Chemical Kinetics

3
Chapter

Intext Exercise

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.

Ans: The average rate of the reaction can be calculated by dividing the change in the rate of decreasing the rate of reactant by the time taken. This is given below:

$$\text{Average rate} = -\frac{d[R]}{dt}$$

This can be written as:

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

$R_1 = 0.03$ M

$R_2 = 0.02$ M

$t_2 - t_1 = 25$ min

Putting the values, we get:

$$\text{Average rate} = -\frac{0.02-0.03}{25}$$

$$\text{Average rate} = -\frac{-0.01}{25} = 4 \times 10^{-4}\ \text{M min}^{-1}$$

So, the average rate in minutes will be $4 \times 10^{-4}\ \text{M min}^{-1}$

Now, to find the average rate in seconds we have to divide the above answer by 60.

So, the answer will be:

$$\text{Average rate} = -\frac{4 \times 10^{-4}}{60} = 6.66 \times 10^{-6}\ \text{M s}^{-1}$$

Therefore, the average rate in seconds will be $6.66 \times 10^{-6}\ \text{M s}^{-1}$

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

Ans: The average rate of the reaction can be calculated by dividing the change in the rate of decreasing the rate of reactant by the time taken. This is given below:

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

This is due the fact that the reaction given is:

$2A \rightarrow \text{Products}$

So, the average rate will be written as:

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

$A_1 = 0.5\ M$

$A_2 = 0.4\ M$

$t_2 - t_1 = 10\ min$

Putting the values, we get:

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

$$\text{Average rate} = -\frac{1}{2} \times \frac{-0.1}{10} = 5 \times 10^{-3}\ M\ min^{-1}$$

So, the average rate will be $5 \times 10^{-3}\ M\ min^{-1}$

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

Ans: The order of the reaction can be calculated by adding the stoichiometry coefficients of the reactants in the given rate of the reaction.

Given the rate is $r = k\,[A]^{1/2}\,[B]^2$

So, the order will be:

$$\text{Order} = 2 + \frac{1}{2} = 2.5$$

So, the order of the reaction is 2.5

4. **The conversion of the 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: The reaction will be:

$$X \rightarrow Y$$

As the question says that this reaction follows the second order reaction, we can write the rate law equation as:

$$\text{Rate} = k[X]^2 = ka^2$$

If [X] = a mol/ L

It is said that the concentration of X increases by three times, so we can write:

[X] = 3a mol/ L

Therefore, the rate of reaction will be:

$$\text{Rate} = k\,(3a)^2 = 9\,ka^2$$

Thus, the rate of the reaction will increase by 9 times or the rate formation will increase by 9 times.

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

Ans: The initial amount of the reactant is given as 5 g. We can write:

$[R]_0 = 5$ g

The final amount of the reactant is given as 3 g. We can write:

[R] = 3 g

We are also given the value of rate constant as:

Rate constant = 1.15×10^{-3} s^{-1}

We know that the reaction is a 1st order reaction, the time can be calculated by:

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

Putting the values in the above formula, we get:

$$t = \frac{2.303}{1.15 \text{ x } 10^{-3}}\log\frac{5}{3}$$

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

t = 444 seconds

So, the time taken will be 444 seconds.

6. **Time required to decompose SO_2Cl_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: We are given that the decomposition of SO_2Cl_2 is a first order reaction. So, we can write:

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

It is mentioned that the time required for the initial amount to become half is 60 minutes.

$t_{1/2} = 60$ min

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

Putting the value, we get:

$$k = \frac{0.693}{60 \times 60} = 1.925 \times 10^{-4}\ s^{-1}$$

Thus, the rate constant is $1.925 \times 10^{-4}\ s^{-1}$.

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

Ans: An increase of 10 degrees in temperature causes a reaction's rate constant to almost double in size. In any case, the Arrhenius equation gives the exact temperature dependency of a chemical reaction rate.

The Arrhenius equation is given below:

$$k = A\, e^{-E_a/Rt}$$

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.

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

Ans: The formula that can be used to solve the question is:

$$\log\frac{k_1}{k_2} = \frac{E_a}{2.303R}\left[\frac{T_2\text{-}T_1}{T_1T_2}\right]$$

T_1 temperature given is absolute temperature and it is equal to 298 K.

