

## Chapter 4 – Chemical Kinetics

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Question 4.1:

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:

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

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

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

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

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

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

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

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Question 4.2:

In a reaction,  $2A \rightarrow \text{Products}$ , the concentration of A decreases from 0.5 mol L<sup>-1</sup> to 0.4 mol L<sup>-1</sup> in 10 minutes. Calculate the rate during this interval?

Answer:

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

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

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

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

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

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


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Question 4.3:

For a reaction,  $A + B \rightarrow \text{Product}$ ; 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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Question 4.4:

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

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

$$= ka^2$$

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

Now, the rate equation will be:

$$\text{Rate} = k (3a)^2$$

$$= 9(ka^2)$$

Hence, the rate of formation will increase by 9 times.

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Question 4.5:

A first order reaction has a rate constant  $1.15 \times 10^{-3} \text{ s}^{-1}$ . How long will 5 g of this reactant take to reduce to 3 g?

Answer:

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

Initial amount = 5 g

Final concentration = 3 g

Rate constant =  $1.15 \times 10^{-3} \text{ s}^{-1}$

We know that for a 1<sup>st</sup> order reaction,

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

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

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

$$= 444.38 \text{ s}$$

$$= 444 \text{ s (approx)}$$

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Question 4.6:

Time required to decompose  $\text{SO}_2\text{Cl}_2$  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<sup>st</sup> order reaction,

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

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

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

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

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

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

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

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Question 4.7:

What will be the effect of temperature on rate constant?

Answer:

The rate constant of a reaction is nearly doubled with a  $10^\circ$  rise in temperature. However, the exact dependence of the rate of a chemical reaction on temperature is given by Arrhenius equation,

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

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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Question 4.8:

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  $T_1 = 298 \text{ K}$

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

$$= 308 \text{ K}$$

We also know that the rate of the reaction doubles when temperature is increased by  $10^\circ$ .

Therefore, let us take the value of  $k_1 = k$  and that of  $k_2 = 2k$

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

Now, substituting these values in the equation:

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

We get:

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

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

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

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

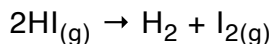
$$= 52.9 \text{ kJ mol}^{-1}$$

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

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Question 4.9:

The activation energy for the reaction



is  $209.5 \text{ kJ mol}^{-1}$  at  $581\text{K}$ . Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Answer:

In the given case:

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

$$T = 581 \text{ K}$$

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

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

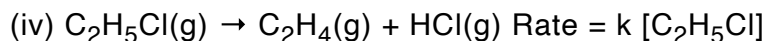
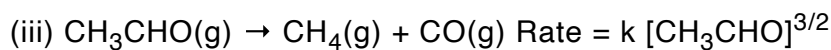
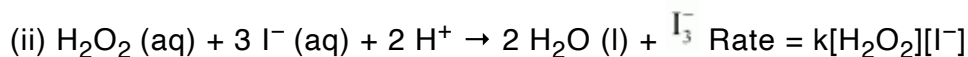
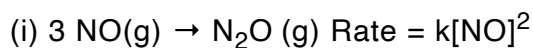
$$x = e^{-E_a/RT} \Rightarrow \ln x = -E_a/RT \Rightarrow \log x = -E_a/2.303RT \Rightarrow \log x = -209500 \text{ J mol}^{-1} / 2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 581 = -18.8323$$

Now,  $x = \text{Antilog } -18.8323 = 1.471 \times 10^{-19}$

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Question 4.1:

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



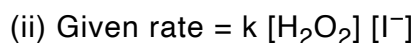
Answer:



Therefore, order of the reaction = 2

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

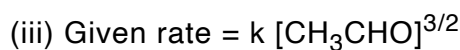
$$\begin{aligned} &= \frac{\text{mol L}^{-1} \text{ s}^{-1}}{(\text{mol L}^{-1})^2} \\ &= \frac{\text{mol L}^{-1} \text{ s}^{-1}}{\text{mol}^2 \text{ L}^{-2}} \\ &= \text{L mol}^{-1} \text{ s}^{-1} \end{aligned}$$



