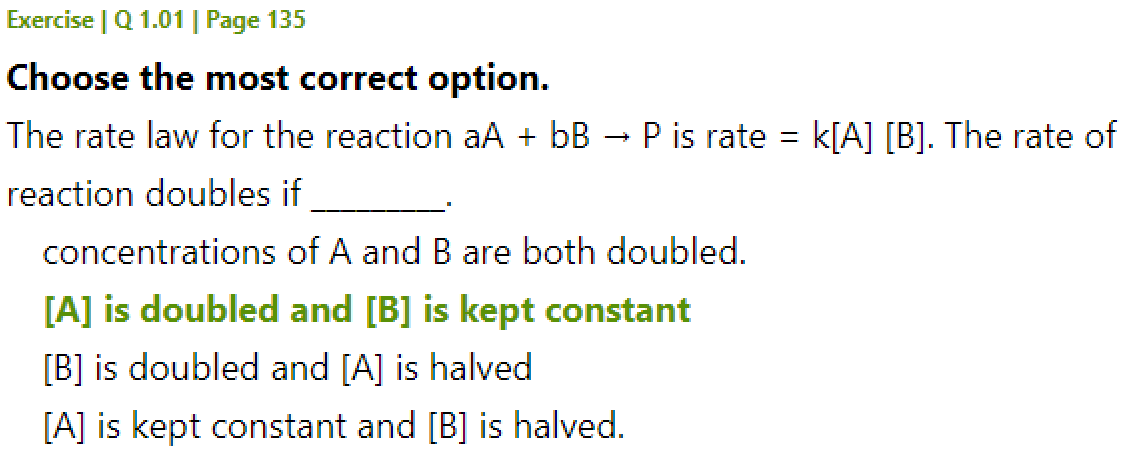
Chemical Kinetics

EXERCISE [PAGES 135 - 137]



Exercise | Q 1.01 | Page 135

Choose the most correct option.

The rate law for the reaction aA + bB → P is rate = k[A] [B]. The rate of reaction doubles if _______.

concentrations of A and B are both doubled.

[A] is doubled and [B] is kept constant

[B] is doubled and [A] is halved

[A] is kept constant and [B] is halved.

Solution:

The rate law for the reaction aA + bB → P is rate = k[A] [B]. The rate of reaction doubles if **[A] is doubled and [B] is kept constant**

Exercise | Q 1.02 | Page 135

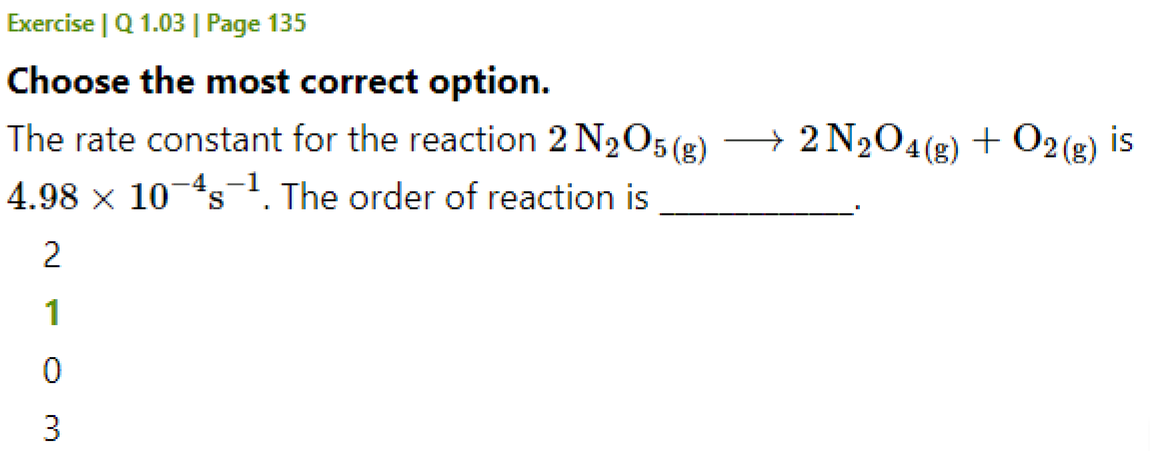
Choose the most correct option.

The order of the reaction for which the units of the rate constant are mol dm^{-3} s^{-1} is _______.

1. 1
2. 3
3. **0**
4. 2

Solution:

The order of the reaction for which the units of the rate constant are mol dm^{-3} s^{-1} is **0**.



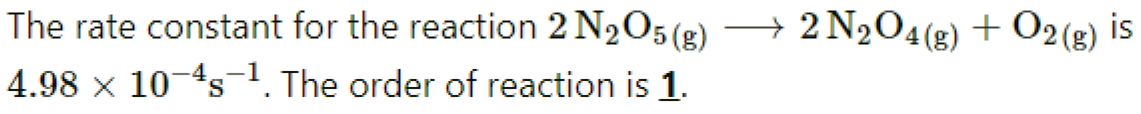
Exercise | Q 1.03 | Page 135

Choose the most correct option.

The rate constant for the reaction $2\,N_2O_{5\,(g)} \longrightarrow 2\,N_2O_{4\,(g)} + O_{2\,(g)}$ is $4.98 \times 10^{-4} s^{-1}$. The order of reaction is __________.

- 2
- **1**
- 0
- 3

Solution:



The rate constant for the reaction $2\,N_2O_{5\,(g)} \longrightarrow 2\,N_2O_{4\,(g)} + O_{2\,(g)}$ is $4.98 \times 10^{-4} s^{-1}$. The order of reaction is <u>**1**</u>.

Exercise | Q 1.04 | Page 135

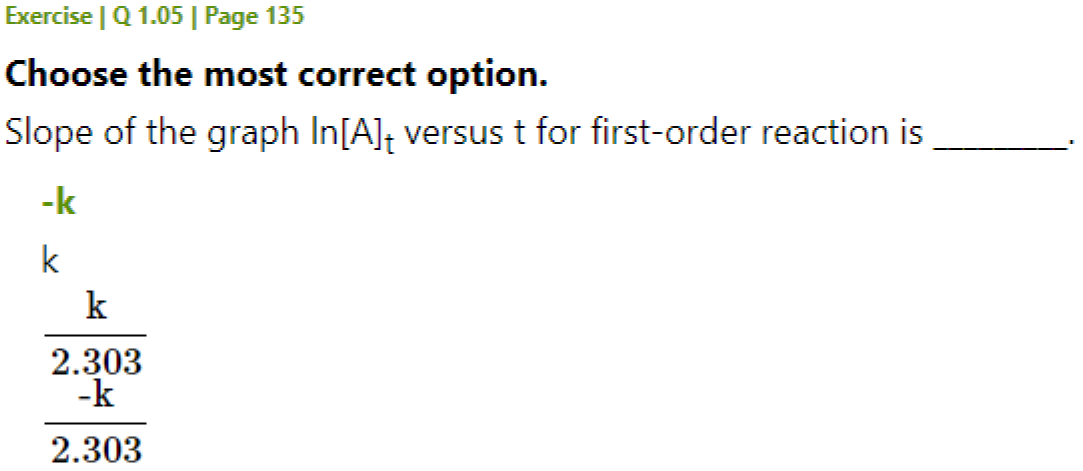
Choose the most correct option.