$T_2 = 298 + 10 = 308$ K

It is given that the rate of the chemical reaction double for an increase of 10 K, therefore, we can write the values of rate constant as:

$k_1 = x$

$k_2 = 2x$

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

Now, putting all the values in the formula, we get:

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

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

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

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

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

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

Ans: We are given the activation energy as $209.5\ \text{kJ mol}^{-1}$

T = 581 K

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

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

$x = e^{E_a/RT}$

$$\ln x = \frac{-E_a}{RT}$$

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

$$\log x = \frac{209500}{2.303 \times 8.314 \times 581} = 18.8323$$

Now, taking the antilog:

x = Antilog (18.8323)

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

NCERT Exercise

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

(i) $3\ NO(g) \rightarrow N_2O(g)$ Rate = $k[NO]^2$

Ans: We are given:

Rate = $k[NO]^2$

From this we can see that the order of the reaction = 2

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

Dimensions will be:

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

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

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

(ii) $\mathbf{H_2O_2(aq)+3I^-(aq)+2H^+ \rightarrow 2H_2O(l)+I_3^-}$ **Rate=k**$\mathbf{[H_2O_2][I^-]}$

Ans: Rate = $k[H_2O_2][I^-]$

From this we can see that the order of the reaction = 2

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

Dimensions will be:

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

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

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

(iii) $\mathbf{CH_3CHO(g) \rightarrow CH_4(g) + CO(g)}$ **Rate =** $\mathbf{k[CH_3CHO]^{3/2}}$

Ans: Rate = $k[CH_3CHO]^{3/2}$

From this we can see that the order of the reaction = $\frac{3}{2}$

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

Dimensions will be:

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

$$= \frac{\text{mol L}^{-1}\ \text{s}^{-1}}{\text{mol}^{\frac{3}{2}}\ \text{L}^{\frac{3}{2}}}$$

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

(iv) $\mathbf{C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)}$ **Rate =** $\mathbf{k[C_2H_5Cl]}$

Ans: Rate = $k[C_2H_5Cl]$

From this we can see that the order of the reaction = 1

$$k = \frac{\text{rate}}{[C_2H_5Cl]}$$

Dimensions will be:

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

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

2. **For a reaction:**

$$\mathbf{2A + B \rightarrow A_2B}$$

The rate = $k[A][B]^2$ with $k = 2.0 \times 10^{-6}$ mol^{-2} L^2 s^{-1}.

Calculate the initial rate of the reaction when [A] = 0.1 mol L^{-1}, [B] = 0.2 mol L^{-1} Calculate the rate of reaction after [A] is reduced to 0.06 mol L^{-1}.

Ans: We are given the rate of the reaction as:

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

Putting the values in this, we get the rate as:

$$\text{rate} = 2.0 \times 10^{-6} \times 0.1 \times (0.2)^2$$

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

When [A] is reduced from $0.10\ \text{mol L}^{-1}$ to $0.06\ \text{mol L}^{-1}$. So, the amount of [A] reacted will be:

$$= 0.10 - 0.06 = 0.04\ \text{mol L}^{-1}$$

Therefore, the concentration of B reacted will be:

$$= \frac{1}{2} \times 0.04 = 0.02\ \text{mol L}^{-1}$$

Hence, new [B] = 0.2 – 0.02 = $0.18\ \text{mol L}^{-1}$

Now, the new rate of the reaction will be:

$$\text{rate} = 2.0 \times 10^{-6} \times 0.06 \times (0.18)^2$$

$$\text{rate} = 3.89 \times 10^{-9}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

Therefore, the rate of the reaction is $3.89 \times 10^{-9}\ \text{mol L}^{-1}\ \text{s}^{-1}$.

3. **The decomposition of NH_3 on the platinum surface there is zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4}\ mol^{-1}\ L\ s^{-1}$?**

Ans: The following equation represents the breakdown of Ammonia on the platinum surface.

$$2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$$

Therefore, we can write the rate of the reaction as:

$$\text{Rate} = -\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt}$$

But we are given that the reaction is a zero order reaction.

$$\text{So, Rate} = -\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = 2.5 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$$

Thus, the rate of production of N_2 will be:

$$\frac{d[N_2]}{dt} = 2.5 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$$

And the rate of production of H_2 will be:

$$\frac{d[H_2]}{dt} = 3 \times 2.5 \times 10^{-4}\ mol\ L^{-1}\ s^{-1} = 7.5 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$$

4. **The decomposition of dimethyl ether leads to the formation of CH_4, H_2 and CO and the reaction rate is given by**

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.,

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

It the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

Ans: If the pressure is measured in bar and time in minutes, then unit of rate will be:

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

We are given the rate of the reaction as: $\text{Rate} = k\,[CH_3OCH_3]^{3/2}$

Therefore, $k = \dfrac{\text{Rate}}{[CH_3OCH_3]^{3/2}}$

So, we can write the units of rate constant as:

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

So, the units are $\text{bar}^{-1/2}\ \text{min}^{-1}$.