Therefore, order of the reaction = 2

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

$$\begin{aligned} &= \frac{\text{mol L}^{-1} \text{ s}^{-1}}{(\text{mol L}^{-1})(\text{mol L}^{-1})} \\ &= \text{L mol}^{-1} \text{ s}^{-1} \end{aligned}$$



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

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

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

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

Therefore, order of the reaction = 1

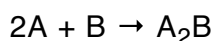
Dimension of  $k = \frac{\text{Rate}}{[\text{C}_2\text{H}_5\text{Cl}]}$

$$\begin{aligned}
 &= \frac{\text{mol L}^{-1} \text{ s}^{-1}}{\text{mol L}^{-1}} \\
 &= \text{s}^{-1}
 \end{aligned}$$


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Question 4.2:

For the reaction:



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

Answer:

The initial rate of the reaction is

$$\begin{aligned}
 \text{Rate} &= k [\text{A}][\text{B}]^2 \\
 &= (2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}) (0.1 \text{ mol L}^{-1}) (0.2 \text{ mol L}^{-1})^2 \\
 &= 8.0 \times 10^{-9} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}
 \end{aligned}$$

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

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

Then, concentration of B available,  $[\text{B}] = (0.2 - 0.02) \text{ mol L}^{-1}$   
 $= 0.18 \text{ mol L}^{-1}$

After  $[\text{A}]$  is reduced to  $0.06 \text{ mol L}^{-1}$ , the rate of the reaction is given by,

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

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

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

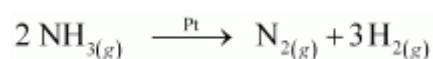

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Question 4.3:

The decomposition of  $\text{NH}_3$  on platinum surface is zero order reaction. What are the rates of production of  $\text{N}_2$  and  $\text{H}_2$  if  $k = 2.5 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$ ?

Answer:

The decomposition of  $\text{NH}_3$  on platinum surface is represented by the following equation.



Therefore,

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

However, it is given that the reaction is of zero order.

Therefore,

$$-\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = k$$

$$= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Therefore, the rate of production of  $\text{N}_2$  is

$$\frac{d[\text{N}_2]}{dt} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

And, the rate of production of  $\text{H}_2$  is

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

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


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Question 4.4:

The decomposition of dimethyl ether leads to the formation of  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{CO}$  and the reaction rate is given by

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

The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.,

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



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

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

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

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

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

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Question 4.5:

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

Answer:

The factors that affect the rate of a reaction are as follows.

- (i) Concentration of reactants (pressure in case of gases)
  - (ii) Temperature
  - (iii) Presence of a catalyst
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Question 4.6:

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  $[A] = a$

$$\text{Rate of reaction, } R = k [A]^2$$

$$= ka^2$$

(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

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

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

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

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

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Question 4.7:

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,

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

where, k is the rate constant,

A is the Arrhenius factor or the frequency factor,

R is the gas constant,

T is the temperature, and

$E_a$  is the energy of activation for the reaction

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Question 4.8:

In a pseudo first order hydrolysis of ester in water, the following results were obtained:

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t/s	0	30	60	90
[Ester]mol L <sup>-1</sup>	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,

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

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

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

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

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

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

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

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

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

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

Question 4.9:

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 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

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

Therefore, the rate of reaction will increase 9 times.

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

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

Therefore, the rate of reaction will increase 8 times.

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Question 4.10:

In a reaction between A and B, the initial rate of reaction ( $r_0$ ) was measured for different initial concentrations of A and B as given below:

A/ mol L <sup>-1</sup>	0.20	0.20	0.40
B/ mol L <sup>-1</sup>	0.30	0.10	0.05
$r_0$ / mol L <sup>-1</sup> s <sup>-1</sup>	$5.07 \times 10^{-5}$	$5.07 \times 10^{-5}$	$1.43 \times 10^{-4}$

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

Answer:

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

Therefore,

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

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

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

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

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

$$\frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{k[0.20]^x[0.30]^y}{k[0.20]^x[0.10]^y}$$

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

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

$$\Rightarrow y = 0$$

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

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

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

$$\Rightarrow 2.821 = 2^x$$

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

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

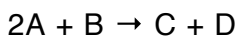
$$= 1.496$$

$$= 1.5 \text{ (approximately)}$$

Hence, the order of the reaction with respect to A is 1.5 and with respect to B is zero.

