

## Chapter - Chemical Kinetics

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

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

$$= -\frac{[R]_2 - [R]_1}{t_2 - t_1}$$
$$\Rightarrow -\frac{0.02 - 0.03}{25} = 4 \times 10^{-4} \text{ Mmin}^{-1}$$

Also, it can be expressed in seconds as:

$$\text{Average rate of reaction} = \frac{4 \times 10^{-4}}{60} = 6.67 \times 10^{-6}$$

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

**Ans:**

$$\text{Average rate} = \frac{1}{2} \frac{\Delta[A]}{\Delta t}$$
$$= \frac{1}{2} \frac{[A]_2 - [A]_1}{t_2 - t_1}$$
$$= \frac{1}{2} \times \frac{0.4 - 0.5}{10} = \frac{1}{2} \times \frac{1 - 0.1}{10}$$
$$= 0.005 \text{ mol L}^{-1} = 5 \times 10^{-3} \text{ M min}^{-1}$$

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

**Ans:**

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

**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?**

**Ans:**

Because the reaction  $X \rightarrow Y$  has second-order kinetics, the rate law equation will be  $\text{Rate} = kC^2$ , with  $C = [x]$ .

The rate law equation for the reaction  $X \rightarrow Y$  will be  $\text{Rate} = kC^2$ , with  $C = [x]$  because it possesses second-order kinetics. So,  $[x] = 3C \text{ mol L}^{-1}$

The rate equation is

$$\begin{aligned}\text{Rate} &= K(3C)^2 \\ &= 9(kC^2)\end{aligned}$$

As a result, the reaction rate will increase by 9 times.

As a result, the rate at which Y is formed will grow by 9 times.

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

**Ans:**

Initial amount  $= [R]_0 = 5g$

Final concentration  $= [R] = 3g$

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

For a first order reaction

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

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

**Ans:**

First order reaction

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{0.693}{k} \\ t_{\frac{1}{2}} &= 60 \text{ min} \\ k &= \frac{0.693}{t_{\frac{1}{2}}} \\ &= \frac{0.693}{60} = 0.01155 \text{ min}^{-1} \\ &= 1.155 \text{ min}^{-1} \\ k &= 1.925 \times 10^{-1} \text{ s}^{-1} \end{aligned}$$

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

**Ans:**

A 10° increase in temperature almost doubles the rate constant of a process. The Arrhenius equation, on the other hand, gives the exact temperature dependency of the rate of a chemical reaction.

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

Where, A stands for the Arrhenius factor, also known as the frequency factor.

T stands for temperature. The gas constant is R. The activation energy is referred to  $E_a$ .

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

**Ans:**

Given,  $T_1 = 298\text{K}$  ,  $T_2 = (298+10)\text{K}$ .

We also know that when the temperature is raised by 10 degrees Celsius, the reaction rate doubles. As a result, we'll use the values  $k_1 = k$ , and  $k_2 = 2k$ .

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

On substitution

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

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

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

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

$$= 52.89 \text{ kJ mol}^{-1}$$

**9. The activation energy for the reaction  $2\text{HI(g)} \rightarrow \text{H}_2 + \text{I}_{2(\text{g})}$  is  $209.5 \text{ kJ mol}^{-1}$  at  $581 \text{ K}$ . Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy.**

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

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

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

The percentage of reactant molecules with energy equal to or greater than activation energy is now:

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

$$\ln = -E_a / RT$$

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

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

$$x = \text{Anti log}(-18.8323) = 1.47 \times 10^{-19}$$

### NCERT Exercise

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



**Ans:**

Given

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

Order of the reaction = 2

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

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

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



**Ans:**

Given,  $k = [H_2O_2][I^-]$

Order of the reaction  $k = \frac{\text{Rate}}{[H_2O_2][I^-]}$

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

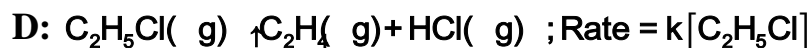


Given,  $\text{rate} = k[CH_3CHO]^{3/2}$

Order of the reaction will be  $\frac{3}{2}$

$$k = \frac{\text{Rate}}{[CH_3CHO]^{3/2}}$$

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



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

Order of the reaction 1

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

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

**2. For the reaction:  $2\text{A} + \text{B} \rightarrow \text{A}_2\text{B}$  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 reaction's beginning rate 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  $0.06 \text{mol L}^{-1}$**

