

NCERT Solutions for Class 12 Chemistry Part 1 Chapter 4

Chemical Kinetics Class 12

Chapter 4 Chemical Kinetics Exercise Solutions

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Q1 :

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.

Answer :

$$= -\frac{\Delta[R]}{\Delta t}$$
Average rate of reaction
$$= -\frac{[R]_2 - [R]_1}{t_2 - t_1}$$

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

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

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

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

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

Q2 :

In a reaction, $2A \rightarrow$ Products, the concentration of A decreases from 0.5 mol L⁻¹to 0.4 mol L⁻¹in 10 minutes. Calculate the rate during this interval?

Answer :



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

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

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

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

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

Q3 :

For a reaction, A + B $\tilde{A} \notin \hat{a} \in$ '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 $X \to Y$ follows second order kinetics.

Therefore, the rate equation for this reaction will be:

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



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

Rate₁ = $k . (a)^2$

 $= ka^2$

If the concentration of X is increased to three times, then $[X] = 3a \mod L^{-1}$ 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 10-3s-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 = $1.15 \ 10^{-3} \text{s}^{-1}$

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

$$k = \frac{0.693}{t_{1/2}}$$
$$= \frac{0.693}{60}$$
$$= 0.01155 \text{ min}^{-1}$$

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

min⁻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,

$$k = \mathrm{Ae}^{-Ea/R}$$

Where,

A is the Arrhenius factor or the frequency factor

Tis 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

∴*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.

Q9 :

The activation energy for the reaction

 $\mathbf{2HI}_{(g)} \rightarrow \mathbf{H}_2 + \mathbf{I}_{2(g)}$

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

 $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ Now, the fraction of molecules of reactants having energy equal to or greater than

activation energy is given as:

 $x = e - E_a/RT \implies In x = -E$

<< Previous Chapter 3 : ElectrochemistryNext Chapter 5 : Surface Chemistry

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) $\tilde{A}\phi \hat{a} \in N_2O(g)$ Rate = $k[NO]^2$

(ii) H₂O₂ (aq) + 3 l · (aq) + 2 H · → 2 H₂O (l) + I_3^- Rate = $k[H_2O_2][I ·]$

(iii) CH₃CHO(g) â†' CH₄(g) + CO(g) Rate = *k* [CH₃CHO]^{3/2}

(iv) C₂H₅Cl(g) â†' C₂H₄(g) + HCl(g) Rate = k [C₂H₅Cl]

Answer :

Dimension

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

Therefore, order of the reaction = 2

$$k = \frac{\text{Rate}}{[\text{NO}]^2}$$

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

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



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Therefore, order of the reaction = 2

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

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

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

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

Therefore, order of reaction = 2

$$k = \frac{\text{Rate}}{[\text{CH}_{3}\text{CHO}]^{\frac{3}{2}}}$$

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

(iv) Given rate = $k [C_2H_5CI]$

Therefore, order of the reaction = 1

 $k = \frac{\text{Rate}}{\left[\text{C}_2\text{H}_5\text{Cl}\right]}$ $=\frac{\text{mol } L^{-1} s^{-1}}{\text{mol } L^{-1}}$ $= s^{-1}$

Q2 :

For the reaction:

 $\mathbf{2A} + \mathbf{B} \to \mathbf{A}_2 \mathbf{B}$

the rate = $k[A][B]^2$ with $k= 2.0 \times 10^{-6}$ mol⁻²L²S⁻¹. Calculate the initial rate of the reaction when [A] = 0.1 mol L⁻¹, [B] = 0.2 mol L⁴. Calculate the rate of reaction after [A] is reduced to 0.06 mol L⁴.



Answer :

The initial rate of the reactionis

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

= $(2.0 \times 10.6 \text{mol}_{2}\text{L}_{2}\text{s}_{1})$ (0.1 mol L-1) (0.2 mol L-1)₂

= 8.0 × 10 - 9mol - 2L2S - 1

When [A] is reduced from 0.1 mol L⁻¹to 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 = $k [A][B]^2$

= $(2.0 \times 10^{-6} \text{mol}^{-2} \text{L}^2 \text{s}^{-1}) (0.06 \text{ mol} \text{L}^{-1}) (0.18 \text{ mol} \text{L}^{-1})^2$ = 3.89 mol L₋₁s₋₁

Q3 :

The decomposition of NH₃on platinum surface is zero order reaction. What are the rates of production of N₂and H₂if $k = 2.5 \times 10^{-4}$ mol⁻¹L s⁻¹?