Question 4.11:

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



Experiment	A/ mol L <sup>-1</sup>	B/ mol L <sup>-1</sup>	Initial rate of formation of D/mol L <sup>-1</sup> min <sup>-1</sup>
I	0.1	0.1	$6.0 \times 10^{-3}$
II	0.3	0.2	$7.2 \times 10^{-2}$
III	0.3	0.4	$2.88 \times 10^{-1}$

IV	0.4	0.1	$2.40 \times 10^{-2}$
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Determine the rate law and the rate constant for the reaction.

Answer:

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

Therefore, rate of the reaction is given by,

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

According to the question,

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

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

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

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

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

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

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

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

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

$$\Rightarrow x = 1$$

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

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \frac{k [0.3]^x [0.4]^y}{k [0.3]^x [0.2]^y}$$

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

$$\Rightarrow 4 = 2^y$$

$$\Rightarrow 2^2 = 2^y$$

$$\Rightarrow y = 2$$

Therefore, the rate law is

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

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

From experiment I, we obtain

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

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

From experiment II, we obtain

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

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

From experiment III, we obtain

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

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

From experiment IV, we obtain

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

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

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

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Question 4.12:

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 <sup>-1</sup>	B/ mol L <sup>-1</sup>	Initial rate/mol L <sup>-1</sup> min <sup>-1</sup>
I	0.1	0.1	$2.0 \times 10^{-2}$
II	—	0.2	$4.0 \times 10^{-2}$
III	0.4	0.4	—
IV	—	0.2	$2.0 \times 10^{-2}$

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,

$$\text{Rate} = k [\text{A}]^1 [\text{B}]^0$$

$$\Rightarrow \text{Rate} = k [\text{A}]$$

From experiment I, we obtain

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

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

From experiment II, we obtain

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

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

From experiment III, we obtain

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

$$= 0.08 \text{ mol L}^{-1} \text{ min}^{-1}$$

From experiment IV, we obtain

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

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

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Question 4.13:

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

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

Answer:

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

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

$$= 3.47$$

$$\times 10^{-3} \text{ s (approximately)}$$

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

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

$$= 0.35 \text{ min (approximately)}$$



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

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

$$= 0.173 \text{ years (approximately)}$$


---

Question 4.14:

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

Answer:

Here,

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

$$= \frac{0.693}{5730} \text{ years}^{-1}$$

It is known that,

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

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

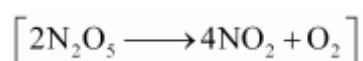
$$= 1845 \text{ years (approximately)}$$

Hence, the age of the sample is 1845 years.

---

Question 4.15:

The experimental data for decomposition of  $\text{N}_2\text{O}_5$



in gas phase at 318K are given below:

t(s)	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [\text{N}_2\text{O}_5] \text{ mol L}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

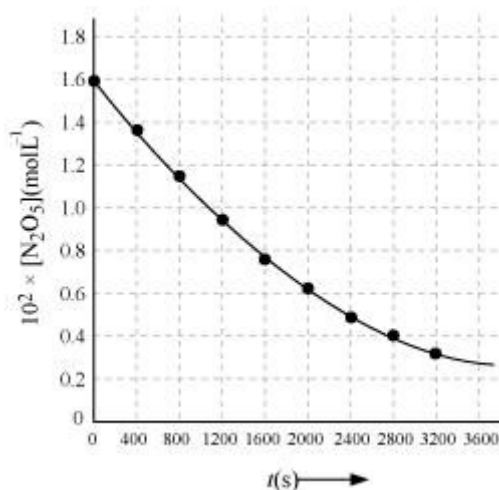
(i) Plot  $[\text{N}_2\text{O}_5]$  against t.