**Ans:**

The initial rate of the reaction is

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

The concentration of A responded when  $[\text{A}]$  was lowered from  $0.1 \text{mol L}^{-1}$  to  $0.06 \text{mol L}^{-1}$ .

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

As a result, B concentration =  $\frac{1}{2} \times 0.04 \text{ mol L}^{-1} = 0.02 \text{ mol L}^{-1}$

After then, the concentration of B responded.

$$[B] = (0.2 \times 0.02) \text{ mol L}^{-1} = 0.18 \text{ mol L}^{-1}$$

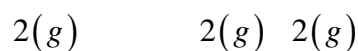
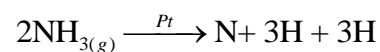
The rate of the reaction is given by once  $[A]$  is lowered to  $0.06 \text{ mol L}^{-1}$ .

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

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

**Ans:** The following equation represents the breakdown of  $\text{NH}_3$  on a platinum surface.



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

It is assumed, however, that the reaction is of zero order.

So,

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

As a result, the rate of  $\text{N}_2$  production is



$$\frac{d[N_2]}{dt} = \frac{2.5 \times 10^{-4}}{2}$$

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

In addition, the rate of  $H_2$  production is increasing.

$$\frac{d[N_2]}{dt} = \frac{3}{2} \times 2.5 \times 10^{-4}$$

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

**4. The decomposition of dimethyl ether leads to the formation of  $CH_4$ ,  $H_2$  and  $CO$  and the reaction rate is given by  $\text{Rate} = k = [CH_3OCH_3]^{3/2}$ . 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.  $\text{Rate} = k = (P_{CH_3OCH_3})^{3/2}$ . If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?**

**Ans:**

In addition, the rate of  $H_2$  production is increasing.

$$\text{Rate} = k = (P_{CH_3OCH_3})^{3/2}$$

$$k = \frac{\text{Rate}}{P_{CH_3OCH_3}}$$

Hence, the unit of rate constants

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

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

**Ans:**

The rate of a reaction is influenced by several things.

(i) Reactant nature: The rate of the reaction is determined by the reactant's nature. Ionic compound reactions, for example, are faster than covalent compound reactions.

(ii) Reactant state: Solid reactions are sluggish, liquid reactions are quick, and gas reactions are very fast.

(iii) Temperature: The rate of reaction is heavily influenced by the temperature. Temperature raises the pace of reaction by 2-3 times for every 100°C increase in temperature.

$$\frac{r_{T+10}}{r_T} = 2-3$$

The temperature coefficient is the name given to this proportion.

The average kinetic energy of reactant molecules increases as the temperature rises. As a result, the rate of collisions rises. The number of molecules with threshold energy grows as the temperature rises. As a result, the rate of reaction accelerates.

iv) Catalyst presence: The rate of reaction also is affected by the presence of a catalyst. Catalysts boost reaction rates by increasing reaction surface area, generating an unstable intermediate with the substrate, and providing a lower-activation-energy alternative path.

**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**

**Ans:** Let the reactant concentration be  $[A] = a$ .

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

If the reactant concentration is doubled,  $[A] = a$ , the reaction rate is

$$R = k(2a)^2 = 4ka^2 = 4R$$

As a result, the reaction rate would increase by four times.

