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

$$=-\frac{\left[\mathbf{R}\right]_{2}-\left[\mathbf{R}\right]_{1}}{t_{2}-t_{1}}$$

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

$$=-\frac{-0.01}{25}$$
 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-1 to 0.4 mol L-1 in 10 minutes. Calculate the rate during this interval?

Answer:

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

$$=-\frac{1}{2}\frac{\left[\mathbf{A}\right]_{2}-\left[\mathbf{A}\right]_{1}}{t_{2}-t_{1}}$$

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

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

= 0.005 mol L⁻¹ min⁻¹

= 5 x10⁻³M min⁻¹

Q3:

For a reaction, A + B $\tilde{A} \notin \hat{a} \in \hat{P}$ roduct; the rate law is given by, $r = k \left[A \right]^{1/2} \left[B \right]^2$. What is the order of the reaction?

Answer:

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

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

= 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 $X \rightarrow Y$ 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 =
$$k \cdot (a)^2$$

$$= ka^2$$

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

Now, the rate equation will be:

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 = $1.15 \cdot 10^{-3} \text{s}^{-1}$

We know that for a 1storder reaction,

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

$$=\frac{2.303}{1.15\times10^{-3}}\log\frac{5}{3}$$

$$=\frac{2.303}{1.15\times10^{-3}}\times0.2219$$

= 444.38 s

= 444 s (approx)

Q6:

Time required to decompose SO₂Cl₂to 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

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

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

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

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

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,

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

Where,

A is the Arrhenius factor or the frequency factor

Tis the temperature

Ris the gas constant

E_ais 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 $T_1 = 298 \text{ K}$

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

$$= 308 K$$

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:

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

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

$$\Rightarrow E_{\rm a} = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2}{10}$$

= 52897.78 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:

 $E_{\rm a} = 209.5 \text{ kJ mol}^{-1} = 209500 \text{ J mol}^{-1}$

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- $E_d/RT \Rightarrow In x=-E$

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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) â†' N₂O(g) Rate = k[NO]²

(ii) H₂O₂ (aq) + 3 I⁻(aq) + 2 H⁺â†' 2 H₂O (I) +
$$I_3^-$$
 Rate = $k[H_2O_2][I^-]$

(iv)
$$C_2H_5CI(g)$$
 \tilde{A} ¢â€ ' $C_2H_4(g)$ + HCI(g) Rate = k [C_2H_5CI]

Answer:

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

Therefore, order of the reaction = 2

$$k = \frac{\text{Rate}}{\left[\text{NO}\right]^2}$$
 Dimension of

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

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

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

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

Therefore, order of the reaction = 2

$$k = \frac{\text{Rate}}{\left[\text{H}_2\text{O}_2\right]\!\!\left[\text{I}^-\right]}$$
 Dimension of

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

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

Therefore, order of reaction = $\overline{2}$

$$k = \frac{\text{Rate}}{\left[\text{CH}_3\text{CHO}\right]^{\frac{3}{2}}}$$

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

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

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

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

Therefore, order of the reaction = 1

$$k = \frac{\text{Rate}}{\left[\text{C}_2\text{H}_5\text{Cl}\right]}$$

Dimension of

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

Q2:

For the reaction:

$$2A + B \rightarrow A_2B$$

the rate = $k[A][B]^2$ with $k= 2.0 \times 10^6$ mol²L²s¹. Calculate the initial rate of the reaction when [A] = 0.1 mol L¹, [B] = 0.2 mol L¹. Calculate the rate of reaction after [A] is reduced to 0.06 mol L¹.

Answer:

The initial rate of the reactionis

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

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

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

When [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

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

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

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

After [A] is reduced to 0.06 mol L⁻¹, the rate of the reaction is given by,

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

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

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

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.

$$2 \text{ NH}_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3 \text{ H}_{2(g)}$$

Therefore,

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,

$$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = k$$
$$= 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$$

Therefore, the rate of production of N2is

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

And, the rate of production of H2is

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

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

Q4:

The decomposition of dimethyl ether leads to the formation of CH₄, H₂and 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.,

