

**Intext Exercise****Question 1:**

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

**Solution 1:**

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

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

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

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

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

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

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

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**Question 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.

**Solution 2:**

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

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

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

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

$$=0.005\text{mol L}^{-1} \text{ min}^{-1} =5\times 10^{-3}\text{M min}^{-1}$$


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**Question 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?

**Solution 3:**

$$\text{The order of the reaction} = \frac{1}{2} + 2 = 2\frac{1}{2} = 2.5$$


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**Question 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?

**Solution 4:**

The reaction  $X \rightarrow Y$  follows second order kinetics hence the rate law equation will be

$$\text{Rate} = kC^2, \text{ where } C = [x]$$

If the concentration of X is increases to three times, now  $[x] = 3\text{Cmol L}^{-1}$

Now, the rate equation will be:

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

$$= 9 (kC^2)$$

Thus the rate of reaction will become 9 times

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

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**Question 5:**

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

**Solution 5:**

$$\text{Initial amount}[R]_0 = 5 \text{ g}$$

$$\text{Final concentration}[R] = 3 \text{ g}$$

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

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

$$\begin{aligned} t &= \frac{2.303}{k} \log \frac{[R]_0}{R} \\ &= \frac{2.303}{1.15 \times 10^{-3}} \log \frac{5}{3} \end{aligned}$$

$$\begin{aligned} &= \frac{2.303}{1.15 \times 10^{-3}} \times 0.2219 \\ &= 444.38 \text{ s} \\ &= 444 \text{ s (approx)} \end{aligned}$$

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**Question 6:**

Time required to decompose  $\text{SO}_2\text{Cl}_2$  to half its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

**Solution 6:**

For a 1<sup>st</sup> order reaction,

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

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

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

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

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

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

$$\text{or, } k = 1.925 \times 10^{-1} \text{ s}^{-1}$$

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**Question 7:**

What will be the effect of temperature on rate constant?

**Solution 7:**

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 8:**

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

**Solution 8:**

Given  $T_1 = 298 \text{ K}$

$$\therefore T_2 = (298 + 10) \text{ K} = 308 \text{ K}$$

We also know that the rate of the reaction doubles when temperature is increased by 10K

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:

We get:

$$\begin{aligned} \log \frac{k_2}{k_1} &= \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right] \\ \log \frac{2k}{k} &= \frac{E_a}{2.303 \times 8.314} \left[ \frac{10}{298 \times 308} \right] \\ \log 2 &= \frac{E_a}{2.303 \times 8.314} \left[ \frac{10}{298 \times 308} \right] \\ E_a &= \frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2}{10} \\ &= 52897.78 \text{ J mol}^{-1} \\ &= 52.89 \text{ kJ mol}^{-1} \end{aligned}$$


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**Question 9:**

The activation energy for the reaction  $2\text{HI}_{(g)} \rightarrow \text{H}_2 + \text{I}_{2(g)}$  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?

**Solution 9:**

In the given case:

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

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

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

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

$$x = e^{E_a/RT}$$

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

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

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

Now  $x = \text{Antilog}(-18.8323)$

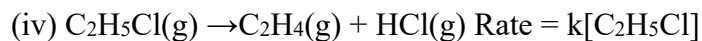
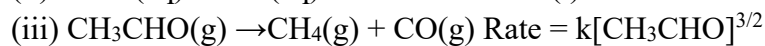
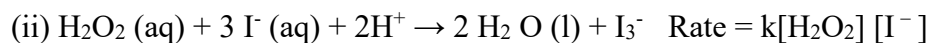
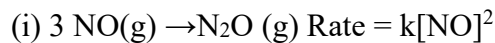
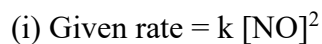
$$= 1.471 \times 10^{-19}$$