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

Ans: Factors that influence a reaction's speed include.

(i) Reactant nature: The rate of reaction is affected by the kind of reactant. For example, ionic compound reactions are quicker than covalent compound reactions.

(ii) The state of the reactants: Solid reactions are sluggish, liquid reactions are rapid, and gas reactions are very quick.

(iii) Temperature: In addition, temperature has a significant impact on response rate. Every 10 degrees Celsius increase in temperature doubles the pace of reaction.

(iv) Presence of catalyst: The rate of reaction is also affected by the presence of a catalyst in the reaction. It enhances the pace of reaction by increasing reaction surface area, by generating unstable intermediates with the substrate, and by offering 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 us assume that the concentration of the reactant be [A] = a

Rate of the reaction will be:

$R = k[A]^2 = ka^2$

It is said that the concentration of A increases by two times, so we can write:

$[A] = 2a$ mol/ L

Therefore, the rate of reaction will be:

$\text{Rate} = k\,(2a)^2 = 4\,ka^2$

Thus, the rate of the reaction will increase by 4 times.

(ii) Reduced to half

It is said that the concentration of A reduced to half, so we can write:

$$[X] = \frac{1}{2}\text{ a mol/ L}$$

Therefore, the rate of reaction will be:

$$\text{Rate} = k\left[\frac{1}{2}a\right]^2 = \frac{1}{4}ka^2$$

Thus, the rate of the reaction will reduce by ¼ times.

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: An increase of 10 degrees in temperature causes a reaction's rate constant to almost double in size. In any case, the Arrhenius equation gives the exact temperature dependency of a chemical reaction rate.

The Arrhenius equation is given below:

$$k = A\,e^{-E_a/Rt}$$

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.

The formula can also be written as:

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2\text{-}T_1}{T_1T_2}\right]$$

Where k_2 is the rate constant at temperature T_2

k_1 is the rate constant at temperature T_1

8. **Ina pseudo first order hydrolysis of ester in water, the following results were obtained**

t/s	**0**	**30**	**60**	**90**
[Ester]mol L^{-1}	**0.55**	**0.31**	**0.17**	**0.085**

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

Ans: Between the time interval of 30 to 60 sec the average rate id reaction will be calculated as:

$$= \frac{d[\text{Ester}]}{dt}$$

Putting the values from the data given in the question, we can write:

$$= \frac{0.31 - 0.17}{60 - 30} = \frac{0.14}{30}$$

$$= 4.67 \times 10^{-3} \text{ mol } L^{-1} \text{ } s^{-1}$$

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

(i) Write the differential rate equation

Ans: The differential rate equation can be written as:

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

(ii) How is the rate affected on increasing the concentration of B three times?

Ans: The concentration of B is increased by 3 times, then B =3B

Therefore, the rate will be:

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

Therefore, the rate will increase by 9 times.

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

Ans: The concentration of A is doubled, then A = 2A

The concentration of B is doubled, then B = 2B

Therefore, the rate will be:

$$-\frac{d[R]}{dt} = k[2A][2B]^2 = 8 \times [A][B]^2$$

Therefore, the rate will increase by 8 times.

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

A/mol L^{-1}	**0.20**	**0.20**	**0.04**
B/mol L^{-1}	**0.30**	**0.10**	**0.05**
r_0/mol L^{-1} s^{-1}	**5.07×10^{-5}**	**5.07×10^{-5}**	**1.43×10^{-4}**

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

Ans: Let us assume that the order of the reaction with respect to A be xand with respect to B be y.

Therefore, we can write:

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

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

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

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

Let us divide (i) by (ii), we get:

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

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

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

Therefore, y = 0

Now, dividing (iii) by (i), we get:

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

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

Because y = 0

$$= 2.821 = 2^x$$

Now, taking log on both the sides.

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

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

$$x = 1.496$$

$$x = 1.5$$

Thus, the order of the reaction according to A is 1.5 and according to B is 0.

