CHAPTER 3

Chemical Kinetics

CLASS 12TH

NCERT EXERCISE AND SOLUTIONS - CHEMISTRY

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

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

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

(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 $= k\left[C_2H_5Cl\right]$

ANSWER:-

(a) Given that

Rate= $k[NO]^2$

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

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

Dimensions will be:

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

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

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

(b) $H_2O_2(aq) + 3I^-(aq) + 2H^+ \rightarrow 2H_2O(I) + I_3^-$ Rate $= k\left[H_2O_2\right][I^-]$

Rate $= k\left[H_2O_2\right]\left[I^-\right]$

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

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

Dimensions will be:

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

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

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

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

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

Dimensions will be:

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

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

Rate $= k[C_2H_5Cl]$

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

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

Dimensions will be:

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

Q. 2. **For the reaction: $2A + B \rightarrow A_2B$ 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 $0.06\ mol\,L^{-1}$.**

ANSWER:-

The initial rate of the reaction is

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

$[A] = 0.1 \text{mol L}^{-1}$, $[B] = 0.2 \text{ mol L}^{-1}$, $k = 2.0 \times 10^{-6}$
$= 2.0 \times 10^{-6} \times 0.1 \times (0.2)^2$
$= 8 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$
When [A] reduces to 0.06 mol L^{-1} i.e. 0.04 mol L^{-1} of A has reacted, then the reactant B
$$= \frac{1}{2} \times 0.04$$
$= 0.02 \text{ mol L}^{-1}$
Hence, the new $[B] = 0.2 - 0.02 = 0.18 \text{ mol L}^{-1}$
Now rate $= 2.0 \times 10^{-6} \times 0.06 \times (0.18)^2$
$= 3.89 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$
Therefore, the rate of the reaction is $3.89 \times 10^{9} \text{ mol L}^{-1} \text{ s}^{-1}$

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

ANSWER:-

The decomposition of NH_3 on platinum surface is represented by the following equation.
$$2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$$
Therefore,
$$\text{Rate} = -\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt}$$
However, it is given that the reaction is of zero order. Therefore,
$$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = k$$
$= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
Therefore, the rate of production of N_2 is
$$\frac{d[N_2]}{dt} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$
And, the rate of production of H_2 is
$$\frac{d[H_2]}{dt} = 3 \times 2.5 \times 10^{-1} \text{ mol L}^{-1} \text{ s}^{-1}$$
$= 7.5 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$

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 = $k\, [CH_3OCH_3]^{3/2}$
The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.,
$$\text{Rate} = k\left(p_{CH_3OCH_3}\right)^{3/2}$$

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

ANSWER:-

If pressure is measured in bar and time in minutes, then Unit of rate = bar min^{-1}

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

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

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

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

So, the unit are $bar^{-1/2}$ min^{-1}

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

ANSWER:-

The factors that affect the rate of a reaction are as follows.

(i) Concentration of reactants (pressure in case of gases)

(ii) Temperature

(iii) Presence of a catalyst

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?

ANSWER:–

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

Rate of reaction, R = k $[A]^2$ = ka^2

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

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

$= 4\ ka^2$

$= 4$ R

Therefore, the rate of the reaction would increase by 4 times.

(ii) If the concentration of the reactant is reduced of 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 would be reduced to $1/4^{th}$

Q. 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?

ANSWER:-

The rate constant is nearly doubled with a rise in temperature by 10° for a chemical reaction.

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

$K = Ae^{-Ea/RT}$

where, k is the rate constant,

A is the Arrhenius factor or the frequency factor,

R is the gas constant,

T is the temperature, and

E_a is the energy of activation for the reaction

Q. 8. In a pseudo first order hydrolysis of ester in water, the following results were obtained:

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

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

(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

ANSWER:-

(i) Average rate of reaction between the time interval, 30 to 60 seconds, $= \frac{d\,[\text{Ester}]}{dt}$

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

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

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

(ii) For a pseudo first order reaction,

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

Now, when t =30 s, then we rate constant will be:

$$k_2 = \frac{2.303}{30} \log \frac{0.55}{0.31} = 1.91 \times 10^{-2} s^{-1}$$

Now, when t = 60s, then we rate constant will be:

$$k_2 = \frac{2.303}{60} \log \frac{0.55}{0.17} = 1.96 \times 10^{-2} s^{-1}$$

Now, when t = 90s, then we rate constant will be:

$$k_3 = \frac{2.303}{90}\log\frac{0.55}{0.085} = 2.075\times10^{-2}\,s^{-1}$$

So, we can calculate the average rate constant as:

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

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

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

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?

ANSWER:-

(i) The differential rate equation will be

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

(ii) 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 rate of reaction will increase 9 times.

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

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

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

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

Therefore, the rate of reaction will increase 8 times.

