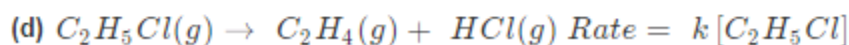
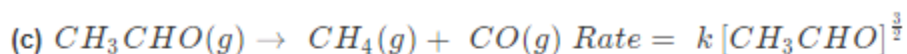
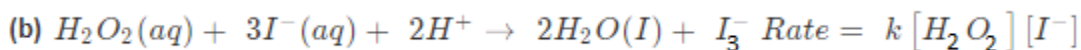
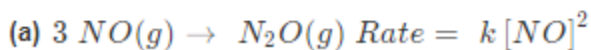


Q 1. From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.



Solution:

(a) Given rate = $k [NO]^2$

Therefore, order of the reaction = 2

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

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

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

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

(b) Given rate = $k [H_2O_2] [I^-]$

Therefore, order of the reaction = 2

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

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

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

(c) Given rate = $k [CH_3CHO]^{\frac{3}{2}}$

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

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

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

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

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

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

Therefore, order of the reaction = 1

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

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

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

Q 2. For the reaction: $2A + B \rightarrow A_2B$ is $k[A][B]^2$ with $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{L}^2 \text{s}^{-1}$.

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

Solution:

The initial rate of reaction is

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

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

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

When $[A]$ is reduced from 0.1 mol L^{-1} to 0.06 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, $[B] = (0.2 - 0.02) \text{ mol L}^{-1} = 0.18 \text{ mol L}^{-1}$

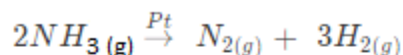
After $[A]$ is reduced to 0.06 mol L^{-1} , the rate of the reaction is given by,

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

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

Solution:

The decomposition of 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 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 H_2 is

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

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

Q 4. The decomposition of dimethyl ether leads to the formation of CH_4 , H_2 , and CO and the

reaction rate is given by $Rate = k [CH_3OCH_3]^{\frac{3}{2}}$

The rate of reaction is followed by an 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.,

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

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

Solution:

If pressure is measured in bar and time in minutes, then

$$\text{Unit of rate} = \text{bar min}^{-1} \quad Rate = k (P_{CH_3OCH_3})^{\frac{3}{2}}$$

$$\Rightarrow k = \frac{Rate}{k (P_{CH_3OCH_3})^{\frac{3}{2}}}$$

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

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

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

Solution:

The factors which are responsible for the effect in chemical reaction's rate are:

- (a) Reaction temperature
- (b) Presence of a catalyst

- (c) The concentration of reactants (pressure in case of gases)
- (d) Nature of the products and reactants
- (e) Radiation exposure
- (f) Surface area

Q 6. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (i) doubled (ii) reduced to half?

Solution:

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

$$\text{Rate of reaction, } R = k[A]^2$$

$$= ka^2$$

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

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

$$= 4ka^2$$

$$= 4R$$

Therefore, the rate of the reaction now will be 4 times the original rate.

(b) 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

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

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

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

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

Q 7. What is the effect of temperature on the rate constant of a reaction? How can this effect of temperature on rate constant be represented quantitatively?

Solution:

When a temperature of 10° rises for a chemical reaction then the rate constant increases and becomes near to double of its original value.

The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation,

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

Where,

k = rate constant,

A = Frequency factor / Arrhenius factor,

R = gas constant

T = temperature

E_a = activation energy for the reaction.

Q 8. In a pseudo-first-order reaction in water, the following results were obtained:

t/s	0	30	60	90
[Ester]mol / L	0.55	0.31	0.17	0.085

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

Solution:

(a) Avg rate of reaction between the time intervals, 30 to 60 seconds,

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

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

$$= \frac{0.14}{30}$$

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

(b) For a pseudo first order reaction,

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

For $t = 30 \text{ s}$

$$k_1 = \frac{2.303}{30} \log \frac{0.55}{0.31}$$

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

For $t = 60 \text{ s}$

$$k_2 = \frac{2.303}{60} \log \frac{0.55}{0.17}$$

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

For $t = 90 \text{ s}$

$$k_3 = \frac{2.303}{90} \log \frac{0.55}{0.085}$$

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

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

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

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

Q 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?

Solution:

(a) The differential rate equation will be

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

(b) If the concentration of B is increased three times, then

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

$$= 9.k[A][B]^2$$

Therefore, the reaction rate will be increased by 9 times.