The time required for 90 % completion of a certain first-order reaction is t. The time required for 99.9 % completion will be _________.

1. t
2. 2t
3. t/2
4. **3t**

Solution:

The time required for 90 % completion of a certain first-order reaction is t. The time required for 99.9 % completion will be **3t** .



Exercise | Q 1.05 | Page 135

Choose the most correct option.

Slope of the graph $\ln[A]_t$ versus t for first-order reaction is _______.

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

Solution:

The slope of the graph ln[A]t versus t for the first-order reaction is **-k.**

Exercise | Q 1.06 | Page 135

Choose the most correct option.

What is the half-life of a first-order reaction if the time required to decrease the concentration of reactant from 0.8 M to 0.2 M is 12 h?

1. 12 h
2. 3 h
3. 1.5 h
4. **6 h**

Solution: 6 h

Exercise | Q 1.07 | Page 135

Choose the most correct option.

The reaction, $3\,ClO^- \longrightarrow ClO_3^- + 2\,Cl^-$ occurs in two steps,

(i) $2\,ClO^- \longrightarrow ClO_2^-$

(ii) $ClO_2^- + ClO^- \longrightarrow ClO_3^- + Cl^-$

The reaction intermediate is ______.

Cl^-

ClO_2^-

ClO_3^-

ClO^-

Solution:

The reaction, $3\,ClO^- \longrightarrow ClO_3^- + 2\,Cl^-$ occurs in two steps,

(i) $2\,ClO^- \longrightarrow ClO_2^-$

(ii) $ClO_2^- + ClO^- \longrightarrow ClO_3^- + Cl^-$

The reaction intermediate is ClO_2^-.

Exercise | Q 1.08 | Page 135

Choose the most correct option.

The elementary reaction $O_{3(g)} + O_{(g)} \longrightarrow 2\,O_{2(g)}$ is _________.

1. unimolecular and second order
2. bimolecular and first order
3. **bimolecular and second order**
4. unimolecular and first order

Solution:

The elementary reaction $O_{3(g)} + O_{(g)} \longrightarrow 2\,O_{2(g)}$ is **bimolecular and second order.**

Exercise | Q 1.09 | Page 135

Choose the most correct option.

Rate law for the reaction, $2\,\mathrm{NO} + \mathrm{Cl_2} \longrightarrow 2\,\mathrm{NOCl}$ is rate = $k[NO_2]^2[Cl_2]$.

Thus of k would increase with __________.

1. **increase in temperature**
2. increase of concentration of NO
3. increase of concentration of Cl_2
4. increase of concentrations of both Cl_2 and NO

Solution:

Rate law for the reaction, $2\,\mathrm{NO} + \mathrm{Cl_2} \longrightarrow 2\,\mathrm{NOCl}$ is rate = $k[NO_2]^2[Cl_2]$.

Thus of k would increase with **increase in temperature.**

Exercise | Q 1.1 | Page 135

Choose the most correct option.

For an endothermic reaction, X ⇌ Y. If E_f is the activation energy of the forward reaction and E_r that for the reverse reaction, which of the following is correct?

1. $E_f = E_r$
2. $E_f < E_r$
3. **$E_f > E_r$**
4. $\Delta H = E_f - E_r$ is negative

Solution: $E_f > E_r$

Exercise | Q 2.01 | Page 136

Answer the following in one or two sentences.

For the reaction,

$\mathrm{N_{2\,(g)}} + 3\,\mathrm{H_{2\,(g)}} \longrightarrow 2\,\mathrm{NH_{3\,(g)}}$,

what is the relationship among $\frac{d[N_2]}{dt}$, $\frac{d[H_2]}{dt}$ and $\frac{d[NH_3]}{dt}$?

Solution:

The relationship between $\frac{d[N_2]}{dt}$, $\frac{d[H_2]}{dt}$ and $\frac{d[NH_3]}{dt}$ is $-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

Exercise | Q 2.02 | Page 136

Answer the following in one or two sentences.

For the reaction,

$\mathrm{CH_3Br_{(aq)}} + \mathrm{OH^-_{(aq)}} \longrightarrow \mathrm{CH_3OH^-_{(aq)}} + \mathrm{Br^-_{(aq)}}$, rate law is rate = k $[\mathrm{CH_3Br}][\mathrm{OH^-}]$

a. How does the reaction rate change if $[\mathrm{OH^-}]$ is decreased by a factor of 5?

b. What is the change in rate if concentrations of both reactants are doubled?

Solution:

For the reaction

$$CH_3Br_{(aq)} + Br^-_{(aq)} \longrightarrow CH_3OH_{(aq)} + Br^-_{(aq)}$$

Rate = $k[CH_3Br]\left[OH^-\right]$

i. If $\left[OH^-\right]$ is increased by a factor of 5, keeping $[CH_3Br]$ constant rate will increase by a factor of 5.

ii. If concentrations of CH_3Br and OH^- are doubled, rate will increase by a factor of 4.

Exercise | Q 2.03 | Page 136

Answer the following in one or two sentences.

What is the relationship between coefficients of reactants in a balanced equation for an overall reaction and exponents in the rate law? In what case the coefficients are the exponents?

Solution:

Coefficients of reactants in a balanced chemical equation may or may not be the same as the exponents in rate law for the same reaction. For elementary reaction, coefficients in a balanced chemical equation are the same as the exponents in the rate law.

Exercise | Q 2.04 | Page 136

Answer the following in one or two sentences.

Why all collisions between reactant molecules do not lead to a chemical reaction?

Solution:

All collisions of reactant molecules do not lead to a chemical reaction because the colliding molecules need to possess certain energy which is greater than the activation energy E_a and proper orientation.

Exercise | Q 2.05 | Page 136

Answer the following in one or two sentences

What is the activation energy of a reaction?

