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

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

(b) $H_2O_2(aq) +\ 3I^-(aq) +\ 2H^+ \rightarrow\ 2H_2O(I) +\ I^-\ Rate =\ k\left[H^2O^2\right]\left[I^-\right]$

(c) $CH_3CHO(g) \rightarrow\ CH_4(g) +\ CO(g)\ Rate =\ k\left[CH_3CHO\right]^{\frac{3}{2}}$

(d) $C_2H_5Cl(g) \rightarrow\ C_2H_4(g) +\ HCl(g)\ Rate =\ k\left[C_2H_5Cl\right]$

Ans:

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

Therefore, order of the reaction = 2

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

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

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

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

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

Therefore, order of the reaction = 2

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

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

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

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

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

Dimensions of $k = \frac{Rate}{[CH_3CHO]^{\frac{3}{2}}}$

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

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

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

(d) Given rate = $k = [C_2H_5Cl]$

Therefore, order of the reaction = 1

Dimension of $k = \frac{Rate}{[C_2H_5Cl]}$

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

$= s^{-1}$

Q 2. For the reaction: $2A + B \rightarrow A_2B$ **is** $k[A][B]^2$ **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:

The initial rate of reaction is

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

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

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

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

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

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

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

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

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

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

Q 3. The decomposition of NH3 on platinum surface is zero order reaction. What are the rates of production of N2 and H2 if k = 2.5 × 10−4 mol−1 L s −1?

Ans:

The decomposition of NH3 on platinum surface is represented by the following equation.

$$2NH^{3(g)} \overset{Pt}{\rightarrow}\ N_{2(g)} + 3H_{2(g)}$$

Therefore,

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

However, it is given that the reaction is of zero order.

Therefore,

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

$$= 2.5 \times\ 10^{-4}\ mol L^{-1} s^{-1}$$

Therefore, the rate of production of N_2 is

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

And, the rate of production of H_2 is

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

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

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

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

$$= 4ka^2$$

$$= 4\ R$$

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?

Ans:

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.

Ans:

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

$$= \frac{0.31 – 0.17}{60 – 30}$$

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

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

(b) For a pseudo first order reaction,

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

$$For\ t = 30\ s$$

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

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

$$For\ t = 60\ s$$

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

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

$$For\ t = 90\ s$$

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

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

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

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

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

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?

Ans:

(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 rat will be increased by 9 times.

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

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

$$8.k\,[A]\,[B]^2$$

Therefore, the rate of reaction will increase 8 times.

Q10. In a reaction between A and B, the initial rate of reaction (r0) 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
$r_0/mol\ L^{\ 1}\ s^{\ 1}$	$5.07\times\ 10^{\ 5}$	$5.07\times\ 10^{\ 5}$	$1.43\times\ 10^{\ 4}$

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

Ans:

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

Then,

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

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

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

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

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

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

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

$$\Rightarrow\ y = 0$$

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

$$\frac{1.43\times10^{-4}}{5.07\times10^{-5}} = \frac{k[0.40]^x[0.05]^y}{k[0.20]^x[0.30]^y}$$

$$\Rightarrow\ \frac{1.43\times10^{-4}}{5.07\times10^{-5}} = \frac{[0.40]^x}{[0.20]^x} \qquad \left[\begin{matrix} Since\ y=0, \\ [0.05]^y = [0.30]^y = 1\end{matrix}\right]$$

$$\Rightarrow\ 2.821 = 2^x$$

$$\Rightarrow\ \log 2.821 = x\log 2 \qquad (taking\ log\ on\ both\ sides)$$

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

$$= 1.496$$

$$= 1.5\ (Approximately)$$

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 → C + D

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

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

Ans:

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, According to the question,

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

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

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

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

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

$$\frac{2.4\times10^{-2}}{6.0\times10^{-3}} = \frac{k[0.4]^x[0.1]^y}{k[0.1]^x[0.1]^y} \quad 4 = \frac{[0.4]^x}{[0.1]^x} \quad 4 = \left(\frac{0.4}{0.1}\right)^x \quad (4)^1 = (4)^x$$

x = 1

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

$$\frac{2.88\times10^{-1}}{7.2\times10^{-2}} = \frac{k[0.3]^x[0.4]^y}{k[0.3]^x[0.2]^y} \quad 4 = \left(\frac{0.4}{0.2}\right)^y \quad 4 = 2^y \quad 2^2 = 2^y$$

y = 2

Hence, the rate law is

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

From experiment 1, we get

$$k = \frac{6.0\times10^{-3} mol\ L^{-1}\ min^{-1}}{(0.1\ mol\ L^{-1})(0.1\ mol\ L^{-1})^2}$$

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

From experiment 2, we get

$$k = \frac{7.2\times10^{-2} mol\ L^{-1}\ min^{-1}}{(0.3\ mol\ L^{-1})(0.2\ mol\ L^{-1})^2}$$