Answer :

The decomposition of NH₃on platinum surface is represented by the following equation.

$$2 \operatorname{NH}_{3(g)} \xrightarrow{Pt} \operatorname{N}_{2(g)} + 3 \operatorname{H}_{2(g)}$$

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,

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

Therefore, the rate of production of N2is

$$\frac{d[N_2]}{dt} = 2.5 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{s}^{-1}$$

And, the rate of production of H₂is

$$\frac{d[H_2]}{dt} = 3 \times 2.5 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{s}^{-1}$$

= 7.5 × 10⁻⁴mol L⁻¹s⁻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 [CH₃OCH₃]^{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.,

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

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

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

 $(k) = \frac{\operatorname{bar} \min^{-1}}{\operatorname{bar}^{\frac{3}{2}}}$

Therefore, unit of rate constants



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

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 :

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

 $\mathbf{R}' = k \left(2a\right)^2$

 $= 4ka^{2}$

= 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



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

Therefore, the rate of the reaction would be reduced to ${}^4\!$

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?

 $1^{\,\text{th}}$

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, kis the rate constant,

A is the Arrhenius factor or the frequency factor,

R is the gas constant,

Tis 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:

Answer :



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.

2.075×10

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

d[Ester] dt

(i) Average rate of reaction between the time interval, 30 to 60 seconds,

$$=\frac{\frac{0.31-0.17}{60-30}}{=\frac{0.14}{30}}_{=4.67}$$

x 10-3mol L-1S-1

(ii) For a pseudo first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$
For $t = 30$ s, $k_1 = \frac{2.303}{30} \log \frac{0.55}{0.31}$

$$= 1.911 \times 10^{-2} \text{s}^{-1}$$
For $t = 60$ s, $k_2 = \frac{2.303}{60} \log \frac{0.55}{0.17}$

$$= 1.957 \times 10^{-2} \text{s}^{-1}$$
For $t = 90$ s, $k_3 = \frac{2.303}{90} \log \frac{0.55}{0.085}$

$$= 2.075 \times 10^{-2} \text{s}^{-1}$$
Then, average rate constant, $k = \frac{k_1 + k_2 + k_3}{3}$

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

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

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

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

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

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

Therefore, the rate of reaction will increase 9 times.

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

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

Therefore, the rate of reaction will increase 8 times.

Q10 :

In a reaction between A and B, the initial rate of reaction (r₀) 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
^o r / 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,

$$\mathbf{r}_{0} = k [\mathbf{A}]^{x} [\mathbf{B}]^{y}$$

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

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

$$5.07 \times 10^{-4} = k [0.20] [0.10]$$
(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

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

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

$$\Rightarrow 2.821 = 2^x$$

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

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

= 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 → C + D

Experiment	A/ mol L-1	B/ mol L-1	Initial rate of formation of D/mol L-1 min-1	
Ι	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,

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

According to the question,

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

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

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

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

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

$$\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k \left[0.4\right]^x \left[0.1\right]^y}{k \left[0.1\right]^x \left[0.1\right]^y}$$
$$\Rightarrow 4 = \frac{\left[0.4\right]^x}{\left[0.1\right]^x}$$
$$\Rightarrow 4 = \left(\frac{0.4}{0.1}\right)^x$$
$$\Rightarrow (4)^1 = 4^x$$
$$\Rightarrow x = 1$$

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



Therefore, the rate law is

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

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

From experiment I, we obtain

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

= 6.0 L²mol⁻²min⁻¹

From experiment II, weobtain

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

= $6.0 L_2 mol_2 min_1$

From experiment III, we obtain

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

= 6.0 L₂mol - 2min - 1

From experiment IV, we obtain

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

= 6.0 L₂mol - 2min - 1

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

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	
Ι	0.1	0.1	2.0 × 10-2	



II		0.2	$4.0 imes 10^{-2}$
III	0.4	0.4	
IV		0.2	2.0×10^{12}

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 x 10⁻²mol L⁻¹min⁻¹ = k (0.1 mol L⁻¹) \Rightarrow k=

