

**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

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

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

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

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

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

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

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

**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

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



$$\begin{aligned} &= -\frac{1}{2} \frac{[A]_2 - [A]_1}{t_2 - t_1} \\ &= -\frac{1}{2} \frac{0.4 - 0.5}{10} \\ &= -\frac{1 - 0.1}{2 \cdot 10} \\ &= 0.005 \text{ mol L}^{-1} \text{ min}^{-1} \\ &= 5 \times 10^{-3} \text{ M min}^{-1} \end{aligned}$$

**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

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

**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:

$$\begin{aligned} \text{Rate}_1 &= k \cdot (a)^2 \\ &= ka^2 \end{aligned}$$

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



Now, the rate equation will be:

$$\begin{aligned}\text{Rate} &= k (3a)^2 \\ &= 9(ka^2)\end{aligned}$$

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

**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,

$$\begin{aligned}t &= \frac{2.303}{k} \log \frac{[R]_0}{[R]} \\ &= \frac{2.303}{1.15 \times 10^{-3}} \log \frac{5}{3} \\ &= \frac{2.303}{1.15 \times 10^{-3}} \times 0.2219 \\ &= 444.38 \text{ s} \\ &= 444 \text{ s (approx)}\end{aligned}$$

**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  $t_{1/2} = 60 \text{ min}$



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

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

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

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

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

**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

**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:

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

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

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

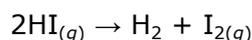
$$= 52897.78 \text{ J mol}^{-1}$$

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

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

#### 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:



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

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

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

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

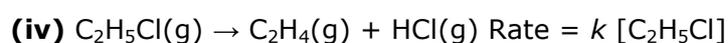
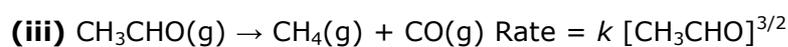
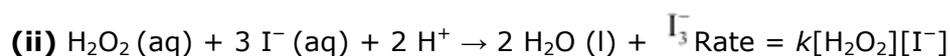
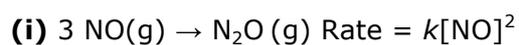
Now,  $x = \text{Anti log}(18.8323)$

$$= \text{Anti log } \overline{19.1677}$$

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

#### Question 4.1:

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





Answer

**(i)** Given rate =  $k [\text{NO}]^2$

Therefore, order of the reaction = 2

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

Dimension of

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

**(ii)** Given rate =  $k [\text{H}_2\text{O}_2] [\text{I}^-]$

Therefore, order of the reaction = 2

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

Dimension of

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

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

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

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

Dimension of

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

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

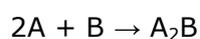


Therefore, order of the reaction = 1

$$\begin{aligned} \text{Dimension of } k &= \frac{\text{Rate}}{[\text{C}_2\text{H}_5\text{Cl}]} \\ &= \frac{\text{mol L}^{-1} \text{ s}^{-1}}{\text{mol L}^{-1}} \\ &= \text{s}^{-1} \end{aligned}$$

**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 =  $(0.1 - 0.06) \text{ mol L}^{-1} = 0.04 \text{ mol L}^{-1}$

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

Then, concentration of B 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,

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

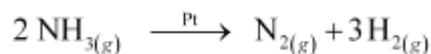
**Question 4.3:**

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,

$$\begin{aligned} -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} &= \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = k \\ &= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

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

$$\begin{aligned} \frac{d[\text{H}_2]}{dt} &= 3 \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \\ &= 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

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



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

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

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

Therefore, unit of rate constants

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

#### 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

#### 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

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

Therefore, the rate of the reaction would be reduced to  $\frac{1}{4}$ <sup>th</sup>.

**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

**Question 4.8:**

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

t/s	0	30	60	90
[Ester]mol L <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,

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

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

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

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

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

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

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

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

$$= \frac{(1.911 \times 10^{-2}) + (1.957 \times 10^{-2}) + (2.075 \times 10^{-2})}{3}$$
$$= 1.98 \times 10^{-2} \text{ s}^{-1}$$