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

If the pressure is measured in bar and time 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 =
$$k \left(p_{\text{CH}_3\text{OCH}_3} \right)^{\frac{3}{2}}$$

$$\Rightarrow k = \frac{\text{Rate}}{\left(p_{\text{CH}_3\text{OCH}_3}\right)^{\frac{3}{2}}}$$

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

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

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

$$=4ka^2$$

$$= 4 R$$

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

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

$$\frac{1}{4}^{th}$$

Therefore, the rate of the reaction would be reduced to

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, kis the rate constant,

A is the Arrhenius factor or the frequency factor,

R is the gas constant,

Tis the temperature, and

E_ais 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,

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

- $= 4.67 \times 10^{-3} \text{mol L}^{-1} \text{s}^{-1}$
- (ii) For a pseudo first order reaction,

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

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

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

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

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

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

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

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

$$=\frac{\left(1.911\times10^{-2}\right)+\left(1.957\times10^{-2}\right)+\left(2.075\times10^{-2}\right)}{3}$$

 $=1.98\times10^{-2} \text{ s}^{-1}$

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

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

(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 (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
$r_{\hspace{-0.05cm} olimits}$ mol $L^{\scriptscriptstyle{-1}}$ $s^{\scriptscriptstyle{-1}}$	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 xand with respect to B be y.

Therefore,

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

$$5.07 \times 10^{-5} = k \left[0.20 \right]^{x} \left[0.30 \right]^{y}$$
(i)
$$5.07 \times 10^{-5} = k \left[0.20 \right]^{x} \left[0.10 \right]^{y}$$
(ii)
$$1.43 \times 10^{-4} = k \left[0.40 \right]^{x} \left[0.05 \right]^{y}$$
(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

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

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

$$\Rightarrow 2.821 = 2^{x}$$

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

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

= 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 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 xand 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

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

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

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

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

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

 $\Rightarrow x = 1$

Therefore, the rate law is

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

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

From experiment I, we obtain

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

= 6.0 L²mol⁻²min⁻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

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

= 6.0 L²mol⁻²min⁻¹

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

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
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 x 10⁻²mol L⁻¹min⁻¹= k (0.1 mol L⁻¹)

 \Rightarrow k= 0.2 min⁻¹

From experiment II, we obtain

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

 \Rightarrow [A] = 0.2 mol L⁻¹

From experiment III, we obtain

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

= 0.08 mol L-1min-1

From experiment IV, we obtain

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

 \Rightarrow [A] = 0.1 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,
$$t_{1/2} = \frac{0.693}{k}$$

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

= 3.47×10^{-3} s (approximately)

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

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

= 0.35 min (approximately)

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

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

= 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:

$$k = \frac{0.693}{t_{\frac{1}{2}}}$$
Here,
$$= \frac{0.693}{5730} \text{ years}^{-1}$$

It is known that,

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

= 1845 years (approximately)

Hence, the age of the sample is 1845 years.

Q15:

The experimental data for decomposition of N_2O_5

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

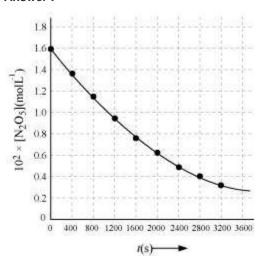
in gas phase at 318K are given below:

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 [N₂O₅] 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)

Answer:



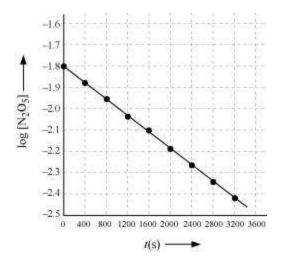
$$\frac{1.630 \times 10^{2}}{2} \, \text{mol} \, L^{-1} = 81.5 \, \text{mol} \, L^{-1},$$

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

is the half life. From the graph,

(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

Rate =
$$k[N_2O_5]$$

(v) From the plot, $\left. \log \left[N_2 O_5 \right] \right._{\text{v/s } \textit{t}, \text{ we obtain}}$

Slope =
$$\frac{-2.46 - (-1.79)}{3200 - 0}$$
$$= \frac{-0.67}{3200}$$

Again, slope of the line of the plot $\log[\mathrm{N_2O_5}]$ 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,

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

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

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

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

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:

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

Here,

It is known that,

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

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

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

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

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

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

$$= 0.7814 \mu g$$

Therefore, 0.7814 μg of 90Sr 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 μg of 90Sr 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

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

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

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

= 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.

$$(CH_3)_2 CHN=NCH(CH_3)_{2(g)} \longrightarrow N_{2(g)} + C_6H_{14(g)}$$
At $t=0$ P_0 0 0
At $t=t$ P_0-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,

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

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

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

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

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

Hence, the average value of rate constant is

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

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

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 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.