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

$2A + B \rightarrow C + D$

Experiment	**A/mol L^{-1}**	**B/mol L^{-1}**	**Initial rate of formation of D/mol $L^{-1}min^{-1}$**
I	**0.1**	**0.1**	**6.0×10^{-3}**
II	**0.3**	**0.2**	**7.3×10^{-2}**
III	**0.3**	**0.4**	**2.88×10^{-1}**
IV	**0.4**	**0.1**	**2.40×10^{-2}**

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

Ans: Let us assume that the order of the reaction with respect to A be x and with respect to B be y.

Therefore, we can write:

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

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

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

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

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

Let us divide (iv) by (i), we get:

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

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

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

Therefore, x = 1

Now, dividing (iii) by (ii), we get:

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

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

$= 4 = 2^{y}$

$= 2^{2} = 2^{y}$

$y = 2$

Thus, the order of the reaction according to A is 1 and according to B is 2.

So, the rate law is:

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

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

Now, putting the values for each experiment, we get:

From experiment I:

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

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

From experiment II:

$$k = \frac{7.3 \times 10^{-2}}{[0.3][0.2]^{2}}$$

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

From experiment III:

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

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

From experiment IV:

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

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

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

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^{-1}**	**B/mol L^{-1}**	**Initial rate D/mol $L^{-1}min^{-1}$**
I	**0.1**	**0.1**	**2.0×10^{-2}**
II	**---**	**0.2**	**4.0×10^{-2}**
III	**0.4**	**0.4**	**----**
IV	**----**	**0.2**	**2.0×10^{-2}**

Ans: We are given that, the reaction between A and B is first order with respect to A and zero order with respect to B.

Therefore, the rate of the reaction is given by:

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

So, we can write:

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

According to the experiment I we can write:

$$2.0 \times 10^{-2} = k(0.1)$$

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

According to the experiment II we can write:

$$4.0 \times 10^{-2} = (0.2)\,[A]$$

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

According to the experiment III we can write:

$$\text{Rate} = 0.2 \times 0.4$$

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

According to the experiment III we can write:

$$2.0 \times 10^{-2} = (0.2)\,[A]$$

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

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

(i) 200 s^{-1}

Ans: Half -life of the reaction can be related with the rate constant of the reaction as:

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

Putting the value of time, we get:

$$k = \frac{0.693}{200} = 3.46 \times 10^{-3}\ s$$

So, the rate of the reaction is $3.46 \times 10^{-3}\ s$

(ii) 2 min^{-1}

Ans: Half-life of the reaction can be related with the rate constant of the reaction as:

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

Putting the value of time, we get:

$$k = \frac{0.693}{2} = 0.346\ \text{min}$$

So, the rate of the reaction is 0.346 min.

(iii) 4 years^{-1}

Ans: Half-life of the reaction can be related with the rate constant of the reaction as:

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

Putting the value of time, we get:

$$k = \frac{0.693}{4} = 0.173\ \text{years}$$

So, the rate of the reaction is 0.173 years.

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

Ans: The given reaction in the above question is radioactive decay and the radioactive decay follows the first order kinetics. Therefore, the decay constant:

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

We are given the half-life time as 5730 years.

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

To find the age of the sample, we can write:

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

80% of the wood is found so, the initial amount can be taken as 100 and the final amount as 80. Putting the values, we get:

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

t = 1845 years

Therefore, the age of the sample is 1845 years.