#### 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.

#### 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

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

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

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

$$\Rightarrow y = 0$$

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

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

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

$$\Rightarrow 2.821 = 2^x$$

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

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

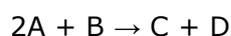
$$= 1.496$$

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

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	$2.40 \times 10^{-2}$

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,

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

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

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

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

From experiment I, we obtain

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

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

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

**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,

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

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

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

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

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

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

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

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

**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

$$\begin{aligned} \text{(i) Half life, } t_{1/2} &= \frac{0.693}{k} \\ &= \frac{0.693}{200 \text{ s}^{-1}} \\ &= 3.47 \text{ s (approximately)} \end{aligned}$$

$$\begin{aligned} \text{(ii) Half life, } t_{1/2} &= \frac{0.693}{k} \\ &= \frac{0.693}{2 \text{ min}^{-1}} \\ &= 0.35 \text{ min (approximately)} \end{aligned}$$

$$\begin{aligned} \text{(iii) Half life, } t_{1/2} &= \frac{0.693}{k} \\ &= \frac{0.693}{4 \text{ years}^{-1}} \\ &= 0.173 \text{ years (approximately)} \end{aligned}$$

**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

$$\begin{aligned} k &= \frac{0.693}{t_{1/2}} \\ \text{Here,} \\ &= \frac{0.693}{5730} \text{ years}^{-1} \end{aligned}$$

It is known that,



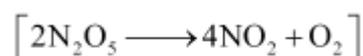
$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$
$$= \frac{2.303}{0.693} \log \frac{100}{80}$$
$$5730$$

= 1845 years (approximately)

Hence, the age of the sample is 1845 years.

**Question 4.15:**

The experimental data for decomposition of  $N_2O_5$



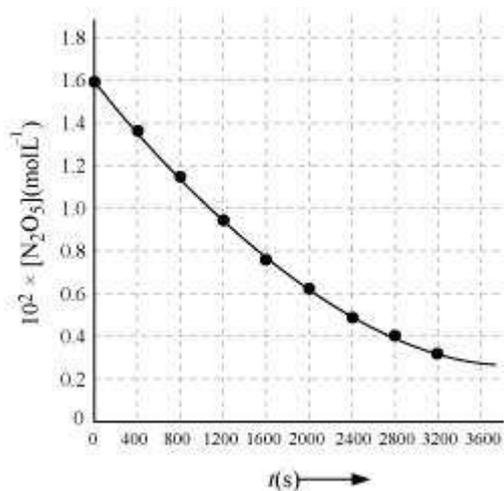
in gas phase at 318K are given below:

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

- (i) Plot  $[N_2O_5]$  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

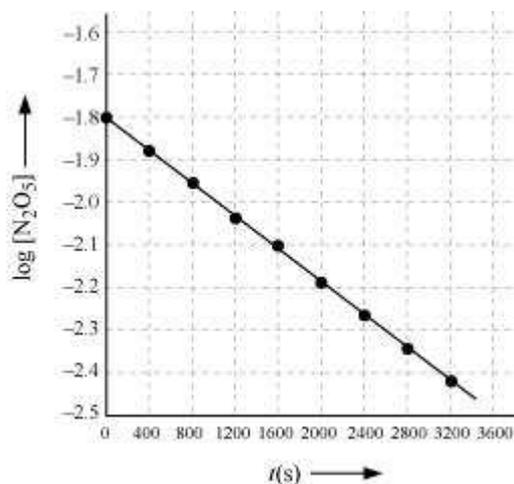
i.



(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)	$10^2 \times [\text{N}_2\text{O}_5] / \text{mol L}^{-1}$	$\log [\text{N}_2\text{O}_5]$
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,  $\log[\text{N}_2\text{O}_5]$  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,



$$\begin{aligned}t &= \frac{2.303}{k} \log \frac{[R]_0}{[R]} \\ \Rightarrow 10 &= \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]} \\ \Rightarrow 10 &= \frac{2.303}{0.693} \left( -\log [R] \right) \\ \Rightarrow \log [R] &= -\frac{10 \times 0.693}{2.303 \times 28.1} \\ \Rightarrow [R] &= \text{antilog} (-0.1071) \\ &= \text{antilog} (\bar{1}.8929) \\ &= 0.7814 \mu\text{g}\end{aligned}$$

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.

