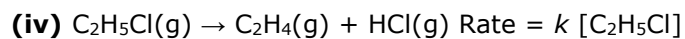
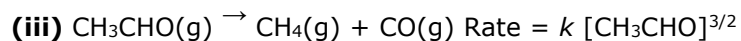
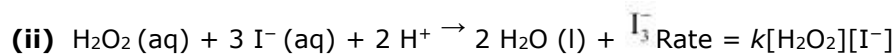
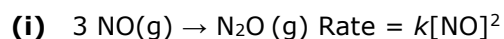


## (Chapter 4)(Chemical Kinetics)

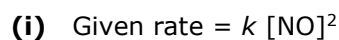
### XII

#### Question 4.1:

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



Answer

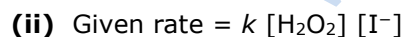


Therefore, order of the reaction = 2

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

Dimension of

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

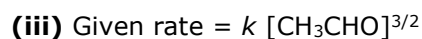


Therefore, order of the reaction = 2

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

Dimension of

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



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

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

Dimension of

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

(iv) Given rate =  $k [\text{C}_2\text{H}_5\text{Cl}]$  Therefore, order of the reaction = 1

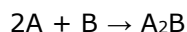
$$k = \frac{\text{Rate}}{[\text{C}_2\text{H}_5\text{Cl}]}$$

Dimension of

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

#### 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

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

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

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

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

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

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

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

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

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

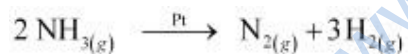
$$= 3.89 \text{ mol L}^{-1} \text{ s}^{-1}$$

#### 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

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

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

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

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

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

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

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  $[A] = a$

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

$$= ka^2$$

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

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

$$= 4ka^2$$

$$= 4R$$

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

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

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

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

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

Therefore, the rate of the reaction would be reduced to  $\frac{1}{4}$ <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  $10^\circ$  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

**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,

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

For  $k_1 = \frac{2.303}{30} \log \frac{0.55}{0.31} \quad t = 30 \text{ s},$   
 $= 1.911 \times 10^{-2} \text{ s}^{-1}$

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



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

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

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

$$\Rightarrow y = 0$$

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

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

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

$$\Rightarrow 2.821 = 2^x$$

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

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

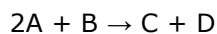
$$= 1.496$$

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

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

**Question 4.11:**

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



Experiment	A/ mol L <sup>-1</sup>	B/ mol L <sup>-1</sup>	Initial rate of formation of D/mol L <sup>-1</sup> min <sup>-1</sup>
I	0.1	0.1	6.0 × 10 <sup>-3</sup>

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

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

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

$$\Rightarrow 4 = 2^y$$

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

$$\Rightarrow y = 2$$

Therefore, the rate law is

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

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

From experiment I, we obtain

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

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

From experiment II, we obtain

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

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

From experiment III, we obtain

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

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

From experiment IV, we obtain

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

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

Therefore, rate constant,  $k = 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$  **Question 4.12:**

The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

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

Answer

The given reaction is of the first order with respect to A and of zero order with respect to B.

Therefore, the rate of the reaction is given by,

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

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

From experiment I, we obtain

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

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

From experiment II, we obtain

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

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

From experiment III, we obtain 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

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

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

**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

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

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

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

**Question 4.14:**

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

Answer

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

Here,

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

It is known that,

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

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

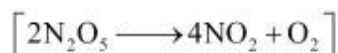
$$= \frac{2.303}{0.693} \log \frac{100}{80}$$

= 1845 years (approximately)

Hence, the age of the sample is 1845 years.

**Question 4.15:**

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



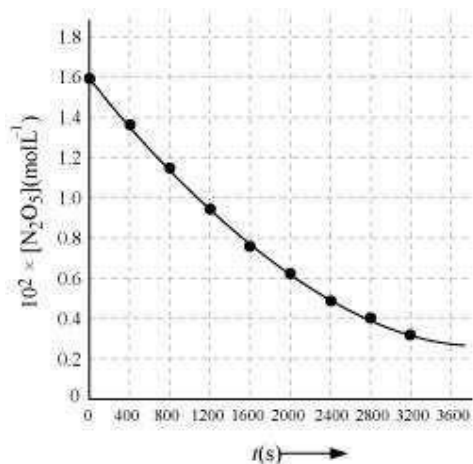
in gas phase at 318K are given below:

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

- (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).