**(ii) reduced to half?**

**Ans:** If the reactant's concentration is cut in half,  $[A] = \frac{1}{2}a$

The rate of reaction will be

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

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

As a result, the reaction rate would be lowered to  $= \frac{1}{4}$

**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?**

**Ans:**

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

Where k is the rate constant,

A denotes the Arrhenius factor or frequency factor,

R denotes the gas constant,

T denotes the temperature, and  $E_a$  denotes the activation energy for the reaction.

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

$k_1$  = rate constant at temperature  $T_1$

$k_2$  = rate constant at temperature  $T_2$

**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.**

**Ans:** Average reaction time between 30 and 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) Calculate the pseudo first order rate constant for the hydrolysis of ester**

**Ans:** pseudo first order reaction

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

When  $t = 30\text{s}$

$$k = \frac{2.303}{30} \times \log \left( \frac{0.55}{0.31} \right) = 1.91 \times 10^{-2} / \text{s}$$

When  $t = 60\text{s}$

$$k = \frac{2.303}{60} \times \log\left(\frac{0.55}{0.17}\right) = 1.96 \times 10^{-2} / \text{s}$$

When  $t = 90\text{s}$

$$k = \frac{2.303}{90} \times \log\left(\frac{0.55}{0.085}\right) = 2.07 \times 10^{-2} / \text{s}$$

$$\text{Average rate constant } k = \frac{k_1 + k_2 + k_3}{3} = 1.98 \times 10^{-2} / \text{s}$$

**9. A reaction is first order in A and second order in B.**

- i. Write the differential rate equation.**
- ii. How is the rate affected on increasing the concentration of three times?**
- iii. How is the rate affected when the concentrations of both A and B are doubled**

**Ans:**

(i) The differential rate equation will be the following:

$$\frac{d[R]}{dt} = k[A][B]^2$$

(ii) If B's concentration is three times higher, then

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

As a result, the reaction rate will rise by 9 times.

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

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

As a result, the reaction rate will rise by eight times.

**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.**

$A/\text{mol L}^{-1}$	0.20	0.20	0.04
$B/\text{mol L}^{-1}$	0.30	0.10	0.05
$r_0/\text{mol L}^{-1} \text{ s}^{-1}$	$5.07 \times 10^{-5}$	$5.07 \times 10^{-5}$	$1.43 \times 10^{-4}$

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

**Ans:** Let the reaction order be  $x$  with respect to A and  $y$  with respect to B. Therefore,

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

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

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

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

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

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

$$\left[ \frac{0.30}{0.10} \right]^x \left[ \frac{0.30}{0.10} \right]^y$$

$$y = 0$$

We get equation (ii) by dividing equation (i) by equation (ii).

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

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

$$[0.05]^y = [0.30]^y = 1$$

$$2.821 = 2^x$$

$$\log 2.821 = x \log 2$$

$$x = \frac{\log 2.821}{\log 2} = 1.496 = 1.5 \text{ (approximately)}$$

As a result, the reaction's order regarding A is 1.5 and zero with respect to B.

**11. The following results have been obtained during the kinetic studies of the reaction:  $2A + B \rightarrow C + D$**

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>
<b>I</b>	<b>0.1</b>	<b>0.1</b>	<b><math>6.0 \times 10^{-3}</math></b>
<b>II</b>	<b>0.3</b>	<b>0.2</b>	<b><math>7.3 \times 10^{-2}</math></b>
<b>III</b>	<b>0.3</b>	<b>0.4</b>	<b><math>2.88 \times 10^{-1}</math></b>
<b>IV</b>	<b>0.4</b>	<b>0.1</b>	<b><math>2.40 \times 10^{-2}</math></b>

**Determine the rate law and the rate constant for the reaction**

**Ans:**

Let the reaction order be x for reaction with respect to A and y for reaction with respect to B. As a result, the reaction rate is given by,

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

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

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

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

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

When we divide equation (iv) by I we get,

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

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

$$x = 1$$

Divide (iii) by (i)