**Question 4.19:**

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

Answer

For a first order reaction,

$$\begin{aligned}t &= \frac{2.303}{k} \log \frac{[R]_0}{[R]} \\ k &= \frac{2.303}{40 \text{ min}} \log \frac{100}{100-30} \\ &= \frac{2.303}{40 \text{ min}} \log \frac{10}{7} \\ &= 8.918 \times 10^{-3} \text{ min}^{-1}\end{aligned}$$

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:**

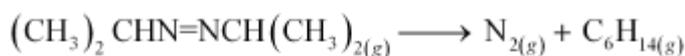
For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

$t$ (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.



$$\text{At } t = 0 \quad \quad \quad P_0 \quad \quad \quad 0 \quad \quad 0$$

$$\text{At } t = t \quad \quad \quad P_0 - p \quad \quad \quad p \quad \quad p$$

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,

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

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

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



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

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

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

Hence, the average value of rate constant is

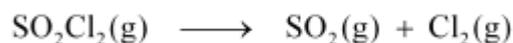
$$k = \frac{(2.175 \times 10^{-3}) + (2.235 \times 10^{-3})}{2} \text{ s}^{-1}$$

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

**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.

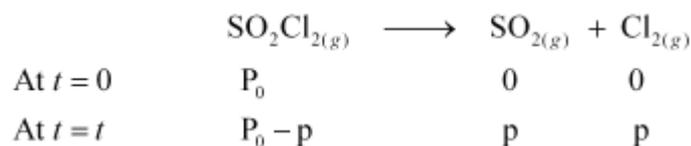


Experiment	Time/s <sup>-1</sup>	Total pressure/atm
1	0	0.5
2	100	0.6

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,

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

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

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

When  $P_t = 0.65 \text{ atm}$ ,

$$P_0 + p = 0.65$$

$$\Rightarrow p = 0.65 - P_0$$

$$= 0.65 - 0.5$$

$$= 0.15 \text{ atm}$$

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,

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

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

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

#### Question 4.22:

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  $E_a$ .

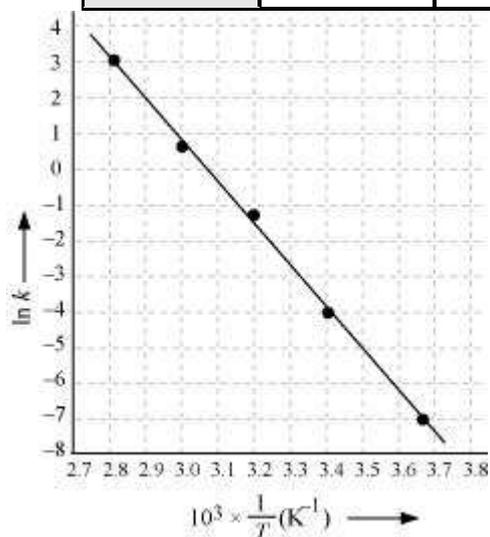
Predict the rate constant at  $30^\circ$  and  $50^\circ\text{C}$ .

Answer



From 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	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,

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

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

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

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

Again,



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

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

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

$$\ln k = -7.147$$

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

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,

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

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

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

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

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

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

$$= 12.5917$$

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,



$$\begin{aligned}\Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} &= \frac{2.303}{100 \text{ s}} \log \frac{1.0}{[A]} \\ \Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} &= \frac{2.303}{100 \text{ s}} (-\log [A]) \\ \Rightarrow -\log [A] &= \frac{2.0 \times 10^{-2} \times 100}{2.303} \\ \Rightarrow [A] &= \text{anti log} \left( -\frac{2.0 \times 10^{-2} \times 100}{2.303} \right)\end{aligned}$$

= 0.135 mol L<sup>-1</sup> (approximately)

Hence, the remaining concentration of A is 0.135 mol L<sup>-1</sup>.

#### 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,

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

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

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



$$\begin{aligned}\Rightarrow \log \frac{[R]_0}{[R]} &= \frac{0.231 \text{ h}^{-1} \times 8 \text{ h}}{2.303} \\ \Rightarrow \frac{[R]_0}{[R]} &= \text{antilog}(0.8024) \\ \Rightarrow \frac{[R]_0}{[R]} &= 6.3445 \\ \Rightarrow \frac{[R]}{[R]_0} &= 0.1576 \text{ (approx)} \\ &= 0.158\end{aligned}$$

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

**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,

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

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

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

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

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

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

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

**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,

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

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

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

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

The given equation is

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

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

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

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

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

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

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

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

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

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

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

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

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



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

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

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

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

$$= 668.95 \text{ K}$$

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

**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,

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

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

$$\begin{aligned} \text{At } 308 \text{ K,} \quad t' &= \frac{2.303}{k'} \log \frac{100}{75} \\ &= \frac{2.2877}{k'} \end{aligned}$$