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**NCERT Exercise**

**Question 1:**

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

**Solution 1:**

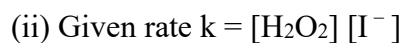
Therefore, order of the reaction = 2

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

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

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

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

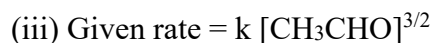


Therefore, order of the reaction = 2

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

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

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



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

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

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

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

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

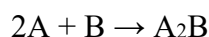
Therefore, order of the reaction = 1  $k = \frac{\text{Rate}}{[\text{C}_2\text{H}_5\text{Cl}]}$

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


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### Question 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  $0.06 \text{ mol L}^{-1}$

### Solution 2:

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

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

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

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

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

$$\begin{aligned}\text{Rate} &= k[\text{A}][\text{B}]^2 \\ &= (2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}) (0.06 \text{ mol L}^{-1}) (0.18 \text{ mol L}^{-1})^2 \\ &= 3.89 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}\end{aligned}$$

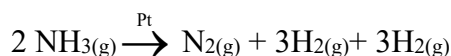

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### Question 3:

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

### Solution 3:

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



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

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

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

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

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

$$\frac{d[\text{N}_2]}{dt} = \frac{2.5 \times 10^{-4}}{2}$$

$$= 1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

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

$$\frac{d[\text{H}_2]}{dt} = \frac{3}{2} \times 2.5 \times 10^{-4}$$

$$= 3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$


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#### Question 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?

#### Solution 4:

If pressure is measured in bar and time in minutes, then unit of rate =  $\text{bar min}^{-1}$

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

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

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

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


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#### Question 5:

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

#### Solution 5:

The factors that affect the rate of a reaction are.

(i) Nature of the reactant: Rate of the reaction depends on nature of reactant. For e.g. Reactions of ionic compounds are faster than that of covalent compounds.

## Chapter 4

### Chemical Kinetics

(ii) State of reactants : Solid reactions are slow and reactions of liquids are fast whereas that of gases are very fast

(iii) Temperature : Rate of reaction largely depends on temperature. It has been observed that every  $10^{\circ}\text{C}$  rise in temperature increases rate of reaction by 2-3 times.

$$\frac{r_{t+10}}{r_t} = 2-3$$

This ratio is called temperature coefficient.

Increase in temperature increases average kinetic energy of reactant molecules. Hence, rate of collision increases. With increase in temperature number of molecules having threshold energy also increases. Hence rate of reaction increases.

iv) Presence of catalyst:

Rate of reaction also depends on presence of catalyst. Catalyst increases rate of reaction by increasing surface area of reaction, by forming unstable intermediate with the substrate and also provides alternate path of lower activation energy.

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#### Question 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?

#### Solution 6:

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

$$\begin{aligned}\text{Rate of reaction, } R &= k[A]^2 \\ &= ka^2\end{aligned}$$

(i) If the concentration of the reactant is double, 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.,  $[A] = \frac{1}{2}a$  the rate of the reaction would be

$$\begin{aligned}R &= k\left(\frac{1}{2}a\right)^2 \\ &= \frac{1}{4}ka^2 \\ &= \frac{1}{4}R\end{aligned}$$

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

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**Question 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?

**Solution 7:**

The rate constant is nearly doubled with a rise in temperature by  $10^\circ$  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

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right] \quad \begin{array}{l} k_1 = \text{rate constant at temperature } T_1 \\ k_2 = \text{rate constant at temperature } T_2 \end{array}$$

**Question 8:**

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

$t/s$	0	30	60	90
$[\text{Ester}]/\text{mol L}^{-1}$	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.

**Solution 8:**

(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,

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

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

$$= 1.91 \times 10^{-2} \text{ s}^{-1}$$

$$\text{For, } t=60 \text{ s, } k_2 = \frac{2.303}{60} \log \frac{0.55}{0.17} = 1.96 \times 10^{-2} \text{ s}^{-1}$$

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

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

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

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


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**Question 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 three times?

(iii) How is the rate affected when the concentrations of both A and B are doubled?

**Solution 9:**

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

Therefore, the rate of reaction will increase 9 times.