15. **The experiment data for decomposition of N_2O_5**

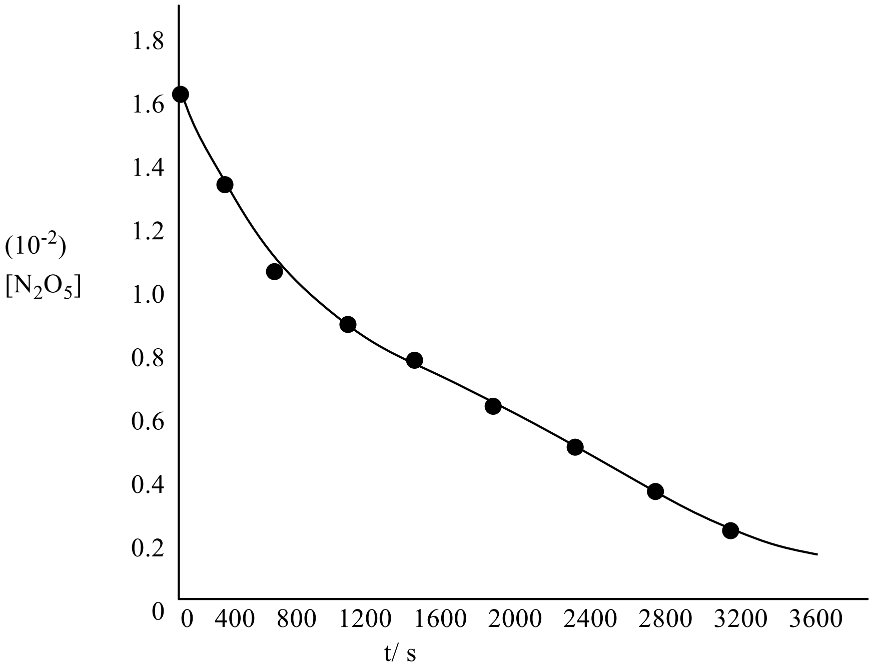
$[2N_2O_5 \rightarrow 4NO_2 + O_2]$

In gas phase at 318 K are given below:

t/s	**0**	**400**	**800**	**1200**	**1600**	**2000**	**2400**	**1800**	**3200**
$10^{-2} \times [N_2O_5]$/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

Ans: The graph is given below:



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

Ans: Time corresponding to the concentration,

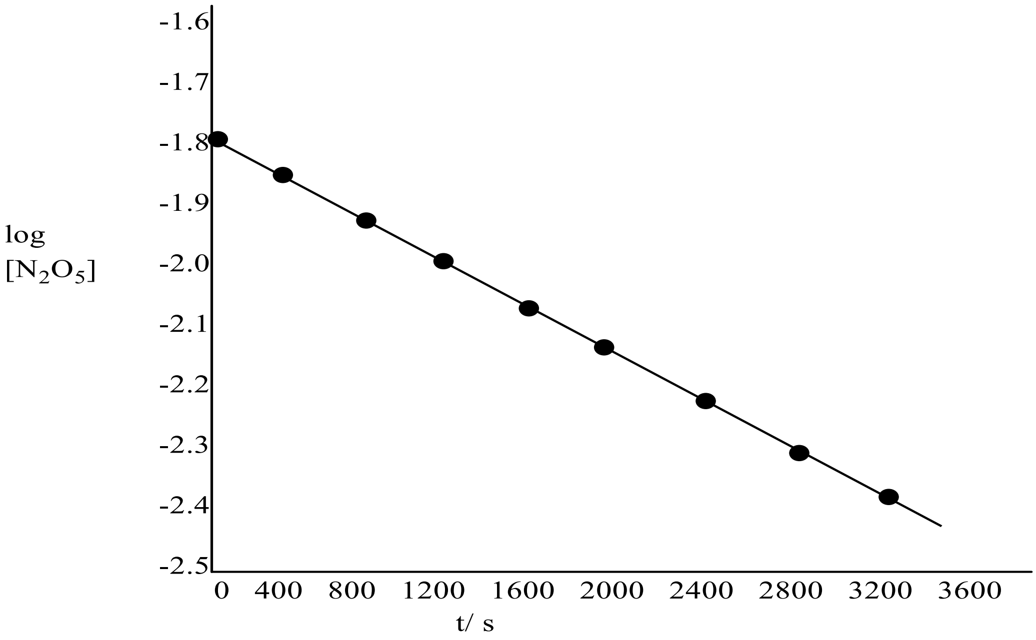
$\frac{1.630 \times 10^{-2}}{2}$ mol L^{-1}=0.815 × 10^{-2} mol L^{-1} is the half-life.

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

(iii) Draw the graph between $\log[N_2O_5]$ and t

Ans:

T(s)	$10^{-2} \times [N_2O_5]$/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) What is the rate law?

Ans: The rate law of the reaction will be:

Rate = $k[N_2O_5]$

(v) Calculate the rate constant.

Ans: From the plot $[N_2O_5]$ v/s t, is given by:

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

Therefore, we obtain:

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

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

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

Ans: Half-life is given by:

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

= 1438 seconds.

The value of half-life calculated from the k is very close to that obtained from the graph.

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

Ans: As we know that:

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

The initial value of the reactant has become 1/16th. Now, putting the values, we get:

$$t = \frac{2.303}{60} \log\frac{16}{1}$$

$$t = \frac{2.303}{60} \log 16 = 4.62 \times 10^{-2} \text{ s}$$

Therefore, the time required will be 4.62×10^{-2} s.

