NCERT SOLUTIONS

CLASS - 12th



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Class : 12th
Subject : Chemistry
Chapter : 4
Chapter Name : Chemical Kinetics

Q4.1 For the reaction R → P, the concentration of a reactant changes from 0.03M to 0.02M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

Answer.

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

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

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

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

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

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

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

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Q4.2 In a reaction, 2A → Products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval?

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

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

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

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

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

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

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Q4.3 For a reaction, A + B → Product; the rate law is given by, $r = k[A]^{1/2}[B]^2$. What is the order of the reaction?

Answer.

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

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

$$= 2.5$$

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Q4.4 The conversion Of molecules X to Y follows second order kinetics. If concentration Of X is increased to three times how will it affect the rate of formation of Y?

Answer. The reaction $X \rightarrow Y$ follows second order kinetics. Therefore. the rate equation for this reaction will be:

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

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

$$\text{Rate}_1 = k \cdot (a)^2$$

$$= ka^2$$

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

NOW, the rate equation Will be: $\text{Rate} = k(3a)^2 = 9\left(ka^2\right)$ Hence, the rate of formation will increase by 9 times.

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Q4.5 A first order reaction has a rate constant $1.1510^{-3}s^{-1}$. How long will 5 g of this reactant take to reduce to 3 g?

Answer.

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

Initial amount = 5g

Final concentration = 39

Rate constant $= 1.1510^{-3}s^{-1}$

We know that for a 1^{s*} order reaction,

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

$$= \frac{2.303}{1.15 \times 10^{-3}}\log\frac{5}{3}$$

$$= \frac{2.303}{1.15 \times 10^{-3}} \times 0.2219$$

$= 444.38s$

$= 444s$(approx)

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Q4.6 Time required to decompose SO_2Cl_2 to half Of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Answer.

We know that for a 1^{st} order reaction,

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

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

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

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

$= 0.01155min^{-1}$

$= 1.155min^{-1}$

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

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Q4.7 What will be the effect of temperature on rate constant?

Answer. The rate Constant of a reaction is nearly doubled with a 10° rise in temperature. However, the exact dependence of the rate of a chemical reaction on temperature is guen by Arrhenius equation,

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

Where,

A is the Arrhenius factor or the frequency factor

T is the temperature

R is the gas constant

E_a is the activation energy

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Q4.8 The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate E_a

Answer.

It is given that $T_1 = 298K$

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

$= 308K$

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, $R = 8.3143K^{-1}mol^{-1}$

Now, substituting these values in the equation:

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

we get:

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

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

$$= 52897.78 \text{Jmol}^{-1}$$

$$= 52.9 \text{k3mol}^{-1}$$

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Q4.9 The activation energy for the reaction $2HI_{(g)} \rightarrow H_2 + I_{2(g)}$ is 209.5k3mol^{-1} at 581KCalculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Answer.

In the given case:

$E_8 = 209.5 \text{kJmol}^{-1} = 209500 \text{Jmol}^{-1}$

$T = 581\text{K}$

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

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

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

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

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

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

Now, $x =$ Anti $\log(\bar{18.8323})$

$=$ Anti log19.1677

$= 1.471 \times 10^{-19}$

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Q4.1 From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

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

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

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

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

Answer.

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

Therefore, order of the reaction $= 2$

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

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

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

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

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

Therefore, order of the reaction $= 2$

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

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

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

(iii) Given rate $= k\left[\text{CH}_3\text{CHO}\right]^{3/2}$

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

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

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

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

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

(iv) Given rate $= k\left[\text{C}_2\text{H}_5\text{Cl}\right]$

Therefore, order of the reaction $= 1$

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

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

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

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Q4.2 For the reaction :

$2\text{A} + \text{B} \rightarrow \text{A}_2\text{B}$

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

Answer.

The initial rate of the reaction is

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

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

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

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

Therefore, concentration of B reacted $= \frac{1}{2} \times 0.04\text{molL}^{-1} = 0.02$ 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 $= k[\text{A}][\text{B}]^2$

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

$= 3.89\text{molL}^{-1}\text{s}^{-1}$

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Q4.3 The decomposition of dimethvl ether leads to the formation of CH., and CO and the reaction rate is given by

$= k\left[\text{CH}_3\text{OCH}_3\right]^{3/2}$

The rate of reaction is followed bv 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 $= k\left(p_{\text{ch, 0CH}_3}\right)^{\frac{3}{2}}$

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 $= k\left(p_{\text{CM, 0cH}}\right)^{3/2}$

Therefore, unit of rate constants $= \frac{\text{bar min}^{-1}}{\text{bar}^3}$

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

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Q4.5 Mention the factors that affect the rate of a chemical reaction.