(c) When the concentrations of both A and B are doubled,

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

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

Therefore, the rate of reaction will increase 8 times.

Q10. 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:

$A/mol L^{-1}$	0.20	0.20	0.40
$B/mol L^{-1}$	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?

Solution:

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

Then,

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

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

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

$$1.43 \times 10^{-4} = k [0.40]^x [0.05]^y \quad (iii)$$

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

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

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

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

$$\Rightarrow y = 0$$

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

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

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

$$\Rightarrow 2.821 = 2^x$$

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

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

$$= 1.496$$

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

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

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

Exp.	$\frac{A}{\text{molL}^{-1}}$	$\frac{B}{\text{molL}^{-1}}$	Initial rate of formation of $\frac{D}{\text{mol L}^{-1} \text{min}^{-1}}$
1	0.1	0.1	6.0×10^{-3}
2	0.3	0.2	7.2×10^{-2}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.4×10^{-2}

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

Solution:

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

Therefore, rate of the reaction is given by,

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

According to the question,

$$6.0 \times 10^{-3} = k [0.1]^x [0.1]^y \text{ --- (1)}$$

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

$$2.88 \times 10^{-1} = k [0.3]^x [0.4]^y \text{ ---(3)}$$

$$2.4 \times 10^{-2} = k [0.4]^x [0.1]^y \text{ ---(4)}$$

Dividing equation (4) by (1), we get

$$\frac{2.4 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k[0.4]^x [0.1]^y}{k[0.1]^x [0.1]^y} \quad 4 = \frac{[0.4]^x}{[0.1]^x} \quad 4 = \left(\frac{0.4}{0.1}\right)^x (4)^1 = (4)^x$$

$$x = 1$$

Dividing equation (3) by (2), we get

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \frac{k[0.3]^x [0.4]^y}{k[0.3]^x [0.2]^y} \quad 4 = \left(\frac{0.4}{0.2}\right)^y \quad 4 = 2^y \quad 2^2 = 2^y$$

$$y = 2$$

Hence, the rate law is

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

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

From experiment 1, we get

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

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

From experiment 2, we get

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

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

From experiment 1, we get

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

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

From experiment 1, we get

$$k = \frac{2.4 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.4 \text{ mol L}^{-1})(0.1 \text{ mol L}^{-1})^2}$$

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

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

Q 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:

Exp.	$\frac{A}{\text{molL}^{-1}}$	$\frac{B}{\text{molL}^{-1}}$	Initial rate $\text{mol L}^{-1} \text{ min}^{-1}$
1	0.1	0.1	2.0×10^{-2}
2	—	0.2	4.0×10^{-2}
3	0.4	0.4	—
4	—	0.2	2.0×10^{-2}

Solution:

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

Thus, the rate of the reaction is given by,

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

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

From experiment 1, we get

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

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

From experiment 2, we get

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

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

From experiment 3, we get

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

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

From experiment 4, we get

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

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

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

(a) 200 s^{-1}

(b) 2 min^{-1}

(c) 4 years^{-1}

Solution:

(a) Half life, $t_{\frac{1}{2}} = \frac{0.693}{k}$

$$= \frac{0.693}{200 \text{ s}^{-1}}$$

$$= 3.47 \times 10^{-3} \text{ s (Approximately)}$$

(b) $t_{\frac{1}{2}} = \frac{0.693}{k}$

$$= \frac{0.693}{2 \text{ min}^{-1}}$$

$$= 0.35 \text{ min (Approximately)}$$

(c) $t_{\frac{1}{2}} = \frac{0.693}{k}$

$$= \frac{0.693}{4 \text{ years}^{-1}}$$

$$= 0.173 \text{ years (Approximately)}$$

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

Solution:

$$\text{Here, } k = \frac{0.693}{t_{\frac{1}{2}}}$$

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

It is known that,

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

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

$$= 1845 \text{ years (approximately)}$$

Hence, the age of the sample is 1845 years.