Solution:

For the reaction to occur the colliding reactant molecules must possess the minimum kinetic energy. This minimum kinetic energy is the activation energy.

Exercise | Q 2.06 | Page 136

Answer the following in one or two sentences.

What are the units for rate constants for zero-order and second-order reactions if time is expressed in seconds and concentration of reactants in mol/L?

Solution:

Units of rate constant

i. Zero-order reaction is mol L^{-1} s^{-1}

ii. The second-order reaction is mol^{-1} L s^{-1}

Exercise | Q 2.07 | Page 136

Answer the following in one or two sentences.

Write the Arrhenius equation and explain the terms involved in it.

Solution:

Arrhenius equation: $k = Ae^{\frac{-E_a}{RT}}$

where k is the rate constant, E_a is the activation energy, R molar gas constant, T temperature in kelvin and A is the pre-exponential factor.

Exercise | Q 2.08 | Page 136

Answer the following in one or two sentences.

What is the rate-determining step?

Solution:

When a chemical reaction occurs in a series of steps, one of the steps is slower than all other steps. Such a slowest step in the reaction is called a rate-determining step.

Exercise | Q 2.09 | Page 136

Answer the following in one or two sentences.

Write the relationships between rate constant and half-life of the first order and zeroth-order reactions.

Solution:

i. First-order reaction: $t_{\frac{1}{2}} = \frac{0.693}{k}$

ii. Zero order reaction: $t_{\frac{1}{2}} = \frac{[A_0]}{2k}$

Exercise | Q 2.1 | Page 136

Answer the following in one or two sentences.

How do the half-lives of the first order and zero-order reactions change with the initial concentration of reactants?

Solution:

i. The half-life of the first-order reaction is independent of the initial concentration of the reactant.

ii. The half-life of zero-order reactions is proportional to the initial concentration of the reactant.

Exercise | Q 3.01 | Page 136

Answer the following in brief.

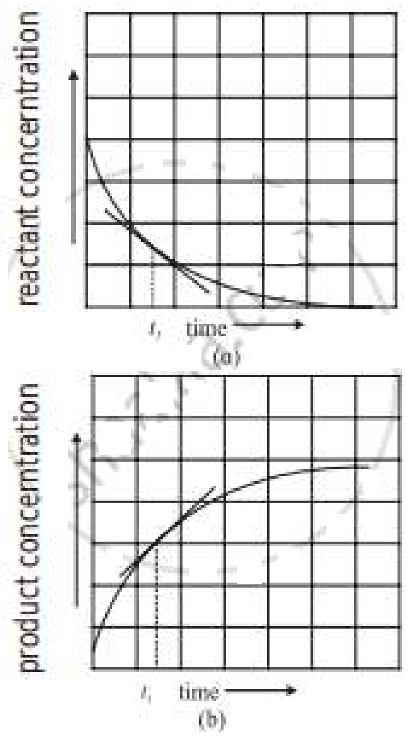
How instantaneous rate of reaction is determined?

Solution:

i. To determine the instantaneous rate of a reaction the progress of a reaction is followed by measuring the concentrations of a reactant or product for different time intervals.

ii. The concentration of a reactant or a product is plotted against time.

iii. A tangent drawn to the curve at time t_1 gives the rate of the reaction. The slope thus obtained gives the instantaneous rate of the reaction at time t_1.



Determination of instantaneous rate

iv. Mathematically the instantaneous rate is expressed by replacing Δ by derivative dc/dt in the expression of the average rate.

Instantaneous rate = $\frac{d[C]}{dt}$

v. For a reaction A → B

Instantaneous rate of consumption of A at time t = $-\frac{d[A]}{dt}$

Instantaneous rate of the formation of B at time t = $\frac{d[B]}{dt}$

Therefore, instantaneous rate of the reaction at time t = $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$

Exercise | Q 3.02 | Page 136

Answer the following in brief.

Distinguish between order and molecularity of a reaction.

Solution:

	Order	**Molecularity**
i.	It is an experimentally determined property.	It is a theoretical entity.
ii.	It is the sum of powers of the concentration terms of reactants that appear in the rate equation.	It is the number of reactant molecules taking part in an elementary reaction.
iii.	It may be an integer, fraction, or zero.	It is an integer.
iv.	It is not based on a balanced chemical equation.	It is based on a balanced chemical equation.

Exercise | Q 3.03 | Page 136

Answer the following in brief.

A reaction takes place in two steps,

1. $NO_{(g)} + Cl_{2(g)} \longrightarrow NOCl_{2(g)}$

2. $NOCl_{2(g)} + NO_{(g)} \longrightarrow 2NOCl_{(g)}$

a. Write the overall reaction.

b. Identify the reaction intermediate.

c. What is the molecularity of each step?

Solution:

i. The overall reaction: $2\,NO_{(g)} + Cl_{2(g)} \longrightarrow 2\,NOCl_{(g)}$

ii. Since, $NOCl_2$ is formed in the first step and consumed in the second step. Hence, it is the reaction intermediate.

iii. The molecularity of each step is 2 because two reactants are involved in each of the steps.

Exercise | Q 3.04 | Page 136

Answer the following in brief.

Obtain the relationship between the rate constant and half-life of a first-order reaction.

Solution:

i. The integrated rate law for the first-order reaction is k =
$$\frac{2.303}{t}\log_{10}\frac{A_0}{A_t}$$

where $[A]_0$ is the initial concentration of a reactant at t = 0. It falls to $[A]_t$ at time t after the start of the reaction. T

ii. The time required for $[A]_0$ to become $\frac{[A]_0}{2}$ is denoted as $t_{\frac{1}{2}}$ or

$[A]_t = \frac{[A]_0}{2}$ at $t = t_{1/2}$

Putting this condition in the integrated rate law we write

$$k = \frac{2.303}{t_{\frac{1}{2}}}\log_{10}\frac{[A]_t}{\frac{[A]_0}{2}} = \frac{2.303}{t_{\frac{1}{2}}}\log_{10}2$$

Substituting value of $\log_{10} 2$,

$$k = \frac{2.303}{t_{\frac{1}{2}}} \times 0.3010$$

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

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

Exercise | Q 3.05 | Page 136

Answer the following in brief.

How will you represent the zeroth-order reaction graphically?