17. **During nuclear explosion, one of the products is ^{90}Sr with a half-life of 28.1 years. If 1 µg of ^{90}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: As radioactive disintegration follows first order kinetics.

Decay constant of ^{90}Sr (k) = $\frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} = 2.466 \times 10^{-2}\ y^{-1}$

To calculate the amount left after 10 years.

a = 1 µg

t = 10 years

$k = 2.466 \times 10^{-2}\ y^{-1}$

(a-x) = ?

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

$$2.466 \times 10^{-2} = \frac{2.303}{10} \log \frac{1}{a-x}$$

log(a-x) = -0.1071

(a-x) = Antilog -0.1071 = 0.7814 µg

To calculate the amount left after 60 years.

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

$$2.466 \times 10^{-2} = \frac{2.303}{60} \log \frac{1}{a-x}$$

log(a-x) = -0.6425

(a-x) = Antilog -0.6425 = 0.2278 µg

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: For first order reaction, we can write:

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

99% completion means that x = 99% of a = 0.99 a

So, we can write:

$$t_{99\%} = \frac{2.303}{k} \log\frac{a}{a\text{-}0.99a}$$

$$t_{99\%} = \frac{2.303}{k} \log 10^2$$

$$t_{99\%} = 2 \times \frac{2.303}{k}$$

90% completion means that x = 90% of a = 0.90 a

$$t_{99\%} = \frac{2.303}{k} \log\frac{a}{a\text{-}0.90a}$$

$$t_{99\%} = \frac{2.303}{k} \log 10$$

$$t_{99\%} = \frac{2.303}{k}$$

Now, we can take the ratio as given below:

$$\frac{t_{99\%}}{t_{90\%}} = \frac{\left(\frac{2 \text{ x } 2.303}{k}\right)}{\left(\frac{2.303}{k}\right)}$$

$$t_{99\%} = 2 \times t_{90\%}$$

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.

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

Ans: 30% decomposition means that x = 30% of a = 0.30 a

Since, the reaction is of 1st order, we can write:

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

Time is given as 40 min. So, putting the values, we get:

$$k = \frac{2.303}{40} \log\frac{a}{a\text{-}0.30a}$$

$$k = \frac{2.303}{40} \log\frac{10}{7}\text{min}^{-1}$$

$$k = \frac{2.303}{40} \times 0.1549 \text{ min}^{-1} = 8.918 \times 10^{-3}\text{min}^{-1}$$

Now, we can calculate the half-life period as we have the rate constant value.

We can write:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.918 \times 10^{-3}} = 7.77 \text{ min}$$

So, the half-life is 7.77 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 decomposition of azoisopropane to hexane and nitrogen at 54.3 k is represent by the following equation.

$$\begin{array}{llll} (CH_3)_2CHN{=}NCH(CH_3)_2 & \longrightarrow & N_2 & + \quad C_6H_{14} \\ \text{At } t = 0 \quad P_o & & 0 & \quad\ 0 \\ \text{At } t = t \quad P_o - P & & p & \quad\ p \end{array}$$

Total pressure after time t, we will be:

$P_t = (P_o\text{-}p) + p + p$

$P_t{=}P_o{+}p$

$p{=}P_t - P_o$

Now, we can substitute the value of p for the pressure of reactant at time t

$=P_o - p$

$=P_o - (P_t - P_o)$

$= 2P_o - P_t$

Now, we can apply the rate constant formula of 1st order reaction.

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

When t = 360 s,

Putting the values, we get:

$$k = \frac{2.303}{360} \log \frac{35.0}{2 \times 35 - 54} = 2.175 \times 10^{-3}\ s^{-1}$$

When t = 720 s,

Putting the values, we get:

$$k = \frac{2.303}{720} \log \frac{35.0}{2 \times 35 - 63} = 2.235 \times 10^{-3}\ s^{-1}$$

Now, we can find the average value:

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

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

21. **The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.**

$SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$

Experiment	**Time/ s**	**Total pressure/ atm**
1	**0**	**0.5**
2	**100**	**0.6**

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

Ans: The given reaction shows the thermal decomposition of SO_2Cl_2 at constant volume.

	SO_2Cl_2	$\longrightarrow$	SO_2	+	Cl_2
At t = 0	P_o		0		0
At t = t	P_o - P		p		p

Total pressure after time t, we will be:

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

$P_t = P_o + p$

$p = P_t - P_o$

Now, we can substitute the value of p for the pressure of reactant at time t

$= P_o - p$

$= P_o - (P_t - P_o)$

$= 2P_o - P_t$

Now, we can apply the rate constant formula of 1st order reaction.