0.2 min⁻¹

From experiment II, we obtain

4.0 x 10⁻²mol L⁻¹min⁻¹= 0.2 min⁻¹[A]

 \Rightarrow [A] = 0.2 mol L⁻¹

From experiment III, we obtain

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Rate = 0.2 min<sup>-1</sup> x 0.4 mol L<sup>-1</sup>
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= 0.08 mol L⁻¹min⁻¹

From experiment IV, we obtain

2.0 x 10⁻²mol L⁻¹min⁻¹= 0.2 min⁻¹[A]

 \Rightarrow [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, $t_{\frac{1}{2}} = \frac{0.693}{k}$ $= \frac{0.693}{200 \text{ s}^{-1}}$ $= 3.47 \times 10^{-3} \text{ s (approximately)}$ (ii) Half life, $t_{\frac{1}{2}} = \frac{0.693}{k}$ $= \frac{0.693}{2 \text{ min}^{-1}}$ = 0.35 min (approximately)(iii) Half life, $t_{\frac{1}{2}} = \frac{0.693}{k}$ $= \frac{0.693}{4 \text{ years}^{-1}}$ = 0.173 years (approximately)

Q14 :

The half-life for radioactive decay of ¹⁴C is 5730 years. An archaeological artifact containing wood had only 80% of the ¹⁴C found in a living tree. Estimate the age of the sample.



Answer :

$$k = \frac{0.693}{t}$$

Here,

$$=\frac{0.693}{5730}$$
 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.

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:

<i>t</i> (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*.

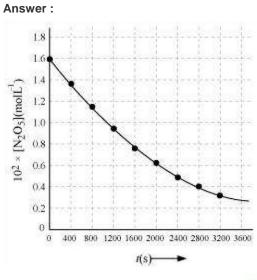
(ii) Find the half-life period for the reaction.

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

(iv) What is the rate law?

(v)





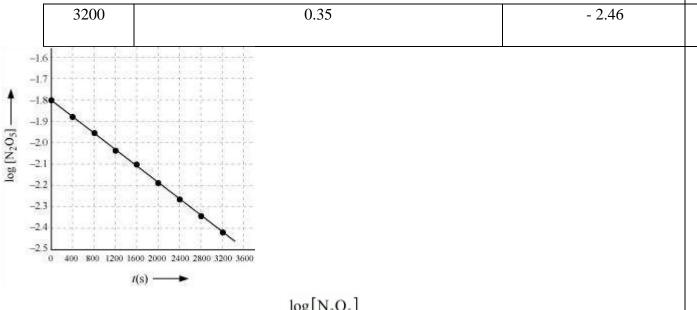
$\frac{1.630 \times 10^2}{2} \text{ mol } L^{-1} = 81.5 \text{ mol } L^{-1},$ is the half life. From the graph,

(ii) Time corresponding to the concentration, the half life is obtained as 1450 s.

(iii)

t(s)	$10^2 \times [N_2O_5] / mol L^1$	$log[N_2O_5]$
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





(iv) The given reaction is of the first order as the plot, $\frac{log \big[N_2 O_5 \big]}{log \big[n_2 O_5 \big]}$ the reaction is

Rate = $k [N_2O_5]$

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

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 1/16thvalue?

v/s *t*, is a straight line. Therefore, the rate law of



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 ⁹⁰Sr with half-life of 28.1 years. If 1μg of ⁹⁰Sr 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 :

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

Here,

It is known that,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$
$$\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$
$$\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}} (-\log[R])$$
$$\Rightarrow \log[R] = -\frac{10 \times 0.693}{2.303 \times 28.1}$$
$$\Rightarrow [R] = \operatorname{antilog} (-0.1071)$$
$$= \operatorname{antilog} (\overline{1.8929})$$
$$= 0.7814 \mu g$$

Therefore, 0.7814 $\tilde{A}\check{Z}\hat{A}^{1\!\!\!/}_{4}g$ of ${}^{\scriptscriptstyle 90}Sr$ will remain after 10 years.