Answer:

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

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

$$\Rightarrow P_{t} = P_{0} + p$$

$$\Rightarrow p = P_t - P_0$$

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

$$= 2 P_0 - P_t$$

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

 $= 2.231 \times 10^{-3} \text{s}^{-1}$ When P = 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 SOCl₂is

$$p_{SOCl_2} = P_0 - p$$

$$= 0.5 - 0.15$$

$$= 0.35 atm$$

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

Rate =
$$k(P_{SOCI_2})$$

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

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

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

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

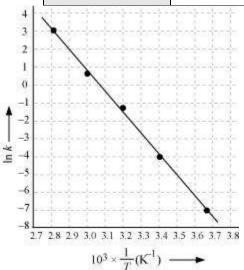
Draw a graph between $\ln k$ and 1/T and calculate the values of A and E_a .

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

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

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,

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

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

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

$$\ln k = -7.147$$

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

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

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

$$\ln k = -2.8$$

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

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

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:

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

 E_a = 179.9 kJ mol⁻¹= 179.9 x 10³J mol⁻¹

According to the Arrhenius equation,

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

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

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

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

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

= (0.3835 - 5) + 17.2082

= 12.5917

Therefore, A = antilog (12.5917)

= $3.9 \times 10^{12} s^{-1}$ (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:

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

T = 100 s

 $[A]_{o} = 1.0 \text{ moL}^{-1}$

Sincethe 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,

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

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

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

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

= 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,

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

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
$$^{-1}$$
 = $\frac{2.303}{8 \text{ h}} log \frac{\left[R\right]_0}{\left[R\right]}$

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

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

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

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

$$= 0.158$$

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

Q26:

The decomposition of hydrocarbon follows the equation

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

Calculate Ea.

Answer:

The given equation is

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

Arrhenius equation is given by,

$$k = Ae^{-E_{\sigma}/RT}$$
 (ii)

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

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

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

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

= 232792 J mol-1

= 232.792 kJ mol-1

Q27:

The rate constant for the first order decomposition of H₂O₂is 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,

$$k = Ae^{-E_{\sigma}/RT}$$

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

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

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

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

= 1.25×10^{4} K × 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,

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

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

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

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

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

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

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

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

= 668.95 K

= 669 K (approximately)

Q28:

The decomposition of A into product has value of k as 4.5 x 10 $^{\circ}$ s⁻¹ at 10 $^{\circ}$ C and energy of activation 60 kJ mol⁻¹. At what temperature would k be 1.5 x 10 $^{\circ}$ s⁻¹?

Answer:

From Arrhenius equation, we obtain

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

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

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

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

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

Then,

$$\log \frac{1.5 \times 10^{4}}{4.5 \times 10^{3}} = \frac{6.0 \times 10^{4} \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{T_{2} - 283}{283 T_{2}} \right)$$

$$\Rightarrow 0.5229 = 3133.627 \left(\frac{T_{2} - 283}{283 T_{2}} \right)$$

$$\Rightarrow \frac{0.5229 \times 283 \ T_{2}}{3133.627} = T_{2} - 283$$

$$\Rightarrow 0.0472 T_{2} = T_{2} - 283$$

$$\Rightarrow 0.9528 \ T_{2} = 283$$

$$\Rightarrow T_{2} = 297.019 \text{ K (approximately)}$$

= 297 K

Hence, *k* would be $1.5 \times 10^4 \, \text{s}^{-1}$ 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 4×10^{10} s⁻¹. Calculate k at 318 K and E_a .

Answer:

For a first order reaction,

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

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

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

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

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

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

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

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

To calculate k at 318 K,

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

Again, from Arrhenius equation, we obtain

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

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

$$= \left(0.6021 + 10\right) - 12.5876$$

$$= -1.9855$$

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.