According to the question,

$$\begin{aligned} t &= t' \\ \Rightarrow \frac{0.1054}{k} &= \frac{2.2877}{k'} \\ \Rightarrow \frac{k'}{k} &= 2.7296 \end{aligned}$$

From Arrhenius equation, we obtain



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

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

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

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

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

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

$$\begin{aligned} \log k &= \log A - \frac{E_a}{2.303RT} \\ &= \log(4 \times 10^{10}) - \frac{76.64 \times 10^3}{2.303 \times 8.314 \times 318} \\ &= (0.6021 + 10) - 12.5876 \\ &= -1.9855 \end{aligned}$$

$$\begin{aligned} \text{Therefore, } k &= \text{Antilog}(-1.9855) \\ &= 1.034 \times 10^{-2} \text{ s}^{-1} \end{aligned}$$

#### 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  $52.86 \text{ kJ mol}^{-1}$ .

Calculate  $\lambda^{\circ m}$  for  $\text{NH}_4\text{OH}$

**CHAPTER-4 CHEMICAL KINETICS**

**5 Marks Chapter**

**Key points**

Thermodynamics helps us to predict the feasibility of chemical reaction by using  $\Delta G$  as parameter but it cannot tell everything about the rate of reaction. Rate of chemical reaction is studied in another branch of chemistry called Chemical Kinetics.

**Chemical kinetics**- The branch of physical chemistry which deals with the study of rate of reaction and their mechanism is called chemical kinetics.

1. **Rate of chemical reaction**- The change in concentration of any reactant or product per unit time is called rate of reaction.

2. TYPES OF RATE OF REACTION-

a) **Average rate of reaction**- The rate of reaction measured over the long time interval is called average rate of reaction.

$$\text{Avg rate } \Delta x/\Delta t = -\Delta[R]/\Delta t = +\Delta[p]/\Delta t$$

b) **Instantaneous rate of reaction**- The rate of reaction measured at a particular time is called instantaneous rate of reaction.

$$\text{Instantaneous rate } dx/dt = -d[R]/dt = +d[P]/dt$$

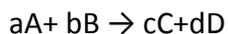
3. FACTORS AFFECTING RATE OF REACTION-

1. Concentration of reactant
2. Surface area
3. Temperature
4. Nature of reactant
5. Presence of catalyst
6. Radiation

4. **RATE CONSTANT (k)**- It is equal to the rate of reaction when molecular concentration of reactant is at unity.

5. **RATE LAW**- The rate of reaction is directly proportional to the product of concentration of reactant and each concentration is raised to some power which may or may not be equal to stereochemistry experimentally.

For a reaction



$$\text{Rate law} = k[A]^p[B]^q$$

Where powers  $p$  and  $q$  are determined experimentally

**6. MOLECULARITY** – The total no. of reactants taking part in elementary chemical reaction is called molecularity.

**7. Elementary reactions** : The reaction which occur in single step is called Elementary reaction.

**8. Complex reactions**: The reaction consist of sequence of elementary reactions are called complex reaction.

**9. ORDER OF REACTION**- The sum of powers to which the concentrations terms are raised in a rate law expression is called order of reactions. For above case order =  $p+q$ : orders of reaction is determined experimentally

**Zero order reaction**: Reactions in which the rate of reaction does not change with the concentration of reaction .

**First order reaction**: Reactions in which the rate of reaction is directly proportional with the concentration of reaction .

## 10. Intregrated rate equation

For First Order :  $k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$

$t$  [R] Remained reactant

For Zero order reaction :  $k = \frac{[R_0] - [R]}{T}$

T

**11. HALF-LIFE PERIOD-** The time during which the concentration of the reactant is reduced to half of its initial concentration is called half-life period.

**Equation for Half life period:**

For First Order :  $t_{1/2} = 0.693/k$

For Zero order reaction :  $t_{1/2} = R_0/2k$

**12. Pseudo first order reaction:** Reactions which are of higher order but follow the kinetics of first order. Eg. Acid catalyzed hydrolysis of ester

**ACTIVATION ENERGY-** The minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to the threshold energy is called activation energy.

Activation energy = Threshold energy – kinetic energy

**TEMPERATURE COEFFICIENT-** The ratio of rate constant at two temperatures having difference of  $10^{\circ}\text{C}$  is called temperature coefficient.