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

When the t = 100 s

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

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

When $P_t = 0.65$ atm

Therefore, pressure of SO_2Cl_2 at time t total pressure is 0.65 atm, is

$P_{SO_2Cl_2} = 2P_o - P_t$

$= 2 \times 0.50 - 0.65$

$= 0.35$ atm

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

$\text{Rate} = k(P_{SO_2Cl_2})$

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

22. **The rate constant for the decomposition of N_2O_5 at various temperature is**

given below:

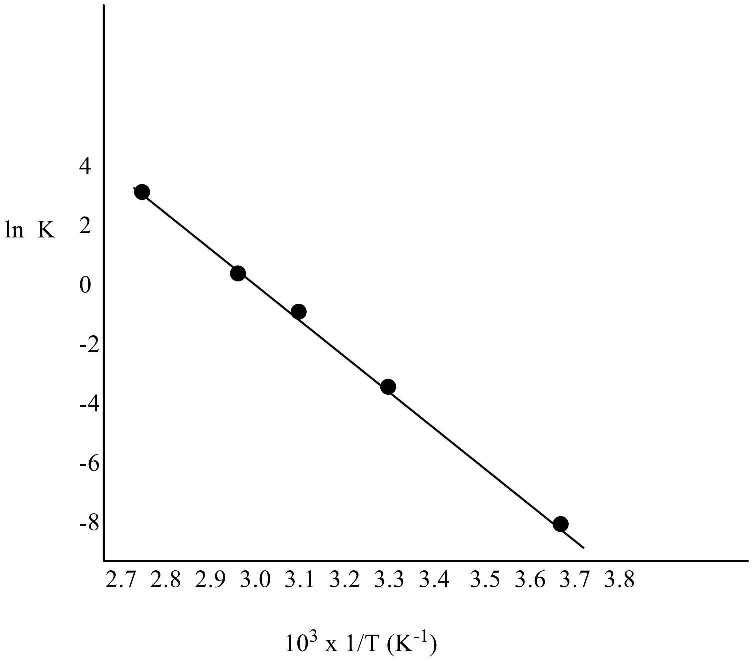
T/°c	**0**	**20**	**40**	**60**	**80**
$10^5 \times$ k/s	**0.0787**	**1.70**	**25.7**	**178**	**2140**

Draw a graph between ln K and 1/T and calculate the values of A and E_a. Predict the rate constant at 30^o and 50^oC.

Ans: As the data is given we can write:

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

The graph is draw below:



Slope of the line, will be given as:

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

According to the Arrhenius equation,

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

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

$= (-12.301)\,(8.314)$

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

Again,

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

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

As T = 273 K and ln k = -7.147

Applying this in the formula, we get:

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

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

When T = 30 + 273 K = 303 K

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

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

$\ln k = -2.8$

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

When T = 50 + 273 K = 323 K

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

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

$\ln k = -0.5$

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

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

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

Ans: We are given some values as:

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

$T = 546\ K$

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

We the Arrhenius equation is:

$k = A\ e^{-E_a/RT}$

In the log form, this can be written as:

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

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

$$\log k = \log (2.418 \times 10^{-5}) - \frac{179.9 \times 10^3}{2.303 \times 8.314 \times 546}$$

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

Therefore, A = antilog (12.5917)

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

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

Ans: We are given some values, that are given below:

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

$t = 100\ s$

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

As we can see that the units of k is given in s^{-1}, this means that the reaction is a first order reaction.

Therefore, we can write:

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

Putting the values, we get:

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

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

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

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

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

Therefore, the remaining amount of A is 0.135 mol L^{-1}.

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 a sample of sucrose remains after 8 hours?**

Ans: The given reaction is a first order reaction. So, we can write:

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

We are given a half-life of 3 hours. Therefore, we can write:

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

So, putting the values in this, we get:

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

Now, we can put this value of rate constant in the first order reaction formula.

$$0.231 = \frac{2.303}{8} \log \frac{[R]_0}{[R]}$$

$$\log \frac{[R]_0}{[R]} = \frac{0.231 \times 8}{2.303}$$

$$\log \frac{[R]_0}{[R]} = 0.8024$$

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

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

Or we can write:

$$\frac{[R]}{[R]_0} = 0.158$$

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

26. The decomposition of hydrocarbon follows the equation $k = (4.5 \times 10^{11}\ s^{-1})e^{-280000K/T}$. Calculate E_a.