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

$$= 4 = \left(\frac{0.4}{0.2}\right)^y = 4 = 2^y$$

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

Rate law

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

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

From experiment I we understand



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

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

From experiment II we understand

$$k = \frac{2.88 \times 10^{-1} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.3 \text{ mol L}^{-1})(0.4 \text{ mol L}^{-1})^2} = 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

From experiment III we understand

$$k = \frac{2.40 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.4 \text{ mol L}^{-1})(0.1 \text{ mol L}^{-1})^2} = 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

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

**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>
<b>I</b>	<b>0.1</b>	<b>0.1</b>	<b>2.0 × 10<sup>-2</sup></b>
<b>II</b>	----	<b>0.2</b>	<b>4.0 × 10<sup>-2</sup></b>
<b>III</b>	<b>0.4</b>	<b>0.4</b>	----
<b>IV</b>	----	<b>0.2</b>	<b>2.0 × 10<sup>-2</sup></b>

**Ans:** With respect to A, the given reaction is first order, whereas with respect to B, it is zero order.

The rate of the reaction

$$Rate = k[A]^1[B]^0$$

$$Rate = k = [A]$$

From 1<sup>st</sup> experiment,

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

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

From 2<sup>nd</sup> experiment,

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

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

From 3<sup>rd</sup> experiment,

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

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

From 4<sup>th</sup> experiment

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

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

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

**Ans:**

$$(i) \text{ Half life } t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{200 \text{ s}^{-1}} = 0.346 \times 10^{-2}$$

$$(ii) \text{ Half life } t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{2 \text{ min}^{-1}} = 0.346 \text{ min}$$

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

**14. The half-life for radioactive decay of C-12 is 5730 years. An archeological artifact containing wood had only 80% of the C-14 found in a living tree. Estimate the age of the sample.**

**Ans:**

The dynamics of radioactive decay are first order. As a result, the decay constant

$$\text{Decay constant } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ year}} = 1.209 \times 10^{-4} / \text{ years}$$

**The rate of counts is proportional to the number of C-14 atoms in the sample.**

$$N_0 = 100, N = 80$$

$$\text{The age of the sample } t = \frac{2.303}{k} \log \left( \frac{N_0}{N} \right)$$

$$t = \frac{2.303}{1.209 \times 10^{-4}} \times \log \left( \frac{100}{80} \right) = 1846 \text{ years}$$

Therefore, the sample age is 1846 years.

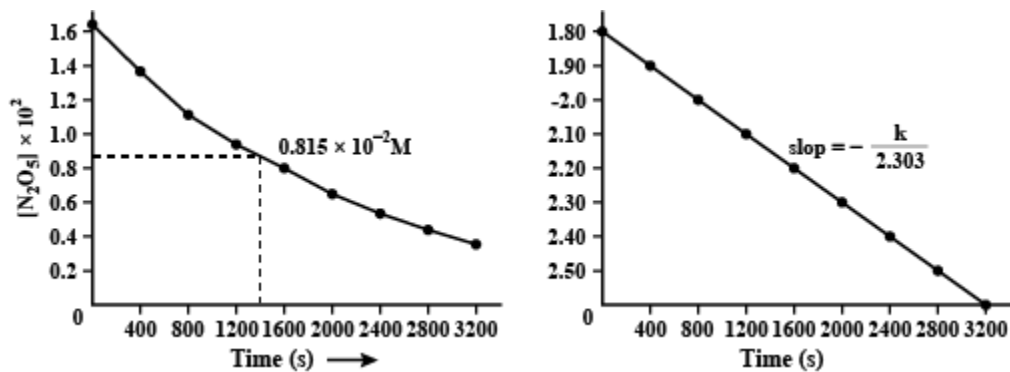
**15. The experimental data for decomposition of  $N_2O_5$  [ $2N_2O_5 \rightarrow 4NO_2 + O_2$ ] in gas phase at 318K are given below:**

t/s	0	4	8	1	1	2	2	1	3
		0	0	2	6	0	4	8	2
		0	0	0	0	0	0	0	0
				0	0	0	0	0	0
	1	1	1	0	0	0	0		

