NCERT Solutions for Class-XII Chemistry

CHAPTER -3

NCERT Chemistry Class 12

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

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

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

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

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

1. (i) Given rate $= k[NO]^2$

Therefore, order of the reaction $= 2$

Dimension of $k = \dfrac{\text{Rate}}{[NO]^2}$

$= \dfrac{\text{molL}^{-1}\ \text{s}^{-1}}{\left(\text{mol L}^{-1}\right)^2} = \dfrac{\text{molL}^{-1}\ \text{s}^{-1}}{\text{mol}^2\ \text{L}^{-2}} = \text{Lmol}^{-1}\ \text{s}^{-1}$

(ii) Given rate $= k\left[H_2O_2\right]\left[I^-\right]$

Therefore, order of the reaction $= 2$

$k = \dfrac{\text{Rate}}{\left[H_2O_2\right]\left[I^-\right]}$

Dimension of

$= \dfrac{\text{molL}^{-1}\ \text{s}^{-1}}{\left(\text{mol L}^{-1}\right)\left(\text{molL}^{-1}\right)}$

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

(iii) Given rate $= k\left[CH_3CHO^{3/2}\right.$

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

Dimension of $= \dfrac{\text{molL}^{-1}\ \text{s}^{-1}}{\left(\text{mol L}^{-1}\right)^{\frac{3}{2}}}$

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

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

(iv) Given rate $= k\left[C_2H_5Cl\right]$ Therefore, order of the reaction $=1$

Dimension of

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

$$= s^{-1}$$

2. For the reaction:

$2\ A + B \rightarrow A_2\ B$

the rate $= k[\ A][B]^2$ with $k = 2.0 \times 10^{-6}\ \text{mol}^{-2}\ L^2\ s^{-1}$. 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 $0.06\ \text{mol}\ L$.

2. The initial rate of the reaction is

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

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

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

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

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

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

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 $0.06\ \text{mol}\ L^{-1}$, the rate of the reaction is given by,

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

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

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

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

3. The decomposition of NH_3 on platinum surface is represented by the following equation.

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

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

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

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

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

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

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.,

$$\text{Rate} = k\left(p^3_{CH_3OCH}\right)^{3/2}$$

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

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

Unit of rate $=$ bar min^{-1}

$$\text{Rate} = k\left(p_{CH_3OH_3}\right)^{3/2}$$

$$\Rightarrow k = \frac{\text{Rate}}{\left(p_{CH_3OCH_3}\right)^{3/2}}$$

Therefore, unit of rate constants

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

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

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

5. Factors that influence a reaction's speed include.

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

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

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

(iv) Presence of catalyst: The rate of reaction is also affected by the presence of a catalyst in the reaction. It enhances the pace of reaction by increasing reaction surface area, by generating unstable intermediates with the substrate, and by offering a lower activation energy alternative path.

6. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is

(i) doubled

(ii) reduced to half?

6. 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

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

$$= 4ka^2$$

$$= 4R$$

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

(ii) 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

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

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

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

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?

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

$k = Ae^{-E_2/Rt^2}$

Where, A is the Arrhenius factor or the frequency factor,
T is the temperature,
R is the gas constant,
E_a is the activation energy.

The formula can also be written as:

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

Where k_2 is the rate constant at temperature T_2
k_1 is the rate constant at temperature T_1

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.

8. (i) Average rate of reaction between the time interval, 30 to 60 seconds,

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

$= \frac{0.14}{30}$

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

(ii) For a pseudo first order reaction,

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

For $k_1 = \frac{2.303}{30}\log\frac{0.55}{0.31}\ t = 30\ s$,

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

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

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

$= 1.98 \times 10^{-2}\ s^{-1}\ 3\ 1$

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?

9. (i) Write the differential rate equation

The differential rate equation can be written as:

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

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

The concentration of B is increased by 3 times, then $B = 3\ B$

Therefore, the rate will be:

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

Therefore, the rate will increase by 9 times.

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

The concentration of A is doubled, then $A = 2\ A$

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

Therefore, the rate will be:

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

Therefore, the rate will increase by 8 times.

10. In a reaction between A and B, the initial rate of reaction (r_0) was measured for different 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

r0/ 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?

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

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

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

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

$1.43\times10^{-4} = k[0.40]^x[0.05]^y$

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

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

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

$\Rightarrow 2.821 = 2^x$

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

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

$2A + B \rightarrow C + D$

Experiment	A/ mol L^{-1}	B/ mol L^{-1}	Initial rate of formation of D/mol L^{-1} min^{-1}

I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-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.

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

Therefore, we can write:

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

$6.0\times10^{-3} = k[0.1]^x[0.1]^y$ ..... (i)

$7.2\times10^{-2} = k[0.3]^x[0.2]^y$ .....(ii)

$2.88\times10^{-1} = k[0.3]^x[0.1]^y$ ..... (iii)

$2.40\times