Temperature coefficient = Rate constant at  $T+10^{\circ}\text{C}$ /Rate constant at  $T^{\circ}\text{C}$

**Arrhenius Equation-**

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

k-rate constant

A-Arrhenius energy

$E_a$ -Activation energy

R- Gas constant

T-Temperature

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

## 2.303RT

Energy of activation can be evaluated as

$$1. \log [k_2/k_1] = \frac{E_a}{2.303R} \frac{(T_2 - T_1)}{(T_1 \times T_2)}$$

$$\log [k_2/k_1] = E_a(1/T_1 - 1/T_2) / 19.15$$

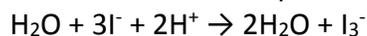
**Collision frequency** : It is the total number of collisions which all molecules undergo in a unit volume in a unit time.

### 1 MARKS QUESTION

1. What is the order of reaction whose rate constant has the same units as the rate of reaction?

Ans. Zero order.

2. State the order with respect to each reactant and overall reaction.

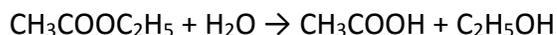


$$\text{Rate} = k[H_2O_2]^1[I^-]^1$$

Ans. Order of reaction = 1+1 = 2

3. Give one example of pseudo first order reaction.

Ans. Hydrolysis of an ester



4. The conversion of molecules X to Y follows the second order of kinetics. If concentration of X is increased 3 times, how will it affect the rate of formation of Y.

Ans. Rate =  $k[A]^2$

$$= k [3A]^2$$

$$= k [9a]^2$$

The rate of formation will become nine times.

5. The rate law for a reaction is  $\text{Rate} = K [A] [B]^{3/2}$

Can the reaction be an elementary process? Explain.

Ans. No, an elementary process would have a rate law with orders equal to its molecularities and therefore must be in integral form.

6. What do you understand by 'rate of reaction'?

7. Name the factors on which the rate of a particular reaction depends.

8. Why rate of reaction does not remain constant throughout?

9. Define specific reaction rate or rate constant.

10. What is half-life period of a reaction?

## 2 MARKS QUESTION

1. The rate of a particular reaction quadruples when the temperature changes from 293K to 313K. Calculate activation energy.

Ans.  $K_2/K_1 = 4,$

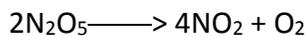
$$T_1 = 293K \quad T_2 = 313K$$

$$\log [k_2/k_1] = E_a(1/T_1 - 1/T_2) / 19.15$$

Thus on calculating and substituting values we get.....

$$E_a = 52.86 \text{ KJ mol}^{-1}$$

2. If the decomposition of nitrogen oxide as



follows a first order kinetics.

- (i) Calculate the rate constant for a 0.05 M solution if the instantaneous rate is  $1.5 \times 10^{-6} \text{ mol/l/s}$ ?

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

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

$$[\text{N}_2\text{O}_5]$$

$$K = \frac{1.5 \times 10^{-6}}{0.05}$$

$$0.05$$

$$K = 3.0 \times 10^{-5}$$

ii) What concentration of  $\text{N}_2\text{O}_5$  would give a rate of  $2.45 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$

$$\text{Rate} = 2.45 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$

$$[\text{N}_2\text{O}_5] = \frac{\text{Rate}}{K} = \frac{2.45 \times 10^{-5}}{3.0 \times 10^{-5}}$$

$$K = 3.0 \times 10^{-5}$$

$$= 0.82 \text{ M}$$

3) Write the difference between order and molecularity of reaction. **CBSE -2014**

Ans. ORDER MOLECULARITY

It is the sum of the powers of

It is the number of reacting speci-

Concentration terms in the rate law expression.

-es undergoing simultaneously

Collision in a reaction.

It is determined experimentally

it is a theoretical concept

Order of reaction need not be a whole number

It is whole no. only

Order of reaction can be zero.