$10^{-2} \times [\text{N}_2\text{O}_5] / \text{mol L}^{-1}$	.	.	.	.	.	.	.		
	6	3	1	9	7	6	5		
	3	6	4	3	8	4	3		

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

Ans. The plot is as follows:



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

Ans: The period that corresponds to the concentration

$$\frac{1.630 \times 10^{-2}}{2} \text{ mol L}^{-1} = 0.815 \times 10^{-2} \text{ mol L}^{-1} \text{ is half-life.}$$

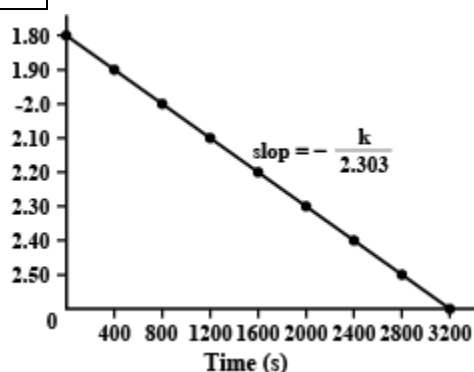
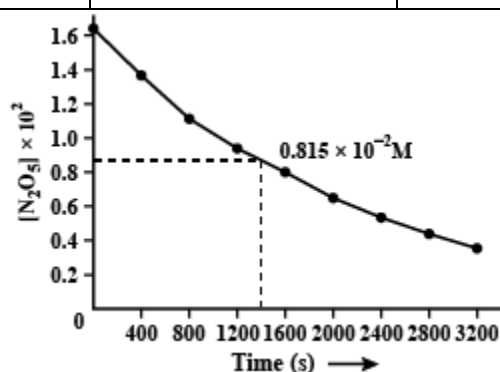
Observing the graph, the half life is 1440s.

(iii) Draw a graph between  $\log[\text{N}_2\text{O}_5]$  and  $t$ .

Ans:

$t(\text{s})$	$10^2 \times [\text{N}_2\text{O}_5] / \text{mol L}^{-1}$	$\text{Log}[\text{N}_2\text{O}_5]$
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) What is the rate law?**

**Ans:** The provided reaction is of first order, as evidenced by the straight-line plot of  $\log \text{N}_2\text{O}_5$  v/s t. As a result, the reaction's rate law is  $\text{Rate} = k[\text{N}_2\text{O}_5]$

**(v) Calculate the rate constant.**

**Ans:** From the plot  $\text{N}_2\text{O}_5$  v/s t, we get

$$\text{slope} = \frac{2.46 - (-1.79)}{3200 - 0} = \frac{-0.67}{3200} = 4.82 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

**(vi) Calculate the half-life period from k and compare it with (ii)**

**Ans:** Half life given by

$$\text{slope} = \frac{2.46 - (-1.79)}{3200 - 0} = \frac{-0.67}{3200} = 4.82 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} = 1438 \text{ s}$$

The value of  $t_{\frac{1}{2}}$  computed from k is extremely close to the value acquired from graph.

**16. 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?**

**Ans:**

$$\begin{aligned} t &= \frac{2.303}{k} \log \frac{[R]}{[R]} \\ &= \frac{2.303}{60 \text{ s}^{-1}} \log \frac{1}{1} \\ &= \frac{2.303}{60 \text{ s}^{-1}} \log 16 \\ &= 4.62 \times 10^{-2} \text{ s} \end{aligned}$$

**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?**

**Ans:**

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

Knowing

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

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

$$= \frac{0.303}{\frac{0.693}{28.1}} (-108[R]) \log [R] - \frac{10 \times 0.303}{2.303 \times 28.1} [R]$$

$$= \text{anti log}(-0.1071) = 0.7814 \mu\text{g}$$

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

Repeating  $k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{28.1} \text{ yr}^{-1}$