(iii) When the concentrations of both A and B are doubled,  $-\frac{d[R]}{dt} = k[A][B]^2$

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

$$= 8.k [A] [B]^2$$

Therefore, the rate of reaction will increase 8 times

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**Question 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	0.04
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?

**Solution 10:**

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

Therefore,

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

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

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

$$1.43 \times 10^{-5} = k[0.40]^x [0.05]^y \dots\dots(iii)$$

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

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

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

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

$$\Rightarrow y = 0$$

Dividing equation (iii) by (ii) we obtain

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

$$\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{k[0.40]^x}{k[0.20]^x} \left[ \frac{[0.05]^y}{[0.30]^y} = 1 \right] \quad \left[ \text{since } y = 0 \right]$$

$$\Rightarrow 2.821 = 2^x$$

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

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

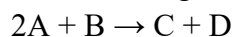
$$= 1.496$$

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

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

**Question 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 × 10 <sup>-3</sup>
II	0.3	0.2	7.3 × 10 <sup>-2</sup>

III	0.3	0.4	$2.88 \times 10^{-1}$
IV	0.4	0.1	$2.40 \times 10^{-2}$

Determine the rate law and the rate constant for the reaction

**Solution 11:**

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,

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

According to the question,

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

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

$$2.88 \times 10^{-1} = k[0.3]^x [0.1]^y \text{ (iii)}$$

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

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

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

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

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

$$\Rightarrow x = 1$$

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

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

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

From experiment I, we obtain

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

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

From experiment II, we obtain

$$k = \frac{7.2 \times 10^3 \text{ mol L}^{-1} \text{ min}^{-1}}{(0.3 \text{ mol L}^{-1})(0.2 \text{ mol L}^{-1})^2}$$

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

From experiment III, we obtain

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

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

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

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 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	$2.0 \times 10^{-2}$

### Solution 12:

The given reaction between A and B is first order with respect to A and 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

$$4.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} = k (0.2 \text{ mol L}^{-1})$$

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

From experiment III, we obtain

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

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

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 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)  $4 \text{ years}^{-1}$

**Solution 13:**

$$\text{(i) Half-life, } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{200 \text{ s}^{-1}}$$

$$= 0.346 \times 10^{-2} = 3.46 \times 10^{-3} \text{ s}$$

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

$$= 0.346 \text{ min}$$

$$\text{(iii) Half life } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4 \text{ years}^{-1}}$$

$$= 0.173 \text{ years}$$


---

**Question 14:**

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

**Solution 14:**

Radioactive decay follows first order kinetics. Therefore, decay constant

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

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

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

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

$$= 1845 \text{ years}$$

Hence, the age of the sample is 1845 years.

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**Question 15:**

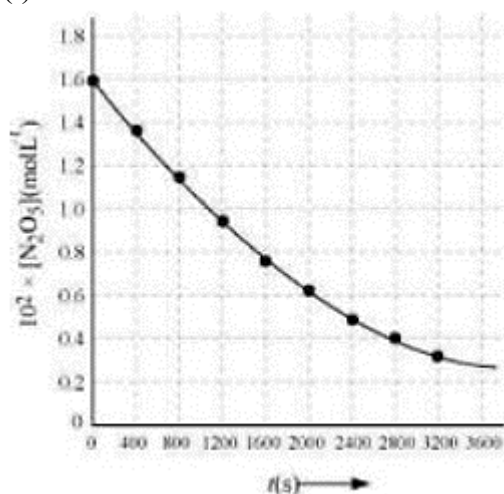
The experimental data for decomposition of  $\text{N}_2\text{O}_5$  [ $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ ] in gas phase at 318K are given below:

t/s	0	400	800	1200	1600	2000	2400	1800	3200
$10^{-2} \times [\text{N}_2\text{O}_5]$ /mol L <sup>-1</sup>	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  $\log [\text{N}_2\text{O}_5]$  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) .