Answer

i.

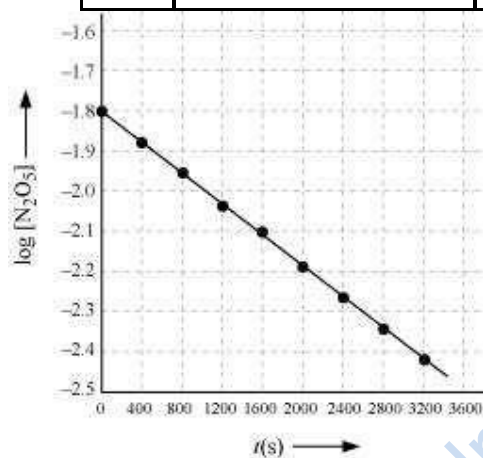


(ii) Time corresponding to the concentration,  $\frac{1.630 \times 10^2}{2} \text{ mol L}^{-1} = 81.5 \text{ mol L}^{-1}$ , is the half life. From the graph, the half life is obtained as 1450 s.

(iii)

t(s)	$10^2 \times [N_2O_5] / \text{mol L}^{-1}$	$\log [N_2O_5]$
0	1.63	- 1.79
400	1.36	- 1.87
800	1.14	- 1.94
1200	0.93	- 2.03
1600	0.78	- 2.11
2000	0.64	- 2.19

2400	0.53	- 2.28
2800	0.43	- 2.37
3200	0.35	- 2.46



(iv) The given reaction is of the first order as the plot,  $\log [N_2O_5]$  v/s  $t$ , is a straight line. Therefore, the rate law of the reaction is

$$\text{Rate} = k [N_2O_5]$$

(v) From the plot,  $\log [N_2O_5]$

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

v/s  $t$ , we obtain

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

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

Therefore, we obtain,



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

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

(vi) Half-life is given by,

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

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

**Question 4.16:**

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

Answer

It is known that,

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

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

**Question 4.17:**

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

Answer

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

Here,

It is known that,

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

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

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

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

$$\begin{aligned} \Rightarrow [R] &= \text{antilog} (-0.1071) \\ &= \text{antilog} (\bar{1}.8929) \\ &= 0.7814 \mu\text{g} \end{aligned}$$

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

Again,

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

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

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

$$\begin{aligned} \Rightarrow [R] &= \text{antilog} (-0.6425) \\ &= \text{antilog} (\bar{1}.3575) \\ &= 0.2278 \mu\text{g} \end{aligned}$$

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,

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

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

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

$$\begin{aligned} t_{1/2} &= \frac{0.693}{k} \\ &= \frac{0.693}{8.918 \times 10^{-3}} \text{ min} \\ &= 77.7 \text{ min (approximately)} \end{aligned}$$

**Question 4.20:**

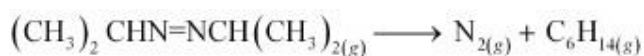
For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

$t$ (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,  $P_t = (P_0 - p) + p + p$

$$\Rightarrow P_t = P_0 + p$$

$$\Rightarrow p = P_t - P_0$$

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

$$= 2P_0 - P_t$$

For a first order reaction,

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

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

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

$$\text{When } t = 360 \text{ s,}$$

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

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

$$\text{When } t = 720 \text{ s,}$$

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

Hence, the average value of rate constant is

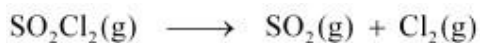
$$k = \frac{(2.175 \times 10^{-3}) + (2.235 \times 10^{-3})}{2} \text{ s}^{-1}$$

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

**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.

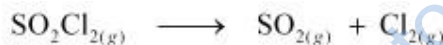


Experiment	Time/s <sup>-1</sup>	Total pressure/atm
1	0	0.5
2	100	0.6

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.