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

$$60 = \frac{0.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$

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

$$[R] = \text{anti log}(-0.6425)$$

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

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

**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**

**Ans:**

The time required for 99 percent completion of a first order reaction is

$$t_1 = \frac{2.303}{k} \log \frac{100}{100-99} = \frac{2.303}{k} \log 100$$

The time required for 90 percent completion of a first order reaction is

$$t_2 = \frac{2.303}{k} \log \frac{100}{100-90} = \frac{2.303}{k} \log 10 = \frac{2.303}{k} t_1 = 2t_2$$

As a result, the time required to complete a first order reaction at 99 percent is twice the time required to complete the reaction at 90%.

**19. A first order reaction takes 40 min for 30% decomposition. Calculate  $t_{\frac{1}{2}}$**

**Ans:**

1<sup>st</sup> order reaction

$$t_2 = \frac{2.303}{k} \log \frac{[R]}{[R]} k = \frac{2.303}{40 \text{ min}} \log \frac{100}{100-30} = \frac{2.303}{40 \text{ min}} \log \frac{10}{7} = 8.918 \times 10^{-3} \text{ min}^{-1}$$

$t_{\frac{1}{2}}$  of the decomposition reaction is

$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{8.918 \times 10^{-3}} \text{ min} = 77.7 \text{ min}$$

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

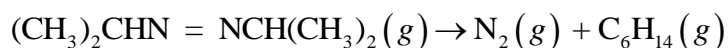
t(sec)	P(mm of Hg)
0	35.0
360	54.0



720	63.0
-----	------

### Calculate the rate constant

**Ans:** The following equation represents the breakdown of azoisopropane to hexane and nitrogen at 54.3 k.



At  $t = 0$        $P_0$

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

Total pressure

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

$$P_t = P_0 + p$$

When the value of  $p$  is substituted for the pressure of the reactant at time  $t$

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

1st order reaction

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

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

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

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

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

Average value of rate constant

$$k = \frac{(2.175 \times 10^{-3}) + (2.235 \times 10^{-3})}{2} \text{ s}^{-1} = 2.20 \times 10^{-3} \text{ s}^{-1}$$

**21. The following data were obtained during the first order thermal decomposition of**

**SO<sub>2</sub>Cl<sub>2</sub> at a constant volume SO<sub>2</sub>Cl<sub>2</sub>(g) → SO<sub>2</sub>(g) + Cl<sub>2</sub>(g)**

Experiment	Time/ s <sup>-1</sup>	Pressure/atm
<b>1</b>	<b>0</b>	<b>0.5</b>
<b>2</b>	<b>100</b>	<b>0.6</b>

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

**Ans:** The following equation represents the thermal breakdown of SO<sub>2</sub>Cl<sub>2</sub> at a constant volume.



At  $t = 0$   $P_0$

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

Total pressure

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

$$P_t = P_0 + p$$

when the value of p is substituted for the pressure of the reactant at time t

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

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

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

when  $t = 100s$

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

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

As a result, the total pressure of  $SO_2Cl_2$

at time  $t$  is  $0.65 \text{ atm}$ .

$$\begin{aligned}
 2 P_{SOCl_2} &= 2P_0 - P_t \\
 &= 2 \times 0.50 - 0.65 \\
 &= 0.35 \text{ atm}
 \end{aligned}$$

As a result, when total pressure is  $0.65 \text{ atm}$ , the rate of equation is

$$\begin{aligned}
 \text{Rate} &= k = (P_{SOCl_2}) \\
 &= (2.33 \times 10^{-3} s^{-1})(0.354 \text{ atm}) = 7.8 \times 10^{-4} \text{ atm s}^{-1}
 \end{aligned}$$