**Solution 15:**

(i)

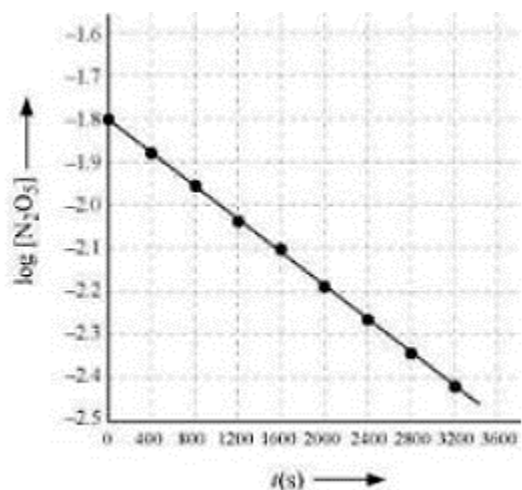


- (ii) Time corresponding to the concentration,  $\frac{1.630 \times 10^{-2}}{2} \text{ mol L}^{-1} = 0.815 \times 10^{-2} \text{ mol L}^{-1}$  is the half-life.

From the graph, the half life is obtained as 1440s.

(iii)

t(s)	$10^2 \times [\text{N}_2\text{O}_5] / \text{mol L}^{-1}$	Log $[\text{N}_2\text{O}_5]$
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  $[\text{N}_2\text{O}_5]$  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  $\log [\text{N}_2\text{O}_5]$  v/s  $t$ , is given by  $-\frac{k}{2.303}$

$$\text{Therefore, we obtain, } -\frac{k}{2.303} = \frac{0.67}{3200}$$

$$\Rightarrow = 4.82 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

(vi) Half-life is given by

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.82 \times 10^{-4} \text{ s}^{-1}}$$

$$= 1.438 \times 10^3 \text{ s}$$

$$= 1438 \text{ s}$$

The value of  $t_{1/2}$  calculated from the value of  $k$  is very close to that obtained from graph.

---

**Question 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?

**Solution 16:**

$$\text{It is known that, } t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

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

$$= 4.62 \times 10^{-2} \text{ s (approximately)}$$

Hence, the required time is  $4.62 \times 10^{-2} \text{ s}$ .

---

**Question 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.

**Solution 17:**

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

Here,

It is known that

$$t = \frac{0.303}{k} \log \frac{[R]_0}{[R]}$$

$$\Rightarrow 10 = \frac{0.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$

$$\Rightarrow 10 = \frac{0.303}{\frac{0.693}{28.1}} (-108 \log [R])$$

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

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

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

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

Again,

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

$$\Rightarrow 60 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$

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

$$\Rightarrow [R] = \text{antilog}(-0.6425)$$

$$= 0.2278 \mu\text{g}$$

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

---

**Question 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.

**Solution 18:**

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.

---

**Question 19:**

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

**Solution 19:**

For a first order reaction,

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

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

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

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

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

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

$$= 77.7 \text{ min}$$


---

**Question 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

**Solution 20:**

The decomposition of azoisopropane to hexane and nitrogen at 54.3 K is represented by the following equation.



$$\text{At } t = 0 \quad P_o \qquad \qquad \qquad 0 \qquad \qquad 0$$

$$\text{At } t = t \quad P_o - p \qquad \qquad \qquad p \qquad \qquad p$$

$$\text{Total pressure after time } t, (P_t) = (P_o - p) + p + p$$

$$\Rightarrow P_t = P_o + p$$

$$\text{or } p = P_t - P_o$$

on substituting the value of  $p$  for the pressure of reactant at time  $t$

$$= P_o - p$$

$$= P_o - (P_t - P_o)$$

$$= 2P_o - P_t$$

For a first order reaction,

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

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

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

$$\text{When } t = 720 \text{ s, } k = \frac{2.303}{720 \text{ s}} \log \frac{35.0}{2 \times 35.0 - 63.0} \times 10^{-3} \text{ s}^{-1}$$