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

- (iii) Draw a graph between  $\log [N_2O_5]$  and  $t$ .
- (iv) What is the rate law?
- (v) Calculate the rate constant.
- (vi) Calculate the half-life period from  $k$  and compare it with (ii).

Answer:

1.

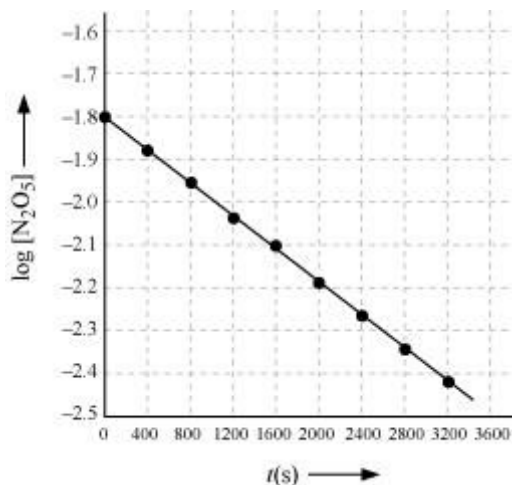


- (ii) Time corresponding to the concentration,  $\frac{1.630 \times 10^2}{2} \text{ mol L}^{-1} = 81.5 \text{ mol L}^{-1}$ , is the half life.

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

(iii)

t(s)	$10^2 \times [N_2O_5] / \text{mol L}^{-1}$	$\log [N_2O_5]$
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,  $\log[\text{N}_2\text{O}_5]$  v/s  $t$ , is a straight line. Therefore, the rate law of the reaction is

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

(v) From the plot,  $\log[\text{N}_2\text{O}_5]$  v/s  $t$ , we obtain

$$\begin{aligned} \text{Slope} &= \frac{-2.46 - (-1.79)}{3200 - 0} \\ &= \frac{-0.67}{3200} \end{aligned}$$

Again, slope of the line of the plot  $\log[\text{N}_2\text{O}_5]$  v/s  $t$  is given by

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

Therefore, we obtain,

$$\begin{aligned} -\frac{k}{2.303} &= -\frac{0.67}{3200} \\ \Rightarrow k &= 4.82 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

(vi) Half-life is given by,

$$\begin{aligned} t_{1/2} &= \frac{0.639}{k} \\ &= \frac{0.693}{4.82 \times 10^{-4}} \text{ s} \\ &= 1.438 \times 10^3 \text{ s} \\ &= 1438 \text{ s} \end{aligned}$$

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

Question 4.16:

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

Answer:

It is known that,

$$\begin{aligned} t &= \frac{2.303}{k} \log \frac{[R]_0}{[R]} \\ &= \frac{2.303}{60 \text{ s}^{-1}} \log \frac{1}{1/16} \\ &= \frac{2.303}{60 \text{ s}^{-1}} \log 16 \\ &= 4.6 \times 10^{-2} \text{ s (approximately)} \end{aligned}$$

Hence, the required time is  $4.6 \times 10^{-2} \text{ s}$ .

---

Question 4.17:

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

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

Here,

It is known that,

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

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

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

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

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

$$= \text{antilog} (1.8929)$$

$$= 0.7814 \mu\text{g}$$

Therefore,  $0.7814 \mu\text{g}$  of  $^{90}\text{Sr}$  will remain after 10 years.

Again,

$$\begin{aligned}
 t &= \frac{2.303}{k} \log \frac{[R]_0}{[R]} \\
 \Rightarrow 60 &= \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]} \\
 \Rightarrow \log [R] &= -\frac{60 \times 0.693}{2.303 \times 28.1} \\
 \Rightarrow [R] &= \text{antilog}(-0.6425) \\
 &= \text{antilog}(\bar{1}.3575) \\
 &= 0.2278 \mu\text{g}
 \end{aligned}$$

Therefore, 0.2278  $\mu\text{g}$  of  $^{90}\text{Sr}$  will remain after 60 years.