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

From experiment 1, we get

$$k = \frac{2.88\times10^{-1} mol\ L^{-1}\ min^{-1}}{(0.3\ mol\ L^{-1})(0.4\ mol\ L^{-1})^2}$$

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

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

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

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

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.	$\frac{A}{mol L^{-1}}$	$\frac{B}{mol L^{-1}}$	Initial rate $mol\ L^{-1}\ min^{-1}$
1	0.1	0.1	$2.0 \times\ 10^{-2}$
2	–	0.2	$4.0 \times\ 10^{-2}$
3	0.4	0.4	–
4	–	0.2	$2.0 \times\ 10^{-2}$

Ans:

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,

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

Rate = $k\,[A]$

From experiment 1, we get

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

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

From experiment 2, we get

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

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

From experiment 3, we get

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

From experiment 4, we get

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

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

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) $4\ years^{-1}$

Ans:

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

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

$= 3.47\ s$ (Approximately)

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

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

$= 0.35\ min$ (Approximately)

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

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

$= 0.173\ years$ (Approximately)

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

Ans:

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

It is known that,

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

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

$$= 1845\ years$$ (approximately)

Hence, the age of the sample is 1845 years.

Q 15. The experimental data for decomposition of N_2O_5

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

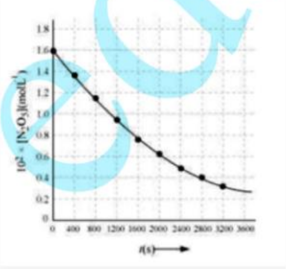
in gas phase at 318K are given below:

T(s)	0	400	800	1200	1600	2000	2400	2800	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

(a) Plot [N2O5] against t.
(b) Find the half-life period for the reaction.
(c) Draw a graph between log[N2O5] 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).

Ans:

(a)



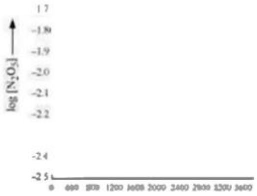
(b) Time corresponding to the concentration, $\frac{1.630 \times 10^2}{2}\ mol\ L^{-1} = 81.5 mol\ L^{-1}$ is the half life.

From the graph , the half life obtained as 1450 s.

(c)

t(s)	$10^2 \times\ [N_2O_5]\, mol\ L^{-1}$	$\log\, [N_2O_5]$

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, $\log\left[N_2O_5\right]$ v/s t, is a straight line.

Therefore, the rate law of the reaction is

Rate = $k\left[N_2O_5\right]$

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

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

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

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

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

Therefore, we obtain,

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

(f) Half – life is given by,

$$t_{\frac{1}{2}} = \frac{0.639}{k}$$

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

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

$$= 1438s$$

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 1/16th value?

Ans:

It is known that,

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

$$= \frac{2.303}{60\ s^{-1}} \log \frac{1}{1/6}$$

$$= \frac{2.303}{60\ s^{-1}} \log 16$$

$$= 4.6 \times 10^{-2}\ (approximately)$$

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

Q 17. During nuclear explosion, one of the products is 90Sr with half-life of 28.1 years. If 1μg of 90Sr 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:

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

Here,

It is known that,

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

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

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

$$\Rightarrow \log[R] = -\frac{10\times0.693}{2.303\times28.1}$$

$$\Rightarrow [R] = antilog\,(-0.1071)$$

$$antiog\,(1.8929)$$

$$= 0.7814\mu g$$

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

Again,

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

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

$$\Rightarrow log[R] = -\frac{60\times0.693}{2.303\times28.1}$$

$$[R] = antilog\ \ (-0.6425)$$

$$antilog\,(1.3575)$$

$$= 0.2278\mu g$$

Therefore, $0.2278\mu g\ of\ {}^{90}Sr$ 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.

Ans:

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

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

$$\frac{2.303}{k}\log100$$

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

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 t1/2.

Ans:

For a first order reaction,

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

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

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

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

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

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

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

$$= 77.7\ min\ (approximately)$$

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.

Ans:

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

$$(CH_3)_2\,CHN = NCH\,(CH_3)_{2(g)} \rightarrow N_{2(g)} + C_6H_{14(g)}$$

At t = 0 P_0 0 0

At t = t $P_0 - P$ p p

After time, t, total pressure, $P_1 = (P_0 - p) + p + p$

$$\Rightarrow P_1 = P_0 + p$$

$$\Rightarrow p = P_1 - P_0$$

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

$$= 2P_0 - P_t$$

For the first order reaction,

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

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

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

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

When t = 720 s,

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

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

Hence the average value of rate constant is.