Hence, the average value of rate constant is

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

$$= 2.20 \times 10^{-3} \text{ s}^{-1}$$


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### Question 21:

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

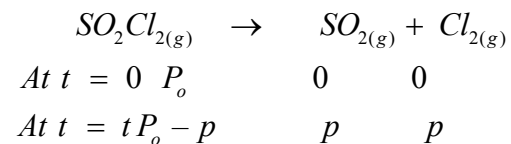


Experiment	Time/s <sup>-1</sup>	Total pressure/atm
1	0	0.5
2	100	0.6

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

### Solution 21:

The thermal decomposition of  $\text{SO}_2\text{Cl}_2$  at a constant volume is represented by the following equation.



Total pressure after time  $t$ ,  $(P_t) = (P_0 - p) + p + p$

$$\Rightarrow P_t = P_0 + p$$

$$\text{or } p = P_t - P_0$$

on substituting the value of  $p$  for the pressure of reactant at time  $t$

$$\begin{aligned} &= P_0 - p \\ &= P_0 - (P_t - P_0) \\ &= 2P_0 - P_t \end{aligned}$$

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

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

When  $t = 100$  s  
 $= 2.231 \times 10^{-3} \text{ s}^{-1}$

When  $P_t = 0.65$  atm,

Therefore pressure of  $\text{SOCl}_2$  at time  $t$  total pressure is 0.65 atm, is

$$P_{\text{SOCl}_2} = 2 P_o - P_t$$

$$= 2 \times 0.50 - 0.65$$

$$= 0.35 \text{ atm}$$

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

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

$$= (2.33 \times 10^{-3} \text{ s}^{-1}) (0.354 \text{ atm}) = 7.8 \times 10^{-4} \text{ atm s}^{-1}$$

### Question 22:

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

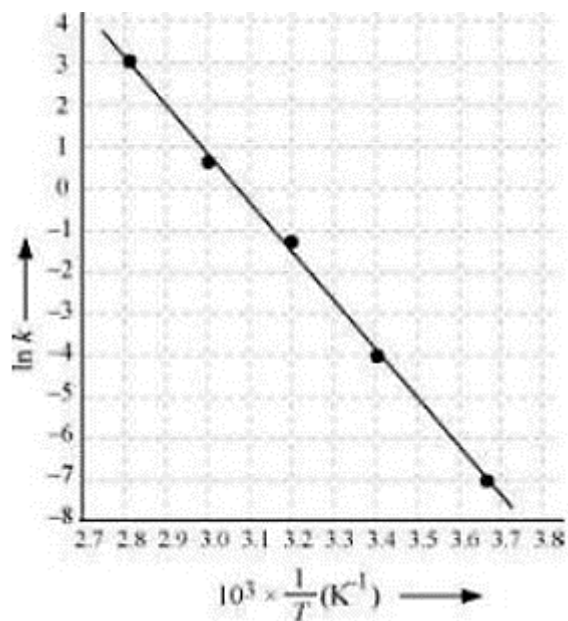
$T/^{\circ}\text{C}$	0	20	40	60	80
$10^5 \times k/\text{s}^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between  $\ln k$  and  $1/T$  and calculate the values of  $A$  and  $E_a$ . Predict the rate constant at  $30^{\circ}$  and  $50^{\circ}\text{C}$ .