**22. The rate constant for the decomposition of  $N_2O_5$  at various temperatures is given below:**

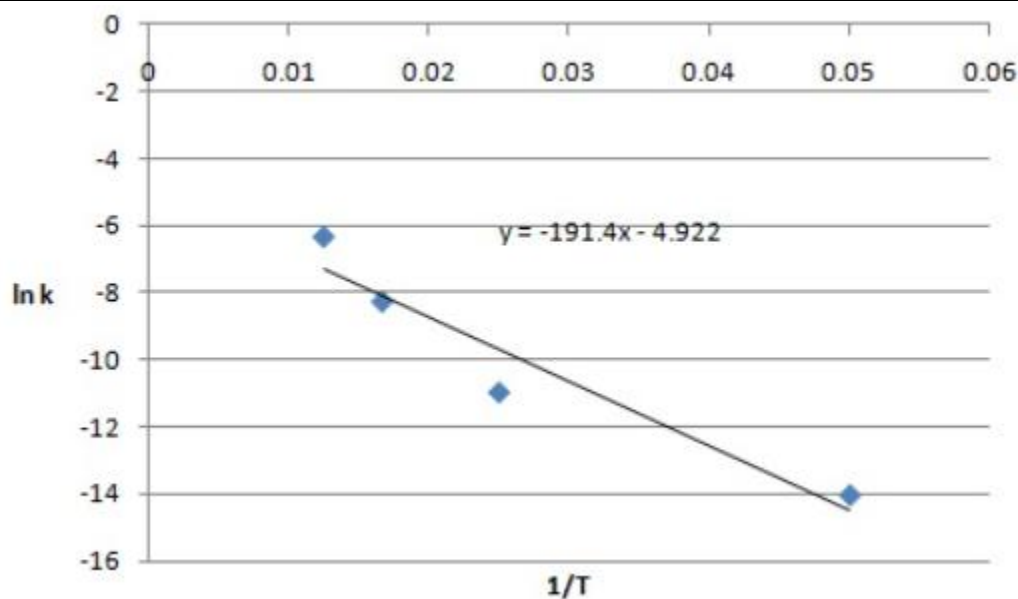
<b>T/°C</b>	<b>0</b>	<b>20</b>	<b>40</b>	<b>60</b>	<b>80</b>
$10^5 \times k/s^{-1}$	<b>0.0787</b>	<b>0.0787</b>	<b>0.0787</b>	<b>178</b>	<b>2140</b>

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

**Ans:**

From the given data, we get:

$T / ^\circ\text{C}$	27	33	40	50	60
$T / \text{K}$	300	306	313	323	333
$1/T \times 10^3 / \text{K}^{-1}$	0.0033366	0.0029334	0.0026185	0.0024768	0.0023153
$10^5 \times k / \text{s}^{-1}$	0.0787	4.075	25.7	178	2140
$\ln k$	-7.147	-4.075	-1.359	-0.577	3.063



Slope of the line

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

Arrhenius

equation,

$$\text{Slope} = -\frac{E_a}{R} \quad E_a = -\text{slope} \times R = -(-12.301K) \times (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) = 102.27 \text{ K J mol}^{-1}$$

Repeating

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

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

Since,

$$T = 273K, \ln k = -7.147$$

So,

$$\ln A = -7.147 + \frac{102.27 \times 10^3}{8.314 \times 273} = 37.911 \ln A = 2.91 \times 10^6$$

$$T = 30 + 273K = 303K$$

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

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

$$\ln k = -2.8$$

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

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

$$\ln k = -0.5$$

$$k = 0.607 s^{-1}$$

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

$$T = 50 + 273K = 323K$$

**23. The rate constant for the decomposition of hydrocarbons is  $2.418 \times 10^{-5} s^{-1}$**

at 546 K. If the energy of activation is 179.9 kJ /mol, what will be the value of pre-exponential factor.