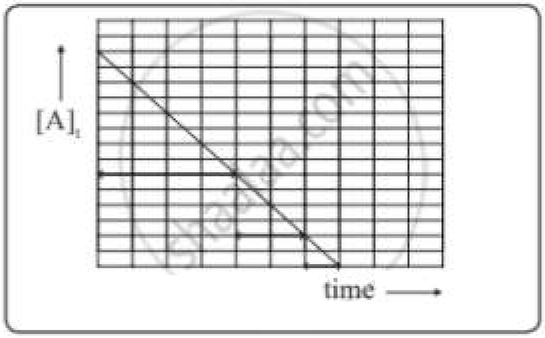
Solution:

Graphical representation of zero-order reactions: The rate law is given as

$$\underset{y}{\underset{\updownarrow}{[A]_t}} = -\underset{m}{\underset{\updownarrow}{k}}\ \underset{x}{\underset{\updownarrow}{t}} + \underset{c}{\underset{\updownarrow}{[A]_0}}$$

which is a straight line given by y = mx + c.

A plot of $[A]_t$ versus t is a straight line.



[A]t vs t for zero-order reaction

The slope of the straight line is -k and its intercept on the y-axis is $[A]_0$.

Exercise | Q 3.06 | Page 136

Answer the following in brief.

What are pseudo-first-order reactions? Give one example and explain why it is pseudo-first-order.

Solution:

i. Certain reactions that are expected to be of higher order follow the first-order kinetics. Such reactions are said to be pseudo-first-order reactions.

ii. **Example**: Consider the hydrolysis of methyl acetate.

$$CH_3COOCH_{3\,(aq)} + H_2O_{(l)} \longrightarrow CH_3COOH_{(aq)} + CH_3OH_{(aq)}$$

The rate law is rate = k' $[CH_3COOCH_3][H_2O]$

iii. **Explanation**: The reaction was expected to follow the second-order kinetics, however, obeys the first order. The reason is that solvent water is present in such large excess that the change in its concentration is negligible compared to the initial one or its concentration remains constant. Thus $[H_2O]$ = constant = k''. The rate law becomes rate = k' $[CH_3COOCH_3]$k'' = k $[CH_3COOCH_3]$

where, k = k'k''

The reaction is thus of first order.

Exercise | Q 3.07 | Page 136

Answer the following in brief.

What are the requirements for the colliding reactant molecules to lead to products?

Solution:

The requirements for colliding molecules to form the product are as follows:

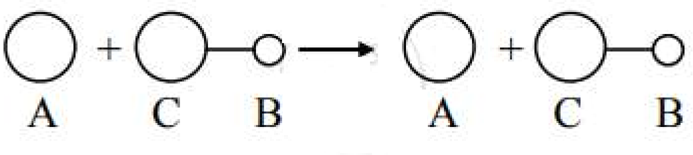
i. Activation energy: For the reaction to occur the colliding reactant molecules must possess the minimum kinetic energy. This minimum kinetic energy is the activation energy. The reaction would occur only if colliding molecules possess kinetic energies equal to or greater than the activation energy.

ii. The orientation of reactant molecules:

a. For reactions involving complex molecules or ions, reactant molecules must collide with proper orientation. The molecules need to be so oriented relative to each other that the reacting groups approach closely.

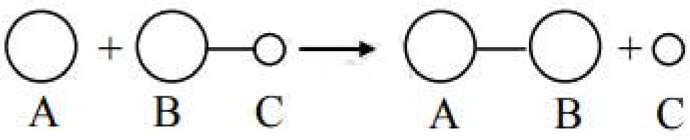
b. Consider, A + C - B → A - B + C

The collision of A with C approaching toward A would not lead to a reaction.



The reactant molecules would collide and separate owing to the improper orientation of C – B.

c. The reaction is successful as a result of proper orientation of C – B. A fraction of such collisions brings forth the conversion of reactants to products.

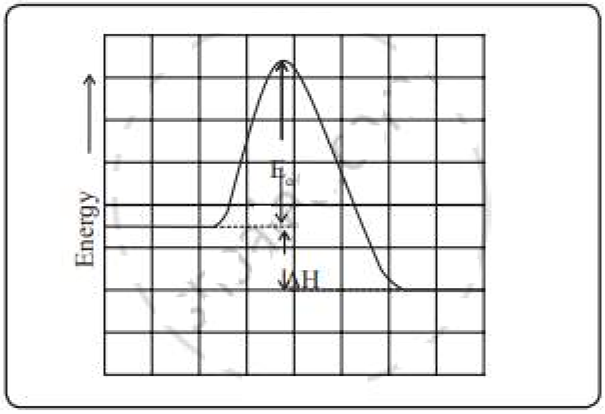


iii. Potential energy barrier:

Consider the reaction A + C – B → A – B + C

a. During a course of the collision, new bond A – B develops, and at the same time bond C – B breaks. An activated complex is formed in which all three atoms are weakly connected together. A + C – B → A-----B-----C → A – B + C

b. To attain the configuration A-----B-----C atoms need to gain energy, which comes from the kinetic energy of colliding molecules. The energy barrier between reactants and products is as shown in the diagram.



Potential energy barrier

c. To form an activated complex, the reactant molecules need to climb up and overcome the energy barrier before they get converted to products.

d. The height of the barrier is called activation energy (E_a). Thus, the reactant molecules transform into products only if they possess energy equal to or greater than such activation energy. As a result, only a few collisions lead to products.

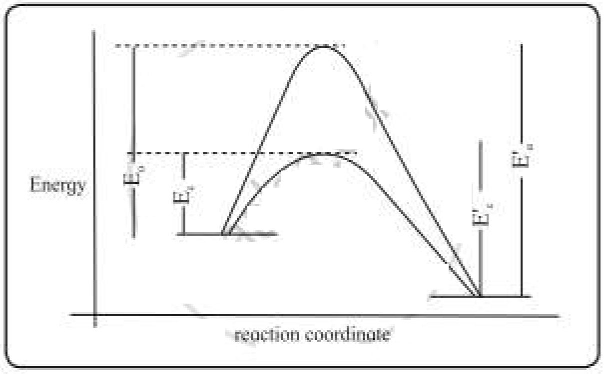
Exercise | Q 3.08 | Page 136

Answer the following in brief.

How a catalyst increases the rate of reaction? Explain with the help of a potential energy diagram for catalyzed and uncatalyzed reactions.

Solution:

i. A catalyst provides an alternative pathway associated with lower activation energy.



Potential energy barriers for catalyzed and uncatalyzed reactions

ii. The potential energy diagram compares the potential energy barriers for the catalysed and uncatalysed reactions. The barrier for uncatalysed reaction (E_a) is larger than that for the same reaction in the presence of a catalyst E_a.

iii. Consider the decomposition of H_2O_2 in aqueous solution catalysed by

I^- ions $2\,H_2O_{2\,(l)} \xrightarrow{I^-} 2\,H_2O_{(l)} + O_{2(g)}$.