It can't be zero or fractional

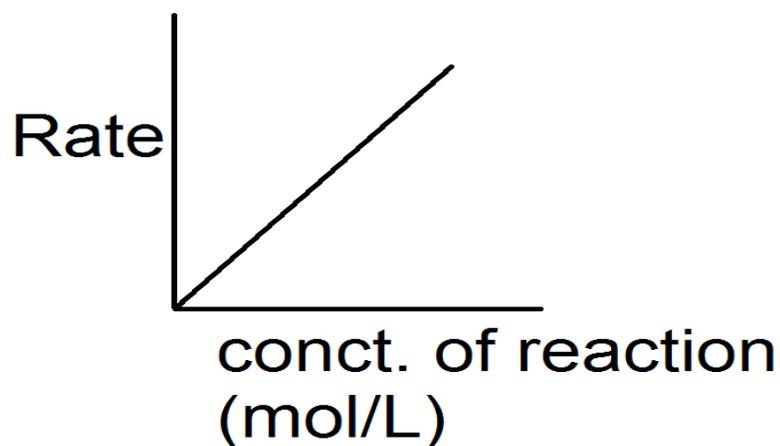
**4)** Define Threshold energy and activation energy. How they are related?

**Ans. Threshold Energy:** It is the minimum amount of energy which the reactant molecules must possess for the effective collision in forming the products.

**Activation Energy:** It is the excess energy required by the reactants to undergo chemical reaction.

Activation energy = Threshold energy – Average kinetic energy of molecules.

**5(a).** Draw a schematic graph showing how the rate of a first order reaction changes in concentration of reactants.



**Variation of rate of first order reaction with concentration.**

**(b).** rate of reaction is given by the equation

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

What are the units of rate constant for this reaction?

Ans. Rate =  $k [A] [B]$

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

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

**6.** List the factors affecting the rate of reaction.

**7.** Explain with suitable example, how the molecularity of a reaction is different from the order of a reaction.

**8.** Define the term 'rate constant' of 'specific reaction rate'.

9. What are Pseudo unimolecular reactions? Explain with the help of a suitable example.

10. What is half life period? Derive an expression for half-life period in case of a first order reaction.

### 3 marks question

Q1. The rate constant for first order reaction is 60/s. How much time will it take to reduce the concentration of the reaction to 1/10 of its initial value.

Ans:-

$$t = \frac{2.303 \log [R_0]}{k [R]}$$

$$t = \frac{2.303 \log 10}{60 \times 1/10}$$

$$t = \frac{2.303 \log 10}{60}$$

$$t = \frac{2.303}{60} = 3.38 \times 10^{-2} \text{ s}^{-1}$$

2. The rate of most of reaction double when their temperature is raised from 298k to 308k. Calculate the activation energy of such a reaction.

Ans:-

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

$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times 0.3010}{1000}$$

$$E_a = 52.89 \text{ kJ/mol}$$

3. A first order reaction takes 69.3 min for 50% completion. Set up an equation for determining the time needed for 80% completion.

Ans.  $k = 0.01$

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

$$= \frac{2.303}{69.3 \text{ min}} \log 2$$

$$= 0.01 \text{ min}^{-1}$$

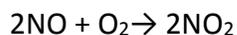
$$T = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$k = 0.01 \quad [R]$$

$$T = \frac{2.303}{0.01} \times \log 5$$

$$T = 160.9 \text{ min}$$

4. Following reaction takes place in one step



How will the rate of the reaction of the above reaction change if the volume of reaction vessel is diminished to 1/3 of its original volume? Will there be any change in the order of reaction with reduced volume?

Ans.  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$

$$\frac{dx}{dt} = k[\text{NO}]^2[\text{O}_2]^1$$

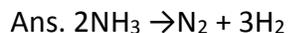
[Since it is one step]

If the volume of reaction vessel is diminished to 1/3, conc. of both [NO] and [O<sub>2</sub>] will become 3 times, the rate of reaction increased 27 times.

No change in the order.

5. The decomposition of  $\text{NH}_3$  on platinum surface is a zero order reaction. What are the rate of production of  $\text{N}_2$  and  $\text{H}_2$ .

$$\text{If } k = 2.5 \times 10^{-4}$$



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

$$\text{rate} = k \times [\text{NH}_3]^0 = k = 2.5 \times 10^{-4}$$

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

dt

$$\frac{d[\text{H}_2]}{dt} = 3 \times \text{rate}$$

dt

$$= 3 \times 2.5 \times 10^{-4} \text{ molL}^{-1}\text{sec}^{-1}$$

6. What is the effect of temperature on the rate of reaction? Explain giving reasons.

7. State the role of activated complex in a reaction and state its relation with activation energy.

#### QUESTIONS CARRYING 5 MARKS

1. What do you understand by the rate of a reaction? How it is expressed? How it is the rate of reaction determined?
2. What do you understand by order of a reaction? How does rate law differ from law of mass action? Give two example of each of the reactions of (i) zero order (ii) first order (iii) second order
3. Derive the equation for the rate constant for a first order reaction. What would be the units of the first order rate constant if the concentration is expressed in mole per litre and time in seconds.
4. Explain why the rate of reaction increases with increase in temperature.
5. Briefly explain the effect of temperature on the rate constant of a reaction.