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

A/ mol L^{-1}	**0.20**	**0.20**	**0.40**
B/mol L^{-1}	**0.30**	**0.10**	**0.05**
ro/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?

ANSWER:-

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

Therefore,

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

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

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

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

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

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

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

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

$\Rightarrow y = 0$

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

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

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

$\Rightarrow 2.821 = 2^x$ (Taking log on both sides

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

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

=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

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^{-1}
II	0.3	0.2	7.2×10^{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.

ANSWER:-

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,

$$6.0\times10^{-3} = k[0.1]^x[0.1]^y \qquad (i)$$
$$7.2\times10^{-2} = k[0.3]^x[0.2]^y \qquad (ii)$$
$$2.88\times10^{-1} = k[0.3]^x[0.4]^y \qquad (iii)$$
$$2.40\times10^{-2} = k[0.4]^x[0.1]^y \qquad (iv)$$

Dividing equation (iv) by (i), we obtain

$$\frac{2.40\times10^{-2}}{6.0\times10^{-3}} = \frac{k[0.4]^x[0.1]^x}{k[0.1]^x[0.1]^x}$$

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

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

$$\Rightarrow (4)^1 = 4^x$$

$$\Rightarrow x = 1$$

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

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

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

$$\Rightarrow 4 = 2^y$$

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

$$\Rightarrow y = 2$$

Therefore, the rate law is

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

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

From experiment I, we obtain

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

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

From experiment II, we obtain

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

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

From experiment III, we obtain

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

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

For experiment IV, we obtain

$$k = \frac{2.40\times10^{-2}\,\text{mol L}^{-1}\,\text{min}^{-1}}{\left(0.4\text{mol L}^{-1}\right)\left(0.1\text{mol L}^{-1}\right)^2}$$

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

Therefore, 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:

Experiment	A/ mol L−1	B/ mol L^{-1}	Initial rate/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}

ANSWER:-

Given that reaction between A & B is first order with respect to A & zero order with respect to B.

Therefore, the rate of the reaction is given by,

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

$\Rightarrow$ Rate = k [A]

From experiment I, we obtain 2.0×10^{-2} mol L^{-1} min^{-1} = k (0.1 mol L^{-1})

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

From experiment II, we obtain 4.0×10^{-2} mol L^{-1} min^{-1} = 0.2 min^{-1} [A]

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

From experiment III, we obtain Rate = 0.2 min^{-1} × 0.4 mol L^{-1} = 0.08 mol L^{-1} min^{-1}

From experiment IV, we obtain 2.0×10^{-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:

(i) **200 s^{-1}** **(ii)** **2 min^{-1}** **(iii)** **4 $years^{-1}$**

ANSWER:-

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

(i) Half life

$t_{1/2}$ = 0.693/200 s^{-1}

= 3.47 s

(ii) Half life

$t_{1/2} = 0.693/2\ min^{-1}$

$= 0.35$ min

(iii) Half life,

$t_{1/2} = 0.693/4 years^{-1}$

$= 0.173$ years

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.**

ANSWER:-

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

Here,

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

It is know that,

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

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

= 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:

	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

(i) **Plot $[N_2O_5]$ against t.**

(ii) **Find the half–life period for the reaction.**

(iii) **Draw a graph between log $[N_2O_5]$ and t.**

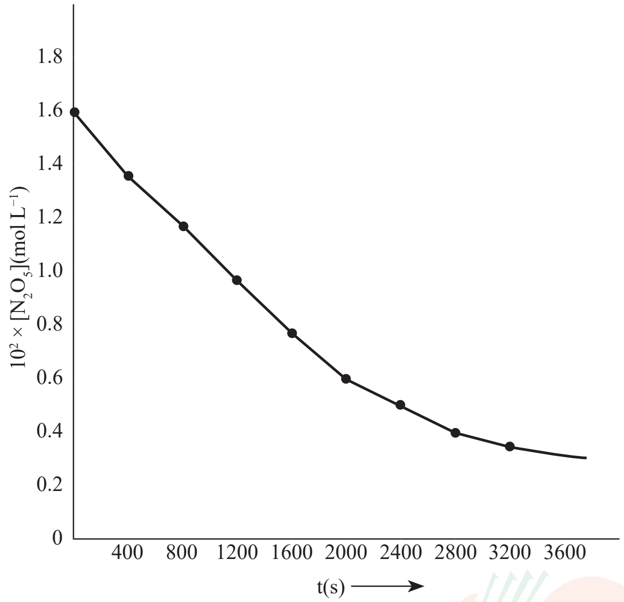
(iv) **What is the rate law?**

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

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

ANSWER:-

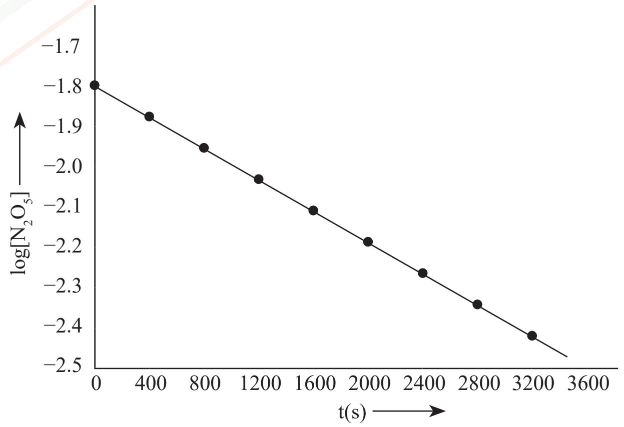
(i)



(ii) 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 is obtained as 1450 s.

(iii)

T(s)	$10_2 \times [N_2O_5]/molL^{-1}$	$log[N]_2\ O_5$
0	1.63	−1.79
400	1.36	−1.87
800	1.14	−1.94
1200	0.93	−2.03
1600	0.78	−2.11
2000	0.64	−2.19
2400	0.53	−2.28
2800	0.43	−2.37
3200	0.35	−2.46



(iv) 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

$$Rate = k[N_2O_5]$$

(v) 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

$$-\frac{\kappa}{2.303}$$

Therefore, we obtain

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

$$\Rightarrow k = 4.82\times10^{-4}\,s^{-1}$$

(vi) Half–life is given by,

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

$$= \frac{0.693}{4.82\times10^{-4}}\,s$$

$$= 1.438\times10^{3}\,s$$

$$= 1438s$$

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?

ANSWER:-

It is known that,

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

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

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

$$= 4.6\times10^{-2}\,s \text{ (approximately)}$$

Hence, the required time is 4.6×10^{-2} s.

Q. 17. During a nuclear explosion, one of the products is ^{90}Sr with a half–life of 28.1 years. If 1μg 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 years if it is not lost metabolically.

ANSWER

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

Here,

It is known that,

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

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

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

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

[R] = antilog (−0.1071) = antiog ($\bar{1}$.8929) = 0.7814 μg

Therefore, 0.7814 μg of ^{90}Sr will remain after 60 years.

Again,

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

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

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

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

$$= \text{antilog } (\bar{1}.3575)$$

$$= 0.2278 \mu g$$

Therefore, 0.2278 μg 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.

ANSWER:-

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

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

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

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

Therefore, $t_1 = 2t_2$

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 $t_{1/2}$**

ANSWER:-

30% decomposition means that x = 30% of a = 0.30a Since, the reaction is of 1st order, we can write:

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

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

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

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

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

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.

Q. 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.

ANSWER:-

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

$(CH_3)_2\ CHN = NCH(CH_3)_2 \rightarrow N_2 + C_6H_{14}$

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 t = 360s,

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 = 720s,

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:

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

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

Q. 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.

ANSWER:-

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

	SO_2Cl_2 $\rightarrow$	SO_2 +	Cl_2
Att = 0	P_o	0	0
Att = 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 substitutable 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 =100s

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

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

When P_t = 0.65 atm

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

$$P_{SO_2Cl_2} = 2P_0 - P_t$$

= 2 × 0.50 – 0.65

= 0.35 atm

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

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

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

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

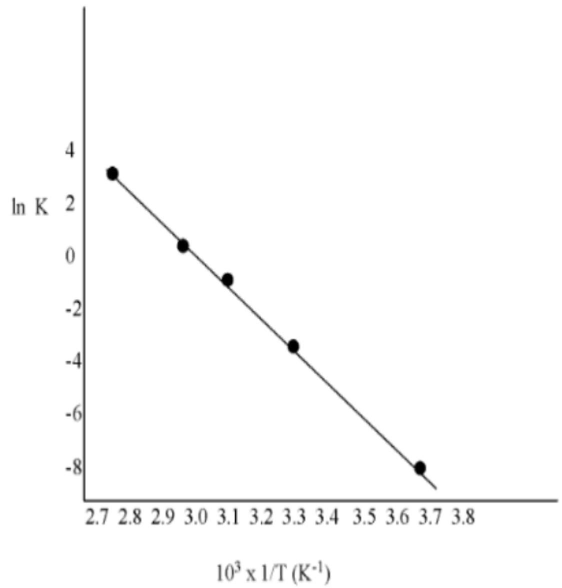
T/ °C	0	20	40	60	80
$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140

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

ANSWER:-

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



Slope of the line, will be given as:

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

According to the Arrhenius equation,

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

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

$$= (-12.301)(8.314)$$

$$= 102.27 KJmol^{-1}$$

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

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

As T = 273 K and in k = –7.147

Applying this in the formula, we get:

$$\ln A = -7.147 - \frac{102.27\times10^3}{8.314\times273} = 37.911$$

So, A = 2.91×10^6

When T = 30 + 273 K = 303 K

$$\frac{1}{\mathbf{T}} = 0.0033K = 3.3\times10^{-3}K$$

Now, at $\frac{1}{T} = 0.0033K = 3.3\times10^{-3}K$

In k = –2.8

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

When T = 50 + 273K = 323K

$$\frac{1}{T} = 0.0031K = 3.1\times10^{-3}K$$

Now, at $\frac{1}{T} = 0.0031K = 3.1\times10^{-3}K$

In k = – 0.5

Therefore, k = 0.607 s^{-1}.

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

ANSWER:-

We are given some values as:

$$K = 2.418\times10^{-5}s^{-1}$$

$$T = 546K$$

$$E_a = 179.9kJmol^{-1} = 179.9\times10^3 Jmol^{-1}$$

We the Arrhenius equation is:

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

In the log form, this can be written as:

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

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

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

$$= \log\left(2.418\times10^{-5}s^{-1}\right) + \frac{179.9\times10^3 \text{ J mol}^{-1}}{2.303\times8.314 \text{ J k}^{-1}\text{ mol}^{-1}\times546\text{K}}$$

= (0.3835 – 5) + 17.2082

=12.5917

Therefor, A = antilog (12.5917)

$$A = 3.912\times10^{12}s^{-1}$$

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

ANSWER:-

We are given some values, that are given below:

$$k = 2.0\times10^{-2}\ s^{-1}$$

$$t = 100\,s$$

$$[A]_0 = 1.0\,mol\,L^{-1}$$

As we can see that the units of k are given in s^{-1}, this meAnswer:-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:

$$2.0\times10^{-2} = \frac{2.303}{100}\log\frac{1.0}{[A]}$$

Putting the values, we get:

$$2.0\times10^{-2} = \frac{2.303}{100}\log\frac{1.0}{[A]}$$

$$2.0\times10^{-2} = \frac{2.303}{100}(-\log[A])$$

$$(-\log[A]) = \frac{2.0\times10^{-2}\times100}{2.303}$$

$$[A] = antilog\left(\frac{2.0\times10^{-2}\times100}{2.303}\right)$$

$$= 0.135 molL^{-1}$$

Therefore, the remaining amount of 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 a sample of sucrose remains after 8 hours?**

ANSWER:-

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

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

It is given that the half−life is 3 hours. Therefore, we can write:

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

So, putting the values in this, we get:

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

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

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

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

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

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

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

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 .

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

ANSWER:-

According to the Arrhenius equation,

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

We are given the equation as:

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

Therefore, the formula can be written as:

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

This can be written as:–

$E_a = 28000 \times R$

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

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

Q. 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?

ANSWER:-

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:

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

We are aiven:

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

Comparing these two, we get:

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

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

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

$E_a = 239.34 kJmol^{-1}$

We are given a half–life of 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:

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

T = 669K

Q. 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 kg mol^{-1}. At what temperature would k be $1.5 \times 10^4\ s^{-1}$?**

ANSWER:-

We are some information:

$k_1 = 4.5 \times 10^3$

$T_1 = 10 + 273 = 283K$

$k_2 = 1.5 \times 10^4$

$T_2 = ?$

$E_a = 60 kJmol^{-1}$

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:

$$\log\frac{1.5\times10^4}{4.5\times10^3} = \frac{60}{2.303\times8.314}\left(\frac{T_2 - 283}{283T_2}\right)$$

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

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

$0.0472\ T_2 = T_2 - 283$

$T_2 = 297$ K

Hence, k would be $1.5 \times 10^4\ s^{-1}$ at 24°C.

Q. 29. **The time required for 10% completion of a first order reaction at 298 k is wqual to that required for its 25% completion at 308 k. As the value of A $4 \times 10^{10}\ s^{-1}$, Calculate k at 318 k and E_a.**

ANSWER:-

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

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

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

$$E_a = 76.623 kJmol^{-1}$$

Now, the calculation of k at 318K

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

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

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

$$= -1.9855$$

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.**

ANSWER:-

We are given that:

$k_2 = 4k_1$

$T_1 = 293$ K

$T_2 = 313$K

According the Arrhenius equation, we get:

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

Putting the values, we get:

$$\log\frac{4k_1}{k_1} = \frac{E_a}{2.303\times8.314}\left(\frac{313-293}{293\times313}\right)$$

$$0.6021 = \frac{E_a}{2.303\times8.314}\left(\frac{313-293}{293\times313}\right)$$

$$E_a = \frac{0.6021\times2.303\times8.314\times293\times313}{20}$$

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

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

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