At room temperature, the rate of reaction is slower in the absence of a catalyst with its activation energy being 76 kJ mol^{-1}. In the presence of catalyst, iodide ion (I^-), the reaction is faster since the activation energy decreases to 57 kJ mol^{-1}.

Exercise | Q 3.09 | Page 136

Answer the following in brief.

Explain with the help of the Arrhenius equation, how do the rate of reaction changes with (a) temperature and (b) activation energy.

Solution:

i. Arrhenius equation $k = e^{\frac{-E_a}{RT}}$ shows that as the temperature rises, $\frac{E_a}{RT}$ decreases, this causes an increase in $-\frac{E_a}{RT}$. This increases k and the rate of reaction.

ii. The decrease in energy of activation (E_a) decreases $\frac{E_a}{RT}$, hence, increases $-\frac{E_a}{RT}$ and the rate of reaction.

Exercise | Q 3.1 | Page 137

Answer the following in brief.

Derive the integrated rate law for the first-order reaction.

Solution:

Consider the first-order reaction,

A → product

The differential rate law is given by

rate = $-\frac{\mathrm{d[A]}}{\mathrm{dt}} = \mathrm{k[A]}$ ...(1)

where, [A] is the concentration of reactant at time t. Rearranging Eq. (1)

$\frac{\mathrm{d[A]}}{\mathrm{[A]}} = -\mathrm{k}$ dt .....(2)

Let $[A]_0$ be the initial concentration of the reactant A at time t = 0.

Suppose $[A]_t$ is the concentration of A at time = t

The equation (2) is integrated between limits $[A] = [A]_0$ at t = 0 and $[A] = [A]_t$ at t = t

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$$

On integration,

$\mathrm{In[A]}_{\mathrm{[A]_0}}^{\mathrm{[A]_t}} = -\mathrm{k\ t}_0^{\mathrm{t}}$

Substitution of limits gives

$\mathrm{In[A]_t - In[A]_0 = -kt}$

or $\mathrm{In}\frac{\mathrm{[A]_t}}{\mathrm{[A]_0}} = -\mathrm{kt}$ ...(3)

or k = $\frac{1}{\mathrm{t}}\mathrm{In}\frac{\mathrm{[A]_0}}{\mathrm{[A]_t}}$

Converting In to $\log_{10}$, we write

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t} \quad \ldots(4)$$

Eq. (4) gives the integrated rate law for the first-order reactions.

Exercise | Q 3.11 | Page 137

Answer the following in brief.

How will you represent first-order reactions graphically?

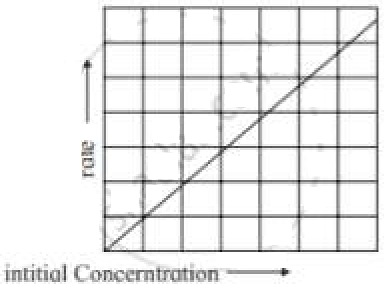
Solution:

i.

The differential rate law for the first-order reaction A → P is

$$\text{rate} = -\underset{\substack{\updownarrow \\ y}}{\frac{d[A]}{dt}} = \underset{\substack{\updownarrow \\ m}}{k}\,\underset{\substack{\updownarrow \\ x}}{[A]_t} + \underset{\substack{\updownarrow \\ c}}{0}$$

The equation is of the form y = mx + c. A plot of rate versus $[A]_t$ is a straight line passing through the origin. The slope of straight line = k.



Variation of rate with [A]

ii.

The integrated rate law is

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

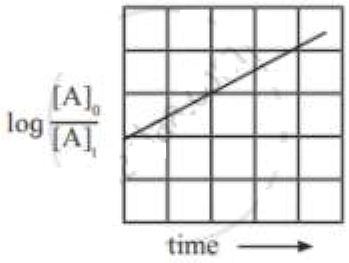
On rearrangement, the equation becomes

$$\frac{kt}{2.303} = \log_{10}[A]_0 - \log_{10}[A]_t$$

Hence,

$$\underset{\overset{\updownarrow}{y}}{\log_{10}[A]_t} = -\underset{\overset{\updownarrow}{m}}{\frac{k}{2.303}}\underset{\overset{\updownarrow}{x}}{t} + \underset{\overset{\updownarrow}{c}}{\log_{10}[A]_0}$$

The equation is of the straight line. A graph of $\log_{10}\frac{A_0}{[A_t]}$ versus t yields a straight line with slope $-\frac{k}{2.303}$ and y-axis intercepts as $\log_{10}[A]_0$.



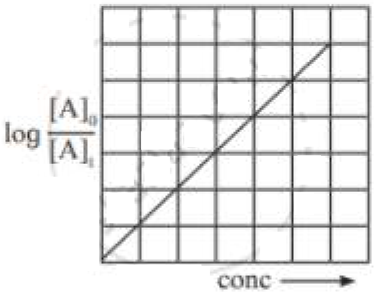
A plot showing log $\frac{[At]_t}{[A]_0}$ vs time

iii.

Rearranging the integrated rate law equation, we get

$$\underset{\underset{\text{v}}{\updownarrow}}{\log_{10}\frac{[A]_0}{[A]_t}} = \underset{\underset{\text{m}}{\updownarrow}}{\frac{k}{2.303}}\,\underset{\underset{x}{\updownarrow}}{t}$$

The equation has a straight-line form y = mx. Hence, the graph of $\log_{10}\frac{[A]_0}{[A]_t}$ versus t is a straight line passing through the origin.



Exercise | Q 3.12 | Page 137

Answer the following in brief.

Derive the integrated rate law for the first-order reaction,

$A_{(g)} \longrightarrow B_{(g)} + C_{(g)}$ in terms of pressure.

Solution:

i. For the gas phase reaction,

$AX_{(g)} \longrightarrow BX_{(g)} + CX_{(g)}$

Let initial pressure of A be P_i that decreases by x within time t.

ii. Pressure of reactant A at time t

$P_A = P_i - x$ ....(1)

The pressures of the products B and C at time t

$P_B = P_C = x$

iii. The total pressure at time t is then

$P = P_i - x + x + x = P_i + x$

Hence, $x = P - P_i$ …(2)

The pressure of A at time t is obtained by substitution of Eq. (1) into Eq. (2).

Thus

$P_A = P_i - (P - P_i) = P_i - P + P_i = 2P_i - P$

iv. The integrated rate law turns out to be

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

The concentration is now expressed in terms of pressures.