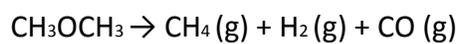
## HOTS

1. The half-life period of two samples are 0.1 and 0.4 seconds. Their initial concentrations are 200 and 50 mol L<sup>-1</sup> respectively. What is the order of reaction?
2. What is the ratio of  $t_{3/4} : t_{1/2}$  for a first order reaction ?
3. Higher molecularity reactions (viz. molecularity, 4 and above) are very rare. Why?
4. Consider the reaction  $2A + B \xrightarrow{\hspace{2cm}}$  Products

When concentration of B alone was doubled, half life time does not change. When conc. of A alone is doubled, the rate increases by two times. What is the unit of K and what is the order of the reaction?

5. For the reaction, the energy of activation is 75KJ / mol. When the energy of activation of a catalyst is lowered to 20KJ / mol. What is the effect of catalyst on the rate of reaction at 20°C.

6. The gas phase decomposition of CH<sub>3</sub>OCH<sub>3</sub> follows first order of kinetics



The reaction is carried out at a constant volume of the container at 500°C and has  $t_{1/2} = 14.5$  min.

Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure of the system after 12 min? Assume ideal behavior.

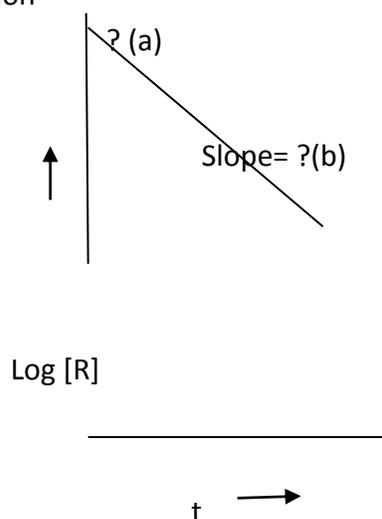
7. From the following data for a chemical reaction between A and B at 300 K

[A] mol/L	[B] mol/L	Initial rate (mol L <sup>-1</sup> sec <sup>-1</sup> )
$2.5 \times 10^{-4}$	$3 \times 10^{-5}$	$5 \times 10^{-4}$
$2.5 \times 10^{-4}$	$6 \times 10^{-5}$	$4 \times 10^{-3}$
$1 \times 10^{-3}$	$6 \times 10^{-5}$	$1.6 \times 10^{-2}$

Calculate (i) the order of reaction with respect to A and with respect to B. (ii) the rate constant 300K

Q 7. See the graph and answer the following question

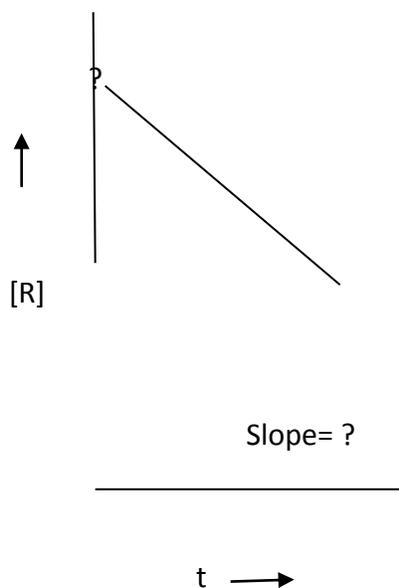
1). What is the order of reaction?



2) what are 'a' and b

q 8. 1) what is the order of reaction?

2) what is the slope and intercept?



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

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Experiment	Time in S	Total Pressure in atm
1	0	0.4
2	100	0.7

Calculate the rate constant. (Given :  $\log 4 = 0.6021$ ,  $\log 2 = 0.3010$ )

Ans.  $k = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t}$

$$k = \frac{2.303}{100} \log \frac{0.4}{2 \times 0.4 - 0.7}$$

$$= \frac{2.303 \times 0.6021}{100} = 0.01387 \text{ s}^{-1}$$

## CHAPTER-5 Surface Chemistry

4 Marks Chapter

The branch of the Chemistry which deals with the study of surface phenomena is called surface Chemistry.