Answer. The factors that affect the rate Of reaction are as follows.
(i) Concentration Of reactants (pressure in case Of gases)
(ii) Temperature
(iii) Presence Of a catalyst

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Q4.6 A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is
(i) Doubled (ii) reduced to half?

Answer.
Let the concentration of the reactant be $[A] = a$

Rate of reaction, $R = k[A]^2$

$= ka^2$

(i)If the concentration Of the reactant is doubled, i.e. [A] = 2a, then the rate of the reaction would be

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

$= 4ka^2$

$= 4R$

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

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

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

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

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

Therefore, the rate of the reaction would be reduced to 4 th

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Q4.7 What is the effect of temperature on the rate constant of a reaction? How can this temperature effect on rate constant be represented quantitatively?

Answer. The rate constant is nearly doubled with a rise in temperature by 10° for a chemical reaction. The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation,

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

Where, k is the rate constant

A is the Arrhenius factor or the frequency factor,

R is the gas constant,

T is the temperature, and

E_a is the energy of activation for the reaction

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Q4.8 In a pseudo first order hydrolysis Of ester in water, the following results were obtained:

t/s	0	30	60	90
[Ester]mol L^{-1}	0.55	0.31	0.17	0.085

(i) Calculate the average rate Of reaction between the time interval 30 to 60 seconds.
(ii) Calculate the pseudo first Order rate constant for the hydrolysis Of ester.

Answer. (i) Average rate Of reaction between the time interval, 30 to 60 seconds,

$= \frac{d[\text{ Ester }]}{dt}$

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

$= \frac{0.14}{30}$

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

(ii) For a pseudo first order reaction,

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

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

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

$k_2 = \frac{2.303}{60}\log\frac{0.55}{0.17}$

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

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

$= \frac{\left(1.91\times10^{-2}\right)+\left(1.957\times10^{-2}\right)+\left(2.075\times10^{-2}\right)}{3}$

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

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Q4.9 A reaction is first order in A and second order in B,
(i) Write the differential rate equation.
(ii) How is the rate affected on increasing the concentration of B three times?
(iii) HOW is the rate affected When the concentrations Of both A and a 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, $-\frac{d[R]}{dt} = k[A][B]^2 = k[2A][B]^2$ Therefore, the rate of reaction will increase 8 times.

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Q4.10 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_0/ mol L^{-1} s^{-1}	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

What is the order of the reaction with respect to A and B?

Answer. Let the order of the reaction With respect to A be x and with respect to 3 be y.
Therefore.

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

$5.07 \times 10^{-5} = k[0.20]^x[0.30]^y$.....(1)

$5.07 \times 10^{-5} = k[0.20]^x[0.10]^y$.....(2)

$1.43 \times 10^{-4} = k[0.40]^x[0.05]^y$.....(3)

Dividing equation (1) by (2), we obtain

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

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

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

$\Rightarrow y = 0$

Dividing equation (3) by (2), we obtain

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

$\Rightarrow \frac{1.43\times10^{-4}}{5.07\times10^{-5}} = \frac{[0.40]^x}{[0.20]^x}$ $\left[\begin{array}{l}\text{since } y = 0\\ [0.05]^y = [0.30]^y = 1\end{array}\right]$

$\Rightarrow 2.821 = 2^x$

$\Rightarrow \log 2.821 = x\log 2$ (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.

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Q4.11 The following results have been obtained during the kinetic studies of the reaction:

$2A + B \rightarrow C + D$

Experiment	A/ mol L^{-1}	B/ mol L^{-1}	Initial rate of formation of D/mol L^{-}
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}

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 be y,

Therefore, rate of the reaction is given by,

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

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

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

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

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

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

$\Rightarrow x = 1$

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

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

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

$\Rightarrow 4 = 2^y$

$\Rightarrow 2^2 = 2^y$

$\Rightarrow y = 2$

Therefore, the rate law is

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

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

$\Rightarrow$ From experiment I, we obtain

$k = \frac{6.0\times10^{-3}\text{molL}^{-1}\text{min}^{-1}}{\left(0.1\text{molL}^{-1}\right)\left(0.1\text{molL}^{-1}\right)^2}$