Thus, $[A]_0 = P_i$ and $[A]_t = P_A = 2P_i - P$

Substitution gives in above

$$k = \frac{2.303}{t} \log_{10} \frac{P_i}{2P_i - P} \quad ...(3)$$

P is the total pressure of the reaction mixture at time t.

Exercise | Q 3.13 | Page 137

Answer the following in brief.

What is a zeroth-order reaction? Derive its integrated rate law. What are the units of the rate constant?

Solution:

i. Reactions in which the rate is independent of the reactant concentration are zeroth-order reaction.

ii. **The integrated rate law for zero-order reactions:**

For zero-order reaction, A → P

the differential rate law is given by

rate = $-\frac{d[A]}{A}$ = $k[A]_0 = k$ ...(1)

Rearrangement of Eq. (1) gives

$d[A] = -k\,dt$ $(\because [A]^0 = 1)$

Integration between the limits

$[A] = [A]_0$ at $t = 0$ and $[A] = [A]_t$ at $t = t$ gives

$$\int_{[A]_0}^{[A]_t} d[A] = -k \int_0^t dt$$

or $[A]_t - [A]_0 = -kt$

Hence, $kt = [A]_0 - [A]_t$ ....(2)

iii. The unit of rate constant for the zero order reaction is mol dm^{-3} s^{-1} .

Exercise | Q 3.14 | Page 137

Answer the following in brief.

How will you determine activation energy:

(a) graphically using Arrhenius equation

(b) from rate constants at two different temperatures?

Solution:

I.

Graphical representation of activation energy

Arrhenius equation is $\mathbf{k} = \mathbf{A}\mathbf{e}^{\frac{-E_a}{RT}}$

Taking the logarithm of both sides of Eqn. we obtain

In k = $-\frac{E_a}{RT} + \text{In A}$

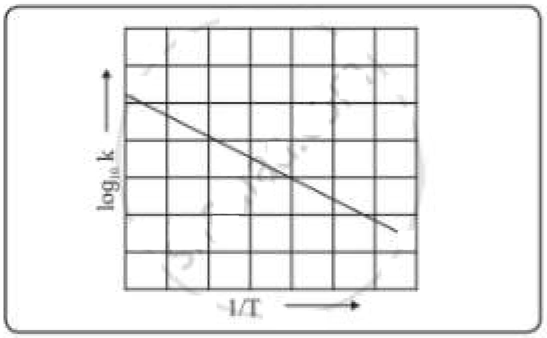
Converting the natural base to base 10 we write

$$\underset{\underset{y}{\updownarrow}}{\log_{10}k} = -\underset{\underset{m}{\updownarrow}}{\frac{E_a}{2.303\,R}}\,\underset{\underset{x}{\updownarrow}}{\frac{1}{T}} + \underset{\underset{c}{\updownarrow}}{\log_{10}A}$$

This equation is of the form of straight-line y = mx + c.

The Arrhenius plot of $\log_{10}k$ versus $\frac{1}{T}$ gives a straight line as shown in the diagram. A slope of the line is $-\frac{E_a}{2.303R}$ with its intercept being $\log_{10}A$.

From a slope of the line, the activation energy can be determined.



Variation of $\log_{10}k$ with 1/T

ii.

Determination of activation energy from rate constants at two different temperatures.

Arrhenius equation is k = $Ae^{\frac{-E_a}{RT}}$

From two different temperatures T_1 and T_2

$$\log_{10}k_1 = \log_{10}A - \frac{E_a}{2.303RT_1} \quad ....(1)$$

$$\log_{10}k_2 = \log_{10}A - \frac{E_a}{2.303RT_2} \quad ....(2)$$

where k_1 and k_2 are the rate constants at temperatures T_1 and T_2 respectively.

Subtracting Eq.(1) from Eq.(2),

$$\log_{10}k_2 - \log_{10}k_1 = -\frac{E_a}{2.303R}\frac{1}{T_2} + \frac{E_a}{2.303R}\frac{1}{T_1}$$

$$\text{Hence, } \log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

Exercise | Q 3.15 | Page 137

Answer the following in brief.

Explain graphically the effect of temperature on the rate of reaction.

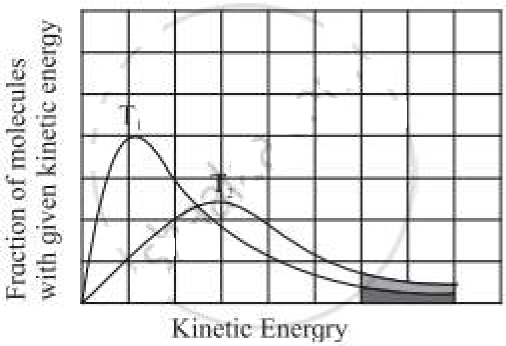
Solution:

i. The average kinetic energy of molecules is proportional to temperature.

ii. At a given temperature, the fraction of molecules with their kinetic energy equal to or greater than E_a may lead to the product.

iii. With an increase in temperature, the fraction of molecules having their energies (E_a) would increases. The rate of the reaction thus would increase.

iv. This is depicted by plotting a fraction of molecules with given kinetic energy versus kinetic energy for two different temperatures T_1 and T_2 ($T_2 > T_1$). The area between the curve and the horizontal axis is proportional to the total number of molecules. The total area is the same at T_1 and T_2.



Comparison of fraction of molecules activated at T_1 and T_2

v. The entire shaded area which represents a fraction of molecules with kinetic energy exceeding E_a is larger at T_2 than at T_1 (since $T_2 > T_1$).

vi. This indicates that a fraction of molecules possessing energies larger than E_a increase with temperature. The rate of reaction increases accordingly.

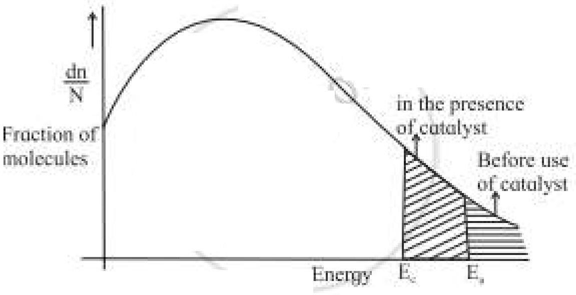
Exercise | Q 3.16 | Page 137

Answer the following in brief.

Explain graphically the effect of a catalyst on the rate of reaction.

Solution:

i. Diagram:



Comparison of fraction of molecules for catalyzed and uncatalyzed reactions

ii. A catalyst lowers the threshold energy.

iii. Consequently, more molecules acquire the minimum amount of energy and tend to cross the energy barrier.

iv. A fraction of activated molecules is greater for the catalyzed reaction. The rate of catalysed reaction thus is larger than the reaction with no catalyst.