---

Question 4.18:

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

$$\begin{aligned}
 t_1 &= \frac{2.303}{k} \log \frac{100}{100-99} \\
 &= \frac{2.303}{k} \log 100 \\
 &= 2 \times \frac{2.303}{k}
 \end{aligned}$$

For a first order reaction, the time required for 90% completion is

$$\begin{aligned}
 t_2 &= \frac{2.303}{k} \log \frac{100}{100-90} \\
 &= \frac{2.303}{k} \log 10 \\
 &= \frac{2.303}{k}
 \end{aligned}$$

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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Question 4.19:

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

Answer:

For a first order reaction,

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

$$\begin{aligned} k &= \frac{2.303}{40 \text{ min}} \log \frac{100}{100-30} \\ &= \frac{2.303}{40 \text{ min}} \log \frac{10}{7} \\ &= 8.918 \times 10^{-3} \text{ min}^{-1} \end{aligned}$$

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

$$\begin{aligned} t_{1/2} &= \frac{0.693}{k} \\ &= \frac{0.693}{8.918 \times 10^{-3}} \text{ min} \end{aligned}$$

= 77.7 min (approximately)

Question 4.20:

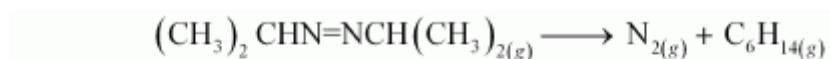
For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

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.



At  $t = 0$                        $P_0$                       0                      0

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

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

$$\Rightarrow P_t = P_0 + p$$

$$\Rightarrow p = P_t - P_0$$

$$\text{Therefore, } P_0 - p = P_0 - (P_t - P_0)$$

$$= 2P_0 - P_t$$

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

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

When  $t = 720$  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

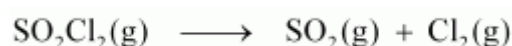
$$k = \frac{(2.175 \times 10^{-3}) + (2.235 \times 10^{-3})}{2} \text{ s}^{-1}$$

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

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

Question 4.21:

The following data were obtained during the first order thermal decomposition of  $\text{SO}_2\text{Cl}_2$  at a constant volume.

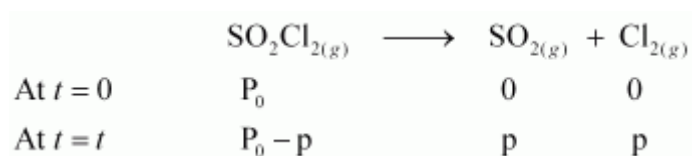


Experiment	Time/s <sup>-1</sup>	Total pressure/atm
1	0	0.5
2	100	0.6

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

Answer:

The thermal decomposition of  $\text{SO}_2\text{Cl}_2$  at 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,  $P_0 - p = P_0 - (P_t - P_0)$

$$= 2 P_0 - P_t$$

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

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

When  $P_t = 0.65$  atm,

$$P_0 + p = 0.65$$

$$\Rightarrow p = 0.65 - P_0$$

$$= 0.65 - 0.5$$

$$= 0.15 \text{ atm}$$

Therefore, when the total pressure is 0.65 atm, pressure of  $\text{SOCl}_2$  is

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

$$= 0.5 - 0.15$$

$$= 0.35 \text{ atm}$$

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

$$\text{Rate} = k(P_{\text{SOCl}_2})$$

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

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

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Question 4.22:

The rate constant for the decomposition of  $\text{N}_2\text{O}_5$  at various temperatures is given below:

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

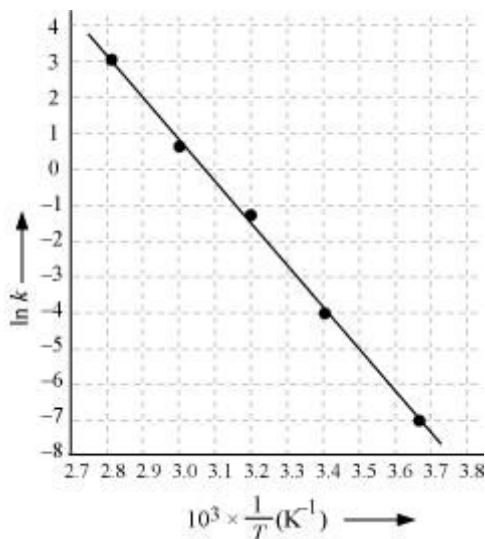
Draw a graph between  $\ln k$  and  $1/T$  and calculate the values of A and  $E_a$ .