Ans: According to the Arrhenius equation,

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

We are given the equation as:

$$k = (4.5 \times 10^{11}\ s^{-1})e^{-280000K/T}$$

Therefore, the formula can be written as:

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

This can be written as:

$$E_a = 28000 \times R$$

$$E_a = 28000 \times 8.314 = 232.79\ \text{kJ mol}^{-1}$$

Therefore, the value of E_a is $232.79\ \text{kJ mol}^{-1}$

27. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

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

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

Ans: According to the Arrhenius equation,

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

This can be written as:

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

In the log form it can be written as:

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

We are given:

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

Comparing these two, we get:

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

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

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

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

We are given half-life time as 256 minutes.

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

$$k = \frac{0.693}{256 \times 60} = 4.51 \times 10^{-5}\ s^{-1}$$

Now, we have the value of rate constant, we can put in the equation:

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

T = 669 K

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

Ans: We are some information:

$$k_1 = 4.5 \times 10^3$$

$$T_1 = 10 + 273 = 283\ K$$

$k_2 = 1.5 \times 10^4$

$T_2 = ?$

$E_a = 60 \text{ kJ mol}^{-1}$

Applying Arrhenius equation:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

Putting the values, we can write:

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60}{2.303 \times 8.314}\left(\frac{T_2 - 283}{283T_2}\right)$$

$$\log 3.333 = 3133.63\left(\frac{T_2 - 283}{283T_2}\right)$$

$$\frac{0.5228}{3133.63} = \left(\frac{T_2 - 283}{283T_2}\right)$$

$0.0472T_2 = T_2 - 283$

$T_2 = 297 \text{ K}$

Or we can write:

$T_2 = 24^{o}\text{C}$

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 4×10^{10} s^{-1} , Calculate k at 318 K and E_a .**

Ans: There are two cases in this question. As the reaction given is first order reaction, we can use:

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

For case 1:

$$k_{298K} = \frac{2.303}{t_1} \log \frac{a}{a - 0.10a}$$

$$k_{298K} = \frac{2.303}{t_1} \log\frac{10}{9}$$

$$k_{298K} = \frac{2.303}{t_1} \times 0.0458$$

$$t_1 = \frac{0.1055}{k_{298K}}$$

For case 2:

$$k_{308K} = \frac{2.303}{t_2} \log\frac{a}{a - 0.25a}$$

$$k_{308K} = \frac{2.303}{t_2} \log\frac{4}{3}$$

$$k_{308K} = \frac{2.303}{t_2} \times 0.125$$

$$t_2 = \frac{0.2879}{k_{308K}}$$

But $t_1 = t_2$

Hence,

$$\frac{0.1055}{k_{298K}} = \frac{0.2879}{k_{308K}}$$

$$\frac{k_{308K}}{k_{298K}} = 2.7289$$

Now, applying the Arrhenius equation,

$$\log\frac{k_{308K}}{k_{298K}} = \frac{E_a}{2.303R}\left(\frac{T_2\text{-}T_1}{T_1T_2}\right)$$

$$\log(2.7289) = \frac{E_a}{2.303 \times 8.314}\left(\frac{308\text{-}298}{298 \times 308}\right)$$

$E_a = 76.623 \text{ kJ mol}^{-1}$

Now, the calculation of k at 318 K

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

$$\log k = \log (4 \times 10^{10}) - \frac{7623}{2.303 \times 8.314 \times 318}$$

$$\log k = 10.6021 - 12.5843 = -1.9822$$

$$k = \text{Antilog}\,(-1.9822) = \text{antilog}\,(\bar{2}.0178) = 1.042 \times 10^{-2}\ s^{-1}$$

Therefore, k is $1.042 \times 10^{-2}\ s^{-1}$.

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.

Ans: We are given that:

$k_2 = 4\ k_1$

$T_1 = 293K$

$T_2 = 313K$

According the Arrhenius equation, we get:

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

Putting the values, we get:

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

$$0.6021 = \frac{E_a}{2.303 \times 8.314}\left(\frac{313-293}{293 \times 313}\right)$$

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

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

$E_a = 52.863\ kJ\ mol^{-1}$

Therefore, the required activation energy is $52.863\ kJ\ mol^{-1}$.