Ans:

Arrhenius equation

$$K = Ae^{-E_a/RT} \ln k = \ln A - \frac{E_a}{RT} \log k = \log A - \frac{E_a}{2.303RT}$$

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

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

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

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

Ans:

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

The given reaction is a first order reaction since the unit of k equals  $s^{-1}$

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \quad 2.0 \times 10^{-2} s^{-1} = \frac{2.303}{100 s} \log \frac{1.0}{[A]} \quad 2.0 \times 10^{-2} s^{-1} = \frac{2.303}{100 s} (-\log [A])$$

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

$$[A] = \text{anti log} \left( \frac{2.0 \times 10^{-1} \times 100}{2.303} \right)$$

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

As a result, the concentration of A left is  $0.135 \text{ mol L}^{-1}$ .

**25. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law with  $t_{\frac{1}{2}} = 3\text{hours}$ . What fraction of sample of sucrose remains after 8 hour?**

**Ans:**

1st order reaction

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

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

$$t_{\frac{1}{2}} = 3 \text{ hours}$$

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

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

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

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

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

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

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

$$\frac{[R]_0}{[R]} = 0.1576$$

$$= 0.158$$

As a result, after 8 hours, 0.158 percent of the sucrose sample remains.

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

**Ans:** From the given equation

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

Arrhenius equation ,

$$k = A e^{-E/RT} \dots (ii)$$

From equation (i) and (ii) we get

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

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

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

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

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

**27. The rate constant for the first order decomposition of H<sub>2</sub>O<sub>2</sub> 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?**

**Ans:** The expression for the rate constant is as follows:

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

Comparing it with Arrhenius equation, we get-

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

$$\text{Therefore, } \frac{E_a}{2.303R} = 1.25 \times 10^4$$

$$E_a = 1.25 \times 10^4 \times 2.303 \times 8.314$$

The activation energy  $= E_a = 239339 \text{ J / mol} = 239.339 \text{ kJ / mol}$

Half life period,  $t_{1/2} = 256 \text{ min} = 256 \times 60 \text{ sec}$



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

$$k = \frac{0.693}{256 \times 60 \text{sec}}$$

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

Substitute in equation (i), we get-

$$\log 4.51 \times 10^{-5} = 14.341.25 \times 10^4 \text{ K} / \text{T}$$

$$-4.35 = 14.341.25 \times 10^4 \text{ K} / \text{T}$$

$$\text{T} = 669 \text{ K}$$

Hence, the temperature at which the half-life period is 256 minutes is 669 K.

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

**Ans:** It is given that the decomposition of A into product has value of  $k = 4.5 \times 10^3 \text{ s}^{-1}$  at  $10^\circ\text{C}$ .

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

$$\log \left( \frac{1.5 \times 10^4}{4.5 \times 10^3} \right) = \frac{60 \times 10^3}{2.303 \times 8.314} \left[ \frac{T' - 283}{283T'} \right]$$

$$0.5228 = 3132.62 \left[ \frac{T' - 283}{283T'} \right]$$

$$T' - 283 = 0.0472T'$$

$$T' = 297.02 \text{ K}$$

$$T' = 297.02 \text{ K} - 273 = 24.02^\circ\text{C}$$

**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  $E_a$ .**

**Ans:**

1st order reaction

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

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

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

$$- \frac{2.303}{k} \log \frac{100}{75}$$

At

$$308\text{K} = \frac{2.2877}{k}$$

Regarding question

$$= \frac{0.1054}{k} \log \frac{0.2877}{k}$$

$$\log \frac{k_1}{k} = 2.7296$$

From Arrhenius equation, we get

$$\log, \log \frac{k_1}{k} = \frac{E_a}{2.303R} \left( \frac{T - T'}{TT'} \right)$$

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

$$E_a = \frac{2.303 \times 8,314 \times 298 \times 308 \times \log(2.7296)}{308 - 298}$$

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

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

calculate  $k$  at 318 K

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

Again, from Arrhenius equation, we get

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

**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 if it does not change with temperature.**

**Ans:**

From Arrhenius equation, we get

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

Given,

$$k_2 = 4k_1$$

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

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

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

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

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

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

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

As a result, the activation energy required is  $52.86 \text{ kJ mol}^{-1}$