Again,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$
$$\Rightarrow 60 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$
$$\Rightarrow \log[R] = -\frac{60 \times 0.693}{2.303 \times 28.1}$$
$$\Rightarrow [R] = \operatorname{antilog} (-0.6425)$$
$$= \operatorname{antilog} (\overline{1.3575})$$
$$= 0.2278 \mu g$$

Therefore, 0.2278 $\tilde{A}\check{Z}\hat{A}^{1\!\!\!/}_{4}g$ of ${}^{\scriptscriptstyle 90}Sr$ 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% completionis

$$t_{1} = \frac{2.303}{k} \log \frac{100}{100 - 99}$$
$$= \frac{2.303}{k} \log 100$$
$$= 2 \times \frac{2.303}{k}$$

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

For a first order reaction, the time required for 90% completion iTherefore, $t_1 = 2t_2$

s

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 $t_{t/2}$.

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

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$
$$= \frac{0.693}{8.918 \times 10^{-3}} \min$$

= 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.

$$(CH_3)_2 CHN = NCH (CH_3)_{2(g)} \longrightarrow N_{2(g)} + C_6 H_{14(g)}$$

At $t = 0$ P₀ 0 0
At $t = t$ P₀ - p p p



After time, *t*, total pressure, $\mathbf{P}_t = (\mathbf{P}_0 - p) + p + p$ $\Rightarrow \mathbf{P}_t = \mathbf{P}_0 + p$ $\Rightarrow p = \mathbf{P}_t - \mathbf{P}_0$

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, $k = \frac{2.303}{360} \log \frac{35.0}{2 \times 35.0 - 54.0}$
= 2.175 × 10⁻³ s⁻¹

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

= 2.235 × 10⁻³ s⁻¹

Hence, the average value of rate constant is

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

= 2.21 × 10-3 S-1

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

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Q21 :

Answer :



The following data were obtained during the first order thermal decomposition of SO₂Cl₂at 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.

The thermal decomposition of SO₂Cl₂at a constant volume is represented by the following equation.

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

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

 $\Rightarrow \mathbf{P}_t = \mathbf{P}_0 + p$ $\Rightarrow p = \mathbf{P}_t - \mathbf{P}_0$

Therefore,
$$\mathbf{P}_{o} - p = \mathbf{P}_{o} - (\mathbf{P}_{t} - \mathbf{P}_{o})$$

 $= 2 P_0 - P_t$

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 $t = 100 \text{ s}$, $k = \frac{2.303}{100 \text{ s}} \log \frac{0.5}{2 \times 0.5 - 0.6}$
= $2.231 \times 10^{-3} \text{s}^{-1}$
When $P_r = 0.65$ 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 $SOCI_2$ is

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

= 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 × 10⁻³s⁻¹) (0.35 atm) = 7.8 × 10⁻⁴atm 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	



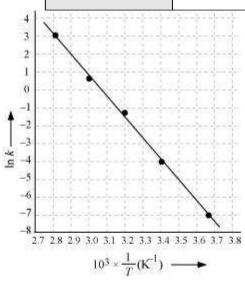
Draw a graph between $\ln k$ and 1/T and calculate the values of A and E_a .

Predict the rate constant at 30 ° and 50 °C.

Answer :

From the given data, we obtain

	T/°C	0	20	40	60	80	
	T/\mathbf{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	
	$10^5 \times k / s^{-1}$	0.0787	1.70	25.7	178	2140	
1125	ln <i>k</i>	- 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,



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

 $\Rightarrow E_a = -Slope \times R$
= $-(-12.301 \text{ K}) \times (8.314 \text{ J K}^{-1} \text{mol}^{-1})$
= $102.27 \text{ kJ mol}^{-1}$
Again,
In $k = \ln A - \frac{E_a}{RT}$
In $A = \ln k + \frac{E_a}{RT}$
When $T = 273 \text{ K}$,
In $k = -7.147$
Then, $\ln A = -7.147 + \frac{102.27 \times 10^3}{8.314 \times 273}$
= 37.911
Therefore, $A = 2.91 \times 10^6$
When $T = 30 + 273 \text{ K} = 303 \text{ K}$,
 $\frac{1}{T} = 0.0033 \text{ K} = 3.3 \times 10^{-3} \text{ K}$,
In $k = -2.8$
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 × 10-5S-1

T= 546 K *E*_a= 179.9 kJ mol⁻¹= 179.9 × 10³J mol⁻¹

According to the Arrhenius equation,

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

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

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

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

$$= \log (2.418 \times 10^{-5} \text{ s}^{-1}) + \frac{179.9 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ Jk}^{-1} \text{ mol}^{-1} \times 546 \text{ K}}$$

= (0.3835 - 5) + 17.2082

= 12.5917

Therefore, A = antilog (12.5917)

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

Q24 :

Consider a certain reaction A \rightarrow 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.

