

$$= \log(4 \times 10^{10}) - \frac{76.64 \times 10^3}{2.303 \times 8.314 \times 318}$$

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

$$= -1.9855$$

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

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

Q30 :

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

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

It is given that, $k_2 = 4k_1$

$T_1 = 293\,K$

$T_2 = 313\,K$

Therefore, $\log \dfrac{4k_1}{k_2} = \dfrac{E_a}{2.303 \times 8.314}\left(\dfrac{313 - 293}{293 \times 313}\right)$

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

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

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

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

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