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

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

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

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

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

Ans:

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

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

$$\begin{matrix} mol\ L^{\ 1} S^{\ 1} \\ (mol\ L^{\ 1})(mol\ L^{\ 1}) \end{matrix}$$

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

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

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: $2A + B \to A_2B$ 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 = $k[A][B]^2$

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

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

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

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

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

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

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

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

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

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

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,

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

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

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

reaction rate is given by $Rate = k\,[CH_3O\,CH_3]^{\frac{3}{2}}$

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.,

$$Rate = k\,(P_{CH_3O\,CH_3})^{\frac{3}{2}}$$

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

The decomposition of dimethyl ether leads to the formation of CH4, H2 and CO and the reaction rate is given by Rate = k [CH3OCH3] 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, Rate = k p(CH OCH3)3/2. If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

Ans:

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

Unit of rate = $bas\ min^{-1}$ $Rate = k\,(P_{CH_3O\,CH_3})^{\frac{3}{2}}$

$$\Rightarrow k = \frac{Rate}{k(P_{CH_3O\,CH_3})^{\frac{3}{2}}}$$

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

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

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

Ans:

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

(a) Temperature

(b) Presence of a catalyst

(c) The concentration of reactants (pressure in case of gases)

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 ?

Ans:

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

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?

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:

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

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

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

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

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

(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, $k = \frac{k_1+k_2+k_3}{3}$

$$= \frac{\left(1.911\times10^{-2}\right)+\left(1.957\times10^{-2}\right)+\left(2.075\times10^{-2}\right)}{3}$$

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

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

$$\frac{5.07\times10^{-5}}{5.07\times10^{-5}} = \frac{k[0.20]^x[0.30]^y}{k[0.20]^x[0.10]^y}$$

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

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

$$\Rightarrow y = 0$$

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

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

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

$$\Rightarrow 2.821 = 2^x$$

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

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

$$= 1.496$$

$$= 1.5\ (Approximately)$$

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.	$\frac{A}{molL^{-1}}$	$\frac{B}{molL^{-1}}$	Initial rate of formation of $\frac{D}{mol\ L^{-1}\ min^{-1}}$
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.

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

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

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

x = 1

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

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

y = 2

Hence, the rate law is

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

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

From experiment 1, we get

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

= 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

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

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

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

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

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:

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

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

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

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

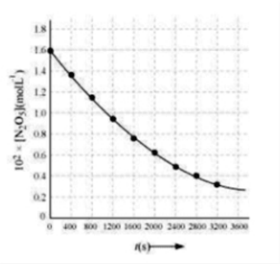
in gas phase at 318K are given below:

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)



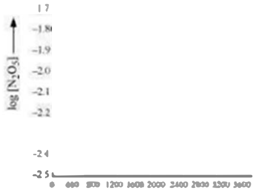
(b) Time corresponding to the concentration, $\frac{1.630 \times 10^2}{2}\ mol\ L^{-1} = 81.5 mol\ L^{-1}$ is the half life.

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,

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

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

(f) Half – life is given by,

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

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

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

$$= 1438 s$$

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 1/16th 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,

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

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

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

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

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

$$antiog\,(1.8929)$$

$$= 0.7814\mu g$$

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

Again,

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

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

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

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

$$antilog\,(1.3575)$$

$$= 0.2278\mu g$$

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

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

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

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

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 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.

$$(CH_3)_2CHN=NCH(CH_3)_{2(g)} \rightarrow N_{2(g)} + C_6H_{14(g)}$$

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,

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

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

When $P_t = 0.65$ atm,

$$P_0 + p = 0.65$$

$$\Rightarrow p = 0.65 – P_0$$

$$= 0.65 – 0.5$$

$$= 0.15\ atm$$

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

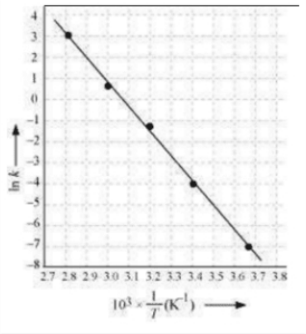
Draw a graph between ln k and 1/T and calculate the values of A and Ea. Predict the rate constant at 30° and 50°C.

Ans:

From the given data, we obtain

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

$\frac{1}{T}/K^{-1}$	3.66×10^{-3}	3.41×10^{-3}	3.19×10^{-3}	3.0×10^{-3}	2.83×10^{-3}
$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140
In 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,

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

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

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

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

Again,

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

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

When T = 273 k,

In k = − 7.147

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

$$= \ 37.911$$

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

When T = 30 + 273 K = 303 K

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

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

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

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

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

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

$$= \ 0.135 \ mol \ L^{-1}$$ (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, $0.231\ h^{-1} = \frac{2.303}{8h} \log \frac{[R]_0}{[R]}$

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

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

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

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

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

$$\Rightarrow log\left(4.51\times10^{-5}\right) = 14.34 - \frac{1.25\times10^{4}\ K}{T}$$

$$\Rightarrow log\left(0.654–05\right) = 14.34 - \frac{1.25\times10^{4}\ K}{T}$$

$$\Rightarrow \frac{1.25\times10^{4}\ K}{T} = 18.686$$

$$= 668.95\ K$$

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

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

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

Also, $k_1 = 4.5\times10^{3}\ s^{-1}\ T_1 = 273+10 = 283\ K\ k_2$

$$= 1.5\times10^{4}\ s^{-1}$$

$$E_a = 60\ kJ\ mol^{-1} = 6.0\times10^{4}\ J\ mol^{-1}$$

Then,

$$\log\frac{1.5\times10^{4}}{4.5\times10^{3}} = \frac{6.0\times10^{4}\ J\ mol^{-1}}{2.303\times8.314\ J\ K^{-1}\ mol^{-1}}\left(\frac{T_2-283}{283\ T_2}\right)$$

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

$$\Rightarrow \frac{0.5229\times283\ T_2}{3133.627} = T_2-283$$

$$\Rightarrow 0.9528\ T_2 = 283$$

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

$$= 297\ K$$

$$= 24^{\circ}$$

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