$$\begin{array}{l} \text{At } t = 0 \quad P_0 \qquad \qquad 0 \qquad 0 \\ \text{At } t = t \quad P_0 - p \qquad \qquad p \qquad p \end{array}$$

$$P_t = (P_0 - p) + p + p$$

After time,  $t$ , total pressure,

$$\Rightarrow P_t = P_0 + p$$

$$\Rightarrow p = P_t - P_0$$

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

For a first order reaction,

$$\begin{aligned} k &= \frac{2.303}{t} \log \frac{P_0}{P_0 - p} \\ &= \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t} \end{aligned}$$

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

$$\begin{aligned} \text{When } & \\ &= 2.231 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

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

$$\begin{aligned}
 P_0 + p &= 0.65 \\
 \Rightarrow p &= 0.65 - P_0 \\
 &= 0.65 - 0.5 \\
 &= 0.15 \text{ atm}
 \end{aligned}$$

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

$$\begin{aligned}
 P_{\text{SOCl}_2} &= P_0 - p \\
 &= 0.5 - 0.15 \\
 &= 0.35 \text{ atm}
 \end{aligned}$$

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

$$\begin{aligned}
 \text{Rate} &= k(P_{\text{SOCl}_2}) \\
 &= (2.23 \times 10^{-3} \text{ s}^{-1})(0.35 \text{ atm}) \\
 &= 7.8 \times 10^{-4} \text{ atm s}^{-1}
 \end{aligned}$$

**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  $E_a$ .

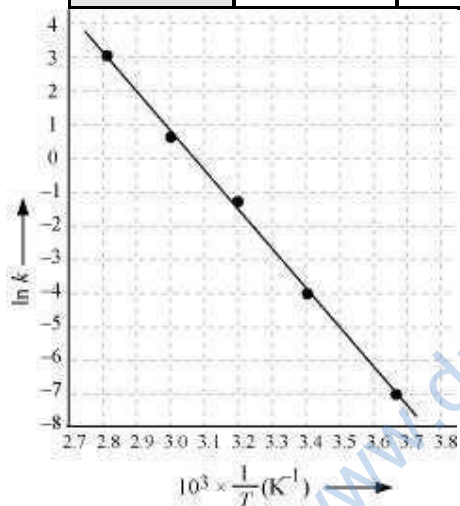
Predict the rate constant at  $30^\circ$  and  $50^\circ\text{C}$ .

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,

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

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

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

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

$$\begin{aligned} &= \log(2.418 \times 10^{-5} \text{ s}^{-1}) + \frac{179.9 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ Jk}^{-1} \text{ mol}^{-1} \times 546 \text{ K}} \\ &= (0.3835 - 5) + 17.2082 \\ &= 12.5917 \end{aligned}$$

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

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

#### Question 4.24:

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

Answer  $k = 2.0 \times 10^{-2} \text{ s}^{-1}$   $T = 100 \text{ s}$

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

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

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

Therefore,

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

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

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

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

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

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

**Question 4.25:**

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

Answer

For a first order reaction,

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

It is given that,  $t_{1/2} = 3.00$  hours

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

Therefore,

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

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

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

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

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

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

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

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

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

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

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

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

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

The given equation is

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\Rightarrow \log(0.654 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

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

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

$$= 668.95 \text{ K}$$

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

**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

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

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

$$T_1 = 273 + 10 = 283 \text{ K } k_2$$

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

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

Then,

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

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

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

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

$$\Rightarrow 0.9528 T_2 = 283$$

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

$$= 297 \text{ K}$$

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

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

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

#### Question 4.29:

The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of  $A$  is  $4 \times 10^{10} \text{ s}^{-1}$ . Calculate  $k$  at 318 K and  $E_a$ .

Answer

For a first order reaction,

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

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

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

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

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

According to the question,

$$t = t'$$

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

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

From Arrhenius equation, we obtain

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

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

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

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

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

To calculate  $k$  at 318 K,

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

Again, from Arrhenius equation, we obtain

$$\begin{aligned} \log k &= \log A - \frac{E_a}{2.303 R T} \\ &= \log(4 \times 10^{10}) - \frac{76.64 \times 10^3}{2.303 \times 8.314 \times 318} \end{aligned}$$

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

$$= -1.9855$$

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

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

**Question 4.30:**



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

Answer

From Arrhenius equation, we obtain

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

It is given that,  $k_2 = 4k_1$

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

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

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

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

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

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

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

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