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

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

Q 21. The following data were obtained during the first order thermal decomposition of SO2Cl2 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 thermal decomposition of SO_2CL_2 at a constant volume is represented by the following equation.

$$SO_2CL_{2(g)} \rightarrow \; SO_{2(g)}CL_2\,(g)$$

At t = 0 P_0 0 0

At t = t $P_0 – p$ 0 0

After time t, total pressure, $P_t \; = \; (P_0 – p) + \; p + \; p$

$$\Rightarrow \; P_t \; = \; P_0 + \; p$$

$$\Rightarrow \; p = \; P_t – P_0$$

$$\therefore \; P_0 – p = \; P_o – (P_t – P_0)$$

$$= \; 2P_0 – P_t$$

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 = 100s,

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

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

$$P_0 + p = 0.65$$

$$\Rightarrow p = 0.65 – P_0$$

$$= 0.65 – 0.5$$

$$= 0.15\ atm$$

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

$$P_{SOCL_2} = P_0 – p$$

$$= 0.5 – 0.15$$

$$= 0.35\ atm$$

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

$$Rate = k\left(P_{SOCL_2}\right)$$

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

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

Q 22. The rate constant for the decomposition of N2O5 at various temperatures is given below:

$T/^{\circ}C$	0	20	40	60	80
$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140

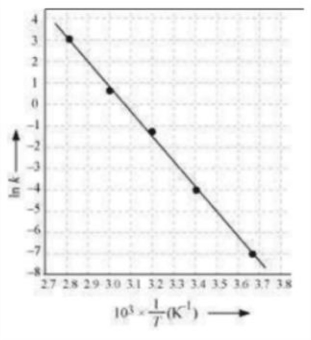
Draw a graph between ln k and 1/T and calculate the values of A and Ea. Predict the rate constant at 30° and 50°C.

Ans:

From the given data, we obtain

$T/^{\circ}C$	0	20	40	60	80
T/K	273	293	313	333	353

$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140
ln K	-7.147	-4.075	-1.359	-0.577	3.063



Slope of the line,

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

According to Arrhenius equation,

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

$$\Rightarrow\ E_a = -Slope \times\ R$$

$$= -(-12.301\, K) \times\ \left(8.314\, JK^{-1}\, mol^{-1}\right)$$

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

Again,

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

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

When T = 273 k,
ln k = – 7.147

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

$$= 37.911$$

$$\therefore\ A =\ 2.91\ \times\ 10^6$$

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

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

$$In\ k = -2.8$$

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

Again, when T = 50 + 273 K = 323 K

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

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

$$In\ k = -0.5$$

Therefore, k = 0.607 /s

Q 23. The rate constant for the decomposition of hydrocarbons is 2.418 × 10−5s−1 at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.

Ans:

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

T = 546 K

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

According to the Arrhenius equation,

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

$$\Rightarrow In\ k = InA - \frac{E_a}{RT}$$

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

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

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

$$= (0.3835 – 5) + 17.2082$$

$= 12.5917$

Therefore, A = antilog (12.5917)

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

Q 24. Consider a certain reaction A → Products with k = 2.0 × 10−2s−1. Calculate the concentration of A remaining after 100 s if the initial concentration of A is 1.0 mol L−1.

Ans:

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

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

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

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

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

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

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

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

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

Q 25. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with t 1/2 = 3.00 hours. What fraction of sample of sucrose remains after 8 hours ?

For the first order reaction,

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

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

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

$= 0.231\ h^{-1}$

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

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

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

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

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

= 0.158

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

Q 26. The decomposition of hydrocarbon follows the equation

$$k = (4.5 \times 10_{11} S–1)\, e_{–28000} K/T$$

Calculate E_a.

Ans:

The given equation is $k = (4.5 \times 10_{11} S–1)\, e_{–28000} K/T$ ....(i)

The Arrhenius equation is given by,

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

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

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

$$\Rightarrow E_a = R \times 28000\ K$$

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

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

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

Q 27. The rate constant for the first order decomposition of H2O2 is given by the following equation:

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

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

Ans:

Arrhenius equation is given by,

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

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

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

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

The given equation is

$$\log k = 14.34 – 1.25 \times 10^4\ K/T \qquad ...(ii)$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$= 668.95\ K$$

$$= 669\ K \quad (approximately)$$

Q 28. The decomposition of A into product has value of k as 4.5 × 103 s−1 at 10°C and energy of activation 60 kJ mol−1. At what temperature would k be 1.5 × 104s −1?

Ans:

From Arrhenius equation, we obtain

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

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

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

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

Then,

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

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

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

$$\Rightarrow 0.9528\ T_2 = 283$$

$$\Rightarrow T_2 = 297.019\ K \quad (approximately)$$

$$= 297\ K$$

$$= 24^\circ$$

Q 29. 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 × 1010s −1. Calculate k at 318K and Ea.

Ans:

For a first order reaction,

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

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

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

$$at\ 208\ K,\ t' = \frac{2.303}{k'} \log \frac{100}{75}$$

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

According to the question,

$$t = t'$$

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

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

From Arrhenius equation, we get

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

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

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

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

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

To calculate k at 318 K,

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

Again, from Arrhenius equation, we get

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

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

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

$$= -1.9855$$

Therefore, k = Antilog(-1.9855)

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

Q 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:

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, $K_2 = 4K_1$

$$T_1 = 293\ K$$

$$T_2 = 313\ K$$

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

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

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

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

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

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