Answer :

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

T= 100 s

[A]₀= 1.0 moL⁻¹

Since the unit of k is s⁻¹, the given reaction is a first order reaction.

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

Therefore,



$$\Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} = \frac{2.303}{100 \text{ s}} \log \frac{1.0}{[\text{A}]}$$
$$\Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} = \frac{2.303}{100 \text{ s}} \left(-\log[\text{A}]\right)$$
$$\Rightarrow -\log[\text{A}] = \frac{2.0 \times 10^{-2} \times 100}{2.303}$$
$$\Rightarrow [\text{A}] = \operatorname{anti} \log \left(-\frac{2.0 \times 10^{-2} \times 100}{2.303}\right)$$

= 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,

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

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

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

Therefore,

$$=\frac{0.693}{3}$$
 h⁻¹

= 0.231 h⁻¹

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



$$\Rightarrow \log \frac{\left[R\right]_{0}}{\left[R\right]} = \frac{0.231 \text{ h}^{-1} \times 8 \text{ h}}{2.303}$$
$$\Rightarrow \frac{\left[R\right]_{0}}{\left[R\right]} = \text{antilog}(0.8024)$$
$$\Rightarrow \frac{\left[R\right]_{0}}{\left[R\right]} = 6.3445$$
$$\Rightarrow \frac{\left[R\right]_{0}}{\left[R\right]_{0}} = 0.1576 \text{ (approx)}$$
$$= 0.158$$

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 x 1011 S-1) e-28000 K/T Calculate

Ea.

Answer :

The given equation is

k = (4.5 × 1011 S-1) е-28000 к/Т (i)

Arrhenius equation is given by,

 $k = \mathrm{Ae}^{-E_{g}/\mathrm{R}T}$ (ii)

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

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

= 8.314 J K⁻¹mol⁻¹x 28000 K

= 232792 J mol⁻¹ = 232.792 kJ mol⁻¹

Q27 :



The rate constant for the first order decomposition of H₂O₂ is given by the following equation:

log $k = 14.34 - 1.25 \times 10^4 \text{ K/T}$ Calculate E_{a} for this reaction and at what temperature will its half-period be 256 minutes?

Answer :

Arrhenius equation is given by,

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

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

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

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

The given equation is

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

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

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

= 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,

$$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{256}$$

= 2.707 x 10⁻³min⁻¹

= 4.51 × 10.5S-1

It is also given that, log k= 14.34 - 1.25 × 10⁴K/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 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 mol¹. At what temperature would k be 1.5 x 10⁴ s⁻¹?

Answer :

From Arrhenius equation, we obtain

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

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

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

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

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

Then,



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

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

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

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

$$\Rightarrow 0.9528 T_2 = 283$$

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

= 297 K = 24°C

Hence, k would be 1.5×10^4 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 x 10^{10} s⁻¹. Calculate *k* at 318 K and *E*_a.

Answer :



For a first order reaction,

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

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

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

$$t' = \frac{2.303}{k'} \log \frac{100}{75}$$

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

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



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

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

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

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

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

To calculate k at 318 K,

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

Again, from Arrhenius equation, we obtain

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

= $\log (4 \times 10^{10}) - \frac{76.64 \times 10^3}{2.303 \times 8.314 \times 318}$
= $(0.6021 + 10) - 12.5876$
= -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



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

It is given that, $k_2 = 4k_1$
 $T_1 = 293 \,\text{K}$
 $T_2 = 313 \,\text{K}$
Therefore, $\log \frac{4k_1}{k_2} = \frac{E_a}{2.303 \times 8.314} \left(\frac{313 - 293}{293 \times 313} \right)$
 $\Rightarrow 0.6021 = \frac{20 \times E_a}{2.303 \times 8.314 \times 293 \times 313}$
 $\Rightarrow E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20}$
 $= 52863.33 \,\text{J mol}^{-1}$
 $= 52.86 \,\text{kJ mol}^{-1}$

Hence, the required energy of activation is 52.86 kJmol⁻¹.