Q 15. The experimental data for decomposition of N_2O_5



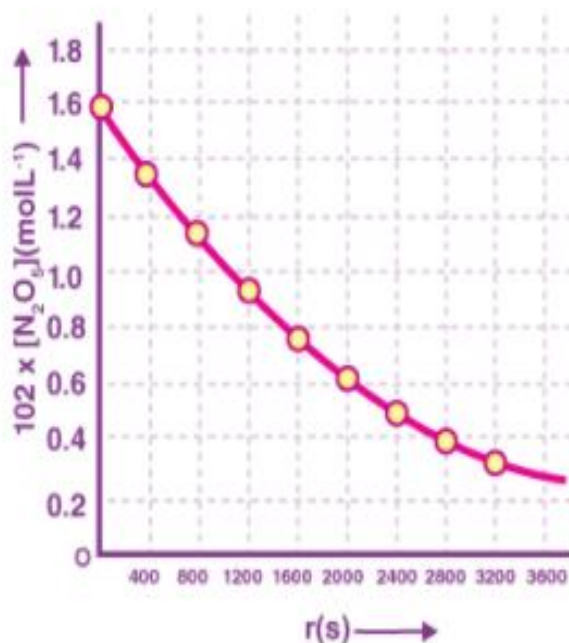
in gas phase at 318K are given below:

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

- (a) Plot $[N_2O_5]$ against t .
 (b) Find the half-life period for the reaction.
 (c) Draw a graph between $\log[N_2O_5]$ and t .
 (d) What is the rate law?
 (e) Calculate the rate constant.
 (f) Calculate the half-life period from k and compare it with (b).

Solution:

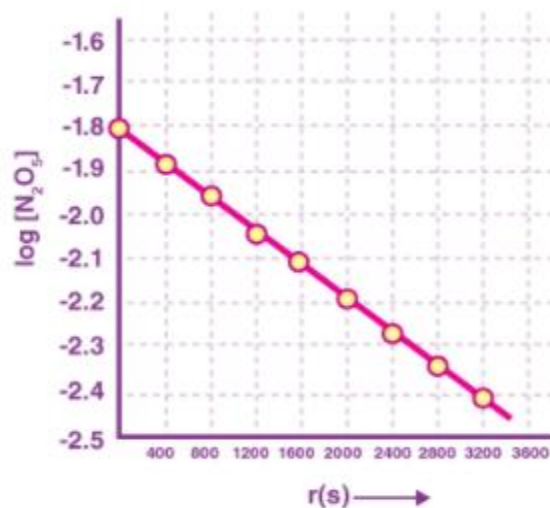
(a)



(b) 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 obtained as 1450 s.

(c)

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



(d) 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

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

(e) From the plot, $\log [N_2O_5]$ v/s t, we obtain

$$\text{Slope} = \frac{-2.46 - (-1.79)}{3200 - 0}$$

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

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

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

Therefore, we obtain,

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

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

(f) Half – life is given by,

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

$$= \frac{0.693}{4.82 \times 10^{-4}} \text{ s}$$

$$= \frac{1.483}{10^3} \text{ s}$$

$$= 1438 \text{ s}$$

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

Q 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 $1/16^{\text{th}}$ value?

Solution:

It is known that,

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

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

Q 17. During the nuclear explosion, one of the products is ^{90}Sr with a half-life of 28.1 years. If $1\mu\text{g}$ 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.

Solution:

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

Here,

It is known that,

$$\begin{aligned}
 t &= \frac{2.303}{k} \log \frac{[R]_0}{[R]} \\
 \Rightarrow 10 &= \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]} \\
 \Rightarrow 10 &= \frac{2.303}{\frac{0.693}{28.1}} (-\log [R]) \\
 \Rightarrow \log [R] &= -\frac{10 \times 0.693}{2.303 \times 28.1} \\
 \Rightarrow [R] &= \text{antilog}(-0.1071) \\
 &= \text{antilog}(1.8929) \\
 &= 0.7814\mu\text{g}
 \end{aligned}$$

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

Again,

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

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

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

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

$$= \text{antilog} (1.3575)$$

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

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

Q 18. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

Solution:

For a first order reaction, the time required for 99% completion is

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

$$= \frac{2.303}{k} \log 100$$

$$= 2 \times \frac{2.303}{k}$$

For a first order reaction, the time required for 90% completion is

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

$$= \frac{2.303}{k} \log 10$$

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

Therefore, $t_1 = 2 t_2$

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.

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

Solution:

For a first order reaction,

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

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

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

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

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

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

$$= \frac{0.693}{8.918 \times 10^{-3}} \text{ min}$$

$$= 77.7 \text{ min (approximately)}$$

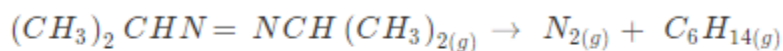
Q 20. For the decomposition of azoisopropane to hexane and nitrogen at 543K, the following data are obtained.

t(sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant.