$= 6.0\text{L}^2\text{mol}^{-2}\text{min}^{-1}$

From experiment II, we obtain

$k = \frac{7.2\times10^{-1}\text{molL}^{-1}\text{min}^{-1}}{\left(0.3\text{molL}^{-1}\right)\left(0.2\text{molL}^{-1}\right)^2}$

$k = \frac{2.88\times10^{-1}\text{molL}^{-1}\text{min}^{-1}}{\left(0.3\text{molL}^{-1}\right)\left(0.4\text{molL}^{-1}\right)^2}$

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

From experiment IV, we obtain

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

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

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

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Q4.12 The reaction between A and a 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

$2.0 \times 10^{-2} mol L^{-1} min^{-1} = k\left(0.1 mol L^{-1}\right)$

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

From experiment II, we obtain

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

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

From experiment III, we obtain

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

$= 0.08 mol L^{-1} min^{-1} = 0.2 min^{-1}[A]$

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

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Q4.13 Calculate the half-life of a first order reaction from their rate constants given below:

(i)$200 s^{-1}$(ii)$2 min^{-1}$(iii)$4 years^{-1}$

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

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

$= 3.47 s$ (approximately)

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

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

$= 0.35 min$ (approximately)

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

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

$= 0.173$ years (approximately)

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Q4.14 The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% Of the ^{14}C found in a living tree. Estimate the age Of the sample.

Answer.

$k = \frac{0.693}{t_{1/2}}$ Here, $1/2 = \frac{0.693}{5730}$ years $^{-1}$ It is known that,

$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} = \frac{2.303}{\frac{0.303}{5730}}\log\frac{100}{80}$ = 1845 years (approximately) Hence, the age of the sample is 1845 years.

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Q4.15 The experimental data for decomposition of N_2O_5,

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

in gas phase at 318K are given below:

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

(i) Plot N_2O_5 against t.

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

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

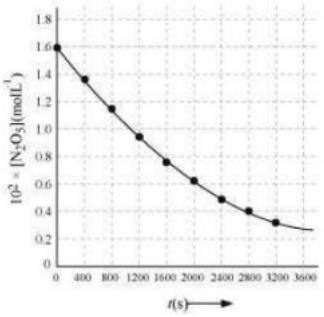
(iv) What is the rate law?

(v) Calculate the rate constant.

(Vi) Calculate the half-life genod from k and compare it with (ii).

Answer.

i.

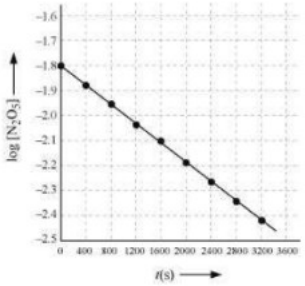


(ii) Time corresponding to the concentration, $\frac{1.630\times10^2}{2}molL^{-1} = 81.5molL^{-1}$,

life. From the graph, the half life is obtained as 1450s .

(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
3200	0.35	− 2.46



(iv) The given reaction is of the first order as the plot, $\log\left[N_2O_5\right]_{v/s} t$ is a straight line.

Therefore, the rate law of the reaction is

Rate $= k\left[N_2O_5\right]$

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

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

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

Again, slope of the line of the plot $\log\left[N_2O_5\right]_{v/s} t$ is given by

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

Therefore, we obtain,

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

$$\Rightarrow k = 4.82 \times 10^{-4} s^{-1}$$

(vi) Half-life is given by,

$$t_{1/2} = \frac{0.639}{k}$$

$$= \frac{0.693}{4.82 \times 10^{-4}} s$$

$$= 1.438 \times 10^3 s$$

$$= 1438 s$$

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

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Q4.16 The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its $1/16^{th}$ value?

Answer.

It is known that

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

$$= \frac{2.303}{60s^{-1}}\log\frac{1}{1/6}$$

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

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

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

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Q4.17 During nuclear explosion, one of the products is 90_{Sr} with half-life of 28.1 years. If 1μg of 90_{Sr} was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

Answer.