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

Answer:

From the given data, we obtain

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



Slope of the line,

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

According to Arrhenius equation,

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

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

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

$$= 102.27 \text{ kJ mol}^{-1}$$

Again,

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

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

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

$$\ln k = -7.147$$

$$\begin{aligned}\text{Then, } \ln A &= -7.147 + \frac{102.27 \times 10^3}{8.314 \times 273} \\ &= 37.911\end{aligned}$$

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

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

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

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

$$\ln k = -2.8$$

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

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

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

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

$$\ln k = -0.5$$

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

Question 4.23:

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

Answer:

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

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

$$E_a = 179.9 \text{ kJ mol}^{-1} = 179.9 \times 10^3 \text{ J mol}^{-1}$$

According to the Arrhenius equation,

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

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

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

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

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

$$= (0.3835 - 5) + 17.2082$$

$$= 12.5917$$

Therefore,  $A = \text{antilog}(12.5917)$

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


---

Question 4.24:

Consider a certain reaction  $A \rightarrow \text{Products}$  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  $1.0 \text{ mol L}^{-1}$ .

Answer:

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

$$T = 100 \text{ s}$$

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

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

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

Therefore,

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

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

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

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

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

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

---

Question 4.25:

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,

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

$$= 0.231 \text{ h}^{-1}$$

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

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

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

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

$$\Rightarrow \frac{[R]}{[R]_0} = 0.1576 \text{ (approx)}$$
$$= 0.158$$

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

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Question 4.26:

The decomposition of hydrocarbon follows the equation

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

Calculate  $E_a$ .

Answer:

The given equation is

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

Arrhenius equation is given by,

$$k = Ae^{-E_a/RT} \quad (\text{ii})$$

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

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

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

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

$$= 232792 \text{ J mol}^{-1}$$

$$= 232.792 \text{ kJ mol}^{-1}$$


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Question 4.27:

The rate constant for the first order decomposition of  $\text{H}_2\text{O}_2$  is given by the following equation:

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

Calculate  $E_a$  for this reaction and at what temperature will its half-period be 256 minutes?

Answer:

Arrhenius equation is given by,

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

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

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

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

The given equation is

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

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

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

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

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

$$= 239339.3 \text{ J mol}^{-1} \text{ (approximately)}$$

$$= 239.34 \text{ kJ mol}^{-1}$$

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

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

$$= \frac{0.693}{256}$$

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

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

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

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

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

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

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

$$= 668.95 \text{ K}$$

$$= 669 \text{ K (approximately)}$$

Question 4.28:

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

Answer:

From Arrhenius equation, we obtain

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

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

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

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

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

Then,

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

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

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

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

$$\Rightarrow 0.9528 T_2 = 283$$

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

$$= 297 \text{ K}$$

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

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

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

Question 4.29:

The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of  $A$  is

$4 \times 10^{10} \text{ s}^{-1}$ . Calculate  $k$  at 318 K and  $E_a$ .

Answer:

For a first order reaction,

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

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

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

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

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

According to the question,

$$t = t'$$

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

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

From Arrhenius equation, we obtain

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

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

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

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

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

To calculate k at 318 K,

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

Again, from Arrhenius equation, we obtain

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

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

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

$$= -1.9855$$

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

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

Question 4.30:

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



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

It is given that,  $k_2 = 4k_1$

$$T_1 = 293 \text{ K}$$

$$T_2 = 313 \text{ K}$$

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

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

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

$$= 52863.33 \text{ J mol}^{-1}$$

$$= 52.86 \text{ kJ mol}^{-1}$$

Hence, the required energy of activation is  $52.86 \text{ kJ mol}^{-1}$ .

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