Solution:

The decomposition of azoisopropane to hexane and nitrogen at 543 K is represented by the following equation.



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

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

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 the first order reaction,

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

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

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

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

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

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

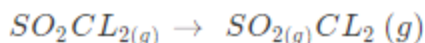
$$= 2.235 \times 10^{-3} \text{ s}^{-1}$$

Hence the average value of rate constant is.

$$k = \frac{2.21 \times 10^{-3} + 2.235 \times 10^{-3}}{2} \text{ s}^{-1}$$

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

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

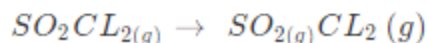


Experiment	Time/s	Total pressure / atm
1	0	0.5
2	100	0.6

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

Solution:

The thermal decomposition of SO_2Cl_2 at a constant volume is represented by the following equation.



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

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

$$\text{After time } t, \text{ total pressure, } P_t = (P_0 - p) + p + p$$

$$\Rightarrow P_t = P_0 + p$$

$$\Rightarrow p = P_t - P_0$$

$$\therefore P_0 - p = P_0 - (P_t - P_0)$$

$$= 2P_0 - P_t$$

For a first order reaction,

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

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

When $t = 100$ s,

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

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

When $P_t = 0.65$ atm,

$$P_0 + p = 0.65$$

$$\Rightarrow p = 0.65 - P_0$$

$$= 0.65 - 0.5$$

$$= 0.15 \text{ atm}$$

Therefore, when the total pressure is 0.65 atm, pressure of SO_2CL_2 is

$$P_{SO_2CL_2} = P_0 - p$$

$$= 0.5 - 0.15$$

$$= 0.35 \text{ atm}$$

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

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

Q 22. 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?

Solution:

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

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

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

According to the Arrhenius equation,

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

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

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

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

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

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

$$= 12.5917$$

Therefore, A = antilog (12.5917)

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

Q 23. 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 mol L^{-1} .

Solution:

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

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

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

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

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

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

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

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

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

Q 24. 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?

Solution:

For the first order reaction,

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

It is given that, $t_{\frac{1}{2}} = 3.00 \text{ hours}$.

$$\text{Therefore, } k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{3} \text{ h}^{-1}$$

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

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

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

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

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

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

$$= 0.158$$

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

Q 25. The decomposition of hydrocarbon follows the equation

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

Calculate E_a .

Solution:

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

The Arrhenius equation is given by,

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

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

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

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

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

$$= 232791 \text{ J mol}^{-1}$$

$$= 232.791 \text{ kJ mol}^{-1}$$

Q 26. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

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

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

Solution:

Arrhenius equation is given by,

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

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

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

The given equation is

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$= 668.95 \text{ K}$$

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

Q 27. The decomposition of A into product has value of k as $4.5 \times 10^3 \text{ s}^{-1}$ at 10°C and energy of activation 60 kJ mol^{-1} . At what temperature would k be $1.5 \times 10^4 \text{ s}^{-1}$?

Solution:

From Arrhenius equation, we obtain

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

$$\text{Also, } k_1 = 4.5 \times 10^3 \text{ s}^{-1} \quad T_1 = 273 + 10 = 283 \text{ K} \quad k_2$$

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

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

Then,

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

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

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

$$\Rightarrow 0.9528 T_2 = 283$$

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

$$= 297 \text{ K}$$

$$= 24^\circ$$

Q 28. The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K. If the value of A is $4 \times 10^{10} \text{ s}^{-1}$. Calculate k at 318K and Ea.

Solution:

For a first order reaction,

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

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

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

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

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

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 get

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

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

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

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

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

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 get

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

$$= \log (4 \times 10^{10}) - \frac{76.64 \times 10^3}{2.303 \times 8.314 \times 318}$$

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

$$= -1.9855$$

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

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

Q 29. The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

Solution:

From Arrhenius equation, we get

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

From the question we have, $K_2 = 4K_1$

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

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

$$\text{Therefore, } \log \frac{4K_1}{K_2} = \frac{E_a}{2.303 \times 8.314} \left(\frac{313 - 293}{293 \times 313} \right)$$

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

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

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

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

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