Exercise | Q 3.17 | Page 137

Answer the following in brief.

For the reaction 2A + B → products, find the rate law from the following data.

[A]/M	[B]/M	rate/M s^{-1}
0.3	0.05	0.15
0.6	0.05	0.30
0.6	0.2	1.20

Solution:

From above observations (i) and (ii)

$0.15 = (0.3)^x (0.05)^y$ ......(i)

$0.30 = (0.6)^x (0.05)^y$ ....(ii)

Dividing (2) by (1)

$$\frac{0.30}{0.15} = 2 = \frac{(0.6)^x(0.05)^y}{(0.3)^x(0.05)^y} = \left(\frac{0.6}{0.3}\right)^x = 2^x$$

Hence, x = 1

From observation (i) and (iii) separately in the rate law gives

$0.15 = (0.3)^x (0.05)^y$ ....(iii)

$1.20 = (0.6)^x (0.2)^y$ ....(iv)

Dividing (4) by (3)

$$\frac{1.20}{0.15} = \frac{0.6}{0.3}\left(\frac{0.2}{0.05}\right)^y \quad (\because x = 1)$$

$$\therefore 8 = 2\left(\frac{0.2}{0.05}\right)^y = 2 \times 4^y$$

$\therefore$ 4 = 4y

Therefore, y = 1

The rate law is rate = k [A][B].

Exercise | Q 4.1 | Page 137

Solve

In a first-order reaction, the concentration of the reactant decreases from 20 mmol dm^{-3} to 8 mmol dm^{-3} in 38 minutes. What is the half-life of reaction?

Solution:

Given:

$[A]_0$ = 20 mmol dm^{-3} , $[A]_t$ = 8 mmol dm^{-3} , t = 38 min

To find:

Half life of reaction $t_{1/2}$

Formulae:

i. $k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$

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

Calculation:

Substituting given value in

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

$$k = \frac{2.303}{38\text{min}}\log_{10}\frac{20}{8}$$

$$= \frac{2.303}{38\ \text{min}}\log_{10}(2.5)$$

$$= \frac{2.303}{38\ \text{min}} \times 0.3979 = 0.0241\ \text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0241} = 28.7\ \text{min}$$

The half life of reaction is 28.7 min.

Exercise | Q 4.2 | Page 137

Solve

The half-life of a first-order reaction is 1.7 hours. How long will it take for 20% of the reactant to react?

Solution:

Given:

Half-life $t_{1/2}$ = 1.7 hours, $[A]_0$ = 100%, $[A]_t$ = 100 - 20 = 80%

To find:

Time for 20% of reactant to react = t

Formulae:

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

ii. $t = \frac{2.303}{K}\log_{10}\frac{[A]_0}{[A]_t}$

Calculation:

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

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.7h} = 0.4076\ h^{-1}$

$t = \frac{2.303}{k}\log_{10}\frac{[A]_0}{[A]_t} = \frac{2.303}{0.4076h^{-1}}\log\frac{100}{80}$

$t = \frac{2.303}{0.4076\ h^{-1}} \times 0.0969 = 0.5475\ h \times \frac{60\ min}{1h} = 32.9\ min$

The time required for 20% of reaction to react is 32.9 min.

Exercise | Q 4.3 | Page 137

Solve

The energy of activation for a first-order reaction is 104 kJ/mol. The rate constant at 25°C is $3.7 \times 10^{-5}\ s^{-1}$. What is the rate constant at 30°C? (R = 8.314 J/K mol)

Solution:

Given:

Activation energy (E_a) = 104 kJ mol^{-1} = 104×10^3 J mol^{-1}

Rate constant (k_1) = $3.7 \times 10^{-5} s^{-1}$

Temperatures; T_1 = 25 + 273 = 298 K, T_2 = 30 + 273 = 303 K

R = 8.314 J K^{-1} mol^{-1}

To find:

Rate constant (k_2) at 30°C

Formula:

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_2T_1}\right)$$

Calculation:

$$\log_{10}\frac{k_2}{3.7\times10^{-5}s^{-1}} = \frac{104\times10^3 J\ mol^{-1}}{2.303\times8.314 J\ K^{-1}mol^{-1}}\left(\frac{303K - 298K}{303K\times298K}\right)$$

$$\therefore \log_{10}\frac{k_2}{3.7\times10^{-5}s^{-1}} = \frac{104000}{2.303\times8.314}\times\frac{5}{303\times298}$$

$$\therefore \log_{10}\frac{k_2}{3.7\times10^{-5}s^{-1}} = 0.301$$

$$\therefore \frac{k_2}{3.7\times10^{-5}s^{-1}} = \text{antilog}(0.301) = 2.00$$

$$k_2 = 2.00\times3.7\times10^{-5}s^{-1} = 7.4\times10^{-5}s^{-1}$$

The rate constant of the reaction is $7.4\times10^{-5}s^{-1}$.

Exercise | Q 4.4 | Page 137

Solve

What is the energy of activation of a reaction whose rate constant doubles when the temperature changes from 303 K to 313 K?

Solution:

Given:

Rate constants; $k_2 = 2k_1$,

Temperatures: $T_1 = 303$ K, $T_2 = 313$ K

To find:

Activation energy of the reaction (E_a)

Formula:

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2\ - T_1}{T_2T_1}\right)$$

Calculation:

$$\log\frac{2k_1}{k_1} = \frac{E_a}{2.303 \times 8.314JK^{-1}mol^{-1}}\left(\frac{313K - 303K}{313K \times 303K}\right)$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314\ J\ mol^{-1}}\left(\frac{10}{313 \times 303}\right)$$

$$0.3010 = \frac{E_a}{19.147\ J\ mol^{-1}} \times 1.0544 \times 10^{-4}$$

$$E_a = \frac{0.3010 \times 19.147}{1.0544 \times 10^{-4}}\ J\ mol^{-1}$$

E_a = 54659 J mol^{-1} = 54.66 kJ mol^{-1}

The energy of activation of the reaction is 54.66 kJ mol^{-1} .

Exercise | Q 4.5 | Page 137

Solve

The rate constant of a reaction at 500°C is $1.6 \times 10^3\ M^{-1}\ s^{-1}$. What is the frequency factor of the reaction if its activation energy is 56 kJ/mol?