### Solution 22:

For the given data, we obtain

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



Slop of the line,

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

According to Arrhenius equation,

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

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

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

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

Again,

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

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

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

$$\ln k = -7.147$$

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

$$\text{Therefore, } A = 2.91 \times 10^6$$

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

In  $k = -2.8$

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

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

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

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

In  $k = -0.5$

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

---

**Question 23:**

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

**Solution 23:**

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

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

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

According to the Arrhenius equation,

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

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

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

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

$$= (0.3835 - 5) + 17.2082 = 12.5917$$

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

$$= 3.912 \times 10^{12} \text{ s}^{-1}$$


---

**Question 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  $1.0 \text{ mol L}^{-1}$ .

**Solution 24:**

$$k = 2.0 \times 10^{-2} \text{ s}^{-1}, t = 100 \text{ s}, [A]_0 = 1.0 \text{ mol L}^{-1}$$

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

$$\begin{aligned}\text{Therefore, } k &= \frac{2.303}{t} \log \frac{[A]_0}{[A]} \\ \Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} &= \frac{2.303}{100\text{s}} \log \frac{1.0}{[A]} \\ \Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} &= \frac{2.303}{100\text{s}} (-\log [A]) \\ \Rightarrow -\log [A] &= \frac{2.0 \times 10^{-2} \times 100}{2.303} \\ \Rightarrow [A] &= \text{antilog} \left( \frac{2.0 \times 10^{-1} \times 100}{2.303} \right) \\ &= 0.135 \text{ mol L}^{-1}\end{aligned}$$

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

---

**Question 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?

**Solution 25:**

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

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

$$\text{Therefore, } k = \frac{0.693}{3} = 0.231 \text{ h}^{-1}$$

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

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

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

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

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

$$= 0.158$$

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

---

**Question 26:**

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

**Solution 26:**

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

Arrhenius equation is given by,  $k = Ae^{-E_a/RT}$  ----- (ii)

From equation (i) and (ii) we obtain

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

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

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

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

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


---

**Question 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?

**Solution 27:**

Arrhenius equation is given by,  $k = Ae^{E_a/RT}$

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

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

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

The given equation is

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

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

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

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

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

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

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

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

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

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

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

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

$$= 668.95 \text{ K}$$

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


---

### Question 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  $1.5 \times 10^4 \text{ s}^{-1}$ ?

### Solution 28:

From Arrhenius equation, we obtain

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

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

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

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

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

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

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

$$\begin{aligned} \Rightarrow 0.0472T_2 &= T_2 - 283 \\ \Rightarrow 0.9528 T_2 &= 283 \\ \Rightarrow T_2 &= 297.019 \text{ K (approximately)} \\ &= 297 \text{ K} \\ &= 24^\circ\text{C} \end{aligned}$$


---

**Question 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  $E_a$

**Solution 29:**

For a first order reaction,

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

$$\begin{aligned} \text{At } 298 \text{ K, } t &= \frac{2.303}{k} \log \frac{100}{90} \\ &= \frac{0.1054}{k} \end{aligned}$$

$$\begin{aligned} t &= \frac{2.303}{k} \log \frac{100}{75} \\ \text{At } 308 \text{ K, } &= \frac{2.2877}{k} \end{aligned}$$

According to the question,  $t = t$

$$\Rightarrow \frac{0.1054}{k} \log \frac{100}{90} = \frac{2.2877}{k}$$

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

From Arrhenius equation, we obtain

$$\log \log \frac{k'}{k} = \frac{E_a}{2.303R} \left( \frac{T'}{TT'} - 1 \right)$$

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

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

$$= 76750.096 \text{ J mol}^{-1}$$

$$= 76.75 \text{ kJ mol}^{-1}$$

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

$$\begin{aligned}\log &= \log A - \frac{E_a}{2.303RT} \\ &= \log(4 \times 10^{10}) - \frac{76.75 \times 10^3}{2.303 \times 8.314 \times 318} \\ &= 10.6021 - 12.6051 = -2.003 \\ \text{Therefore, } k &= \text{Anti log } (-2.003) \\ &= 9.93 \times 10^{-3} \text{ s}^{-1}\end{aligned}$$


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**Question 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.

**Solution 30:**

For Arrhenius equation, we obtain

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

It is given that  $k_2 = 4k_1$

$T_1 = 293 \text{ K}$

$T_2 = 313 \text{ K}$

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

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

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

$$= 52863.00 \text{ J mol}^{-1}$$

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

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

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