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

Here,

It is known that,

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

$$\Rightarrow 10 = \frac{2.303}{\frac{0.303}{28.1}}\log\frac{1}{[R]}$$

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

$$\Rightarrow \frac{10 \times 0.693}{2.303 \times 28.1}$$

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

$= \text{antilog}(1.8929)$

$= 0.7814\mu g$

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

Again,

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

$$\Rightarrow 60 = \frac{2.303}{\frac{0.303}{28.1}}\log\frac{1}{[R]}$$

$\Rightarrow \log[R] = -\frac{60 \times 0.693}{2.303 \times 28.1} \Rightarrow [R] = \text{antilog}(-0.6425) = \text{antilog}(1.3575) = 0.2278\mu g$ Therefore, 0.2278mug of ^{90}Sr will remain after 60 years.

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Q4.18 For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

Answer.

For a first order reaction, the time required for 99% completion is $t_1 = \frac{2.303}{k}\log\frac{100}{100-99} = \frac{2.303}{k}\log 100 = 2 \times \frac{2.303}{k}$

For a first order reaction, the time required for 90% completion is $t_2 = \frac{2.303}{k}\log\frac{100}{100-90} = \frac{2.303}{k}\log 10 = \frac{2.303}{k}$ Therefore, $t_1 = 2t_2$

Hence, the time required for 99% completion Of a first order reaction is twice the time required for the completion Of 90% Of the reaction.

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Q4.19 A first order reaction takes 40 min for decomposition. Calculate $t_{1/2}$

Answer. For first order reaction

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

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

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

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

Therefore, $t_{1/2}$ of the decomposition reaction is $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.918 \times 10^{-3}} \text{min} = 77.7\text{min}$ (approximately)

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Q4.20 For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

t (sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant.

Answer.

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

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

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

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

$\Rightarrow P_t = P_0 + p$

$\Rightarrow p = P_t - P_0$

Therefore, $P_0 - p = P_0 - (P_t - P_0)$

$= 2P_0 - P_t$

For a first order reaction,

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

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

When t = 360 s, $k = \frac{2.303}{360\ \text{s}}\log\frac{35.0}{2\times35.0 - 54.0}$

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

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

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

Hence, the average value of rate constant is

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

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

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Q4.21 The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.

$sO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$

Experiment	**Time/s^{-1}**	**Total pressure/atm**
1	0	0.5
2	100	0.6

Calculate the rate Of the reaction when total pressure is 0.65 atm.

Answer.

following equation.

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

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

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

$\Rightarrow P_t = P_0 + p$

$\Rightarrow p = P_t - P_0$

Therefore, $P_0 - p = P_0 - (P_t - P_0)$

$= 2\,P_0 - P_t$

For a first order reaction,

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

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

When t = 100 s, $k = \frac{2.303}{100\text{ s}}\log\frac{0.5}{2\times0.5-0.6}$

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

When P_t = 0.65 atm,

$P_0 + p = 0.65$

$\Rightarrow p = 0.65 - P_0$

$= 0.65 - 0.5$

$= 0.15$ atm

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

$p_{SOCl_2} = P_0 - p$

$= 0.5 - 0.15$

$= 0.35$ atm

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

Rate = $k(p_{SOCl_2})$

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

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

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Q4.22 The rate constant for the decomposition Of N_2O_5, at various temperatures is given below:

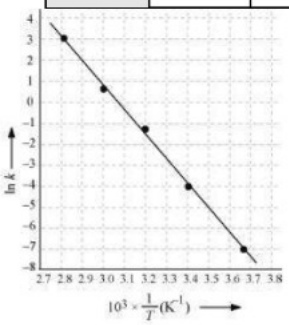
T/°C	0	20	40	60	80
$10^5 \times k/\text{s}^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between in K and 1/ T and calculate the values of A and E_s.

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

Answer. For the given data, we obtain

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



Slope of the line,

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

According to Arrhenius equation,

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

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

$= -(-12.301\text{K}) \times \left(8.314\text{JK}^{-1}\text{mol}^{-1}\right)$

$= 102.27\text{kJmol}^{-1}$

Again

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

$\ln A = \ln k + \frac{E_o}{\text{R}T}$

When $T = 273\text{K}$

$\text{In } k = -7.147$

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

$$= 37.911$$

Therefore, $A = 2.91 \times 10^6$

When $T = 30 + 273\text{K} = 303\text{K}$

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

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

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

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

$\text{In } k = -0.5$

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

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Q4.23 The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5}\text{s}^{-1}$ at 546K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.

Answer.

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

$T = 546\text{K}$

$E_\text{s} = 179.9\text{kJmol}^{-1} = 179.9 \times 10^3\text{Jmol}^{-1}$

According to the Arrhenius equation,

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

$\Rightarrow \ln k = \ln\text{A} - \frac{E_e}{\text{R}T}$

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

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

$$= \log\left(2.418 \times 10^{-4}\text{s}^{-1}\right) + \frac{179.9 \times 10^3\text{Jmol}^{-1}}{2.303 \times 8.314\text{Jk}^{-1}\text{mol}^{-1} \times 546\text{K}}$$

$= (0.3835 - 5) + 17.2082$

$= 12.5917$

Therefore, $A =$ antilog (12.5917)

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

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Q4.24

Consider a certain reaction $A \rightarrow$ products with $k = 2.0 \times 10^{-2}\text{s}^{-1}$. Calculate the concentration of A remaining after 100s if the initial concentration of A is 1.0mol$L$

Answer.

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

$T = 100s$

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

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

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

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

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

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

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

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

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

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Q4.25 Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2}$ = 3.00 hours. What fraction of sample of sucrose remains after 8 hours?

Answer.

For a first order reaction,

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

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

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

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

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

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

$= 0.158$

Hence, the fraction of sample of sucrose that remains after 8 hours is O. 158.

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Q4.26 The decomposition of hydrocarbon follows the equation $k = \left(4.5 \times 10^{11} s^{-1}\right) e^{-28000k/T}$ Calculate E_a

Answer.

The given equation is

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

Arrhenius equation is given by,

$k = A e^{-E, kT}$(ii)

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

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

$$\Rightarrow E_0 = R \times 28000K$$

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

$= 232792 Jmol^{-1}$

$= 232.792 kJmol^{-1}$

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Q4.27

The rate constant for the first order decomposition of H_2O_2 is given by the following equation: $\log k = 14.34 - 1.25 \times 10^4 K/T$ Calculate E_a for this reaction and at w

Answer.

Arrhenius equation is given by,

$k = Ae^{-E/kT}$

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

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

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

The given equation is

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

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

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

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

$= 1.25 \times 10^4 K \times 2.303 \times 8.314 JK^{-1}mol^{-1}$

$= 239339.3 Jmol^{-}1$ (approximately)

$= 239.34 kJmol^{-1}$

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

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

$= \frac{0.693}{256}$

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

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

It is also g ven that, $\log k = 14.34 - 1.25 \times 10^4 K/T$

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

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

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

$= 668.95K$

$= 669K$ (approximately)

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Q4.28 The decomposition of A into product has value of k as $4.5 \times 10^3 s^{-1}$ at 10 ° C and energy of activation $60 kmol^{-1}$ At what temperature would k be $1.5 \times 10^4 s^{-1}$?

Answer.

From Arrhenius equation, we obta

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

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

$T_1 = 273 + 10 = 283K$

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

$E_a = 60\text{kJmol}^{-1} = 6.0 \times 10^4\text{Jmol}^{-1}$

Then,

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

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

$$\Rightarrow \frac{0.5229\times283T_2}{3133.627} = T_2 - 283$$

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

$$\Rightarrow 0.9528T_2 = 283$$

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

$= 297\text{k}$

$= 24^\circ\text{C}$

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

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Q4.29

The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K . If the value of A is $4 \times 10^{10}\text{s}^{-1}$. Ca

Answer.

For a first order reaction,

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

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

$= \frac{0.1054}{k}$

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

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

According to the question,

$t = t'$

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

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

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

$$\log(2.7296) = \frac{E_a}{2.303\times8.314}\left(\frac{308-298}{298\times308}\right)$$

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

$= 76640.096\text{Jmol}^{-1}$

$= 76.64\text{kJmol}^{-1}$

To calculate k at 318K

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

Again, from Arrhenius equation, we obtain

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

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

$= (0.6021 + 10) - 12.5876$

$= -1.9855$

Therefore, $k =$ Antilog (-1.9855)

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

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Q4.30 The rate Of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy Of activation Of the reaction assuming that it does not change With temperature.

Answer.

From Arrhenius equation, we obtain

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

It is given that, $k_2 = 4k_1$

$T_1 = 293\mathrm{K}$

$T_2 = 313\mathrm{K}$

Therefore, $\log\frac{4k_1}{k_2} = \frac{E_a}{2.303 \times 8.314}\left(\frac{313-293}{293\times313}\right)$

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

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

$$= 52863.33\mathrm{Jmol}^{-1}$$

$$= 52.86\mathrm{kJmol}^{-1}$$

Hence, the required energy of activation is $52.86\mathrm{kJmol}^{-1}$

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