Solution:

Given:

Rate constant (k) = $1.6 \times 10^3\ M^{-1}s^{-1}$,

Temperature (T) = 500 + 273 = 773 K,

Activation energy (E_a) = 56 kJ mol^{-1} = 56×10^3 J mol^{-1}

To find:

frequency factor (A)

Formula:

$$\mathrm{K} = \mathrm{A}e^{\frac{-E_a}{RT}}$$

Calculation:

Substituting the given values

$$1.6 \times 10^3 \mathrm{M^{-1}s^{-1}} = \mathrm{A} \times e^{\left(\frac{-56\times10^3\ \mathrm{Jmol^{-1}}}{8.314\ \mathrm{JK^{-1}mol^{-1}}\times773\ \mathrm{K}}\right)}$$

$$\therefore \frac{1.6 \times 10^3 \mathrm{M^{-1}s^{-1}}}{\mathrm{A}} = e^{\left(\frac{-56000}{8.314\times773}\right)}$$

$$\therefore \log\left(\frac{1.6 \times 10^3\ \mathrm{M^{-1}s^{-1}}}{\mathrm{A}}\right) = \frac{-56000}{8.314 \times 773 \times 2.303}$$

$$\therefore \frac{1.6 \times 10^3 \mathrm{M^{-1}s^{-1}}}{\mathrm{A}} = \text{antilog}(-3.7836)$$

$$\therefore \frac{1.6 \times 10^3 \mathrm{M^{-1}s^{-1}}}{\mathrm{A}} = 1.646 \times 10^{-4}$$

$$\therefore \mathrm{A} = \left(\frac{1.6 \times 10^3 \mathrm{M^{-1}s^{-1}}}{1.646 \times 10^{-4}}\right) = 9.72 \times 10^6 \mathrm{M^{-1}s^{-1}}$$

The frequency factor of reaction is $9.72 \times 10^{-6}\ \mathrm{M^{-1}s^{-1}}$.

Exercise | Q 4.6 | Page 137

Solve

Show that time required for 99.9% completion of a first-order reaction is three times the time required for 90% completion.

Solution:

For a first-order reaction,

$$t = \frac{2.303}{k} \log_{10} \frac{[A]_0}{[A]_t}$$

i.

Time is taken for 99.9% completion:

Let the time taken for 99.9% completion of the reaction be $t_{99.9\%}$.

Let initial concentration, $[A]_0$ = a

Then final concentration, $[A]_t$ = a - 99.9% of a

$$= a - \left(\frac{99.9}{100} \times a\right) = 0.001\ a$$

$$t_{99.9\%} = \frac{2.303}{k} \log_{10} \frac{[A]_0}{[A]_t}$$

$$= \frac{2.303}{k} \log_{10} \frac{a}{0.001\ a}$$

$$= \frac{2.303}{k} \log_{10} 1000 \quad ...(1)$$

ii.

Time is taken for 90% completion:

Let the time taken for 90% completion of the reaction be $t_{90\%}$.

Let initial concentration, $[A]_0$ = a

Then, final concentration, $[A]_t$ = a - 90% of a

$$= a - \left(\frac{90}{100} \times a\right) = 0.1a$$

$$t_{90\%} = \frac{2.303}{k} \log_{10} \frac{[A]_0}{[A]_t} = \frac{2.303}{k} \log_{10} \frac{a}{0.1a}$$

$$= \frac{2.303}{k} \log_{10} 10 \quad ...(2)$$

Dividing (1) by (2), we get

$$\frac{t_{99.9\%}}{t_{90\%}} = \frac{\frac{2.303}{k}\log_{10}1000}{\frac{2.303}{k}\log_{10}10} = \frac{\log_{10}1000}{\log_{10}10} = \frac{3}{1}$$

$$\therefore \frac{t_{99.9\%}}{t_{90\%}} = 3$$

$\therefore t_{99.9\%} = 3\ t_{90\%}$

Therefore, for a first-order reaction, the time required for 99.9% completion is 3 times that required for 90% completion.

Exercise | Q 4.7 | Page 137

Solve

A first-order reaction takes 40 minutes for 30% decomposition. Calculate its half-life.

Solution:

Given:

$[A]_0$ = 100%, $[A]_t$ = 100 - 30 = 70%, t = 40 min

To find:

Half life of reaction ($t_{1/2}$)

Formula:

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

Calculation:

Substitution of these in above

$$k = \frac{2.303}{t}\log_{10}\frac{100}{70}$$

$$= \frac{2.303}{40\ \text{min}}\log_{10}(1.429)$$

$$= \frac{2.303}{40\ \text{min}} \times 0.155$$

$= 0.008924\ \text{min}^{-1}$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.008924\ \text{min}^{-1}} = 77.66\ \text{min}$$

The half life of reaction is 77.66 min.

Exercise | Q 4.8 | Page 137

Solve

The rate constant for the first-order reaction is given by $\log_{10} k = 14.34 - 1.25 \times 10^4\ T$. Calculate activation energy of the reaction.

Solution:

The given rate constant equation is

$$\log_{10}k = 14.34 - 1.25 \times 10^4\ T \quad ...(1)$$

Arrhenius equation is

$$k = Ae^{\frac{-E_a}{RT}}$$

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

$$\therefore \log_{10}k = \log_{10}A - \frac{E_a}{2.303RT} \quad ...(2)$$

Comparing (1) and (2),

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

$$\therefore \frac{E_a}{2.303\ R} = 1.25 \times 10^4$$

$$\therefore \frac{E_a}{2.303 \times 8.314} = 1.25 \times 10^4$$

$\therefore E_a = 1.25 \times 10^4 \times 2.303 \times 8.314 = 239339\ \text{K mol}^{-1} = 239.3\ \text{kJ mol}^{-1}$

The energy of activation of the reaction is 239.3 kJ mol^{-1}

Exercise | Q 4.9 | Page 137

Solve

What fraction of molecules in a gas at 300 K collide with an energy equal to the activation energy of 50 kJ/mol?

Solution:

Given:

Activation energy (E_a) = 50 kJ mol^{-1} = 50 × 10^3 J mol^{-1}

Temperature (T) = 300 K

To find:

Fraction of molecule (f) with energy equal to E_a

Formula:

$$f = e^{\frac{-E_a}{RT}}$$

Calculation:

Substituting the given value above

$$f = e^{\left(\frac{-50 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 300 \text{ K}}\right)}$$

$$\log_{10} f = \left(\frac{-50 \times 10^3}{8.314 \times 300 \times 2.303}\right)$$

$$\log_{10} f = -8.70$$

$$f = \text{antilog}(-8.70)$$

$$f = 1.99 \times 10^{-9} \approx 2.0 \times 10^{-9}$$

Fraction of molecules having energy equal to activation energy is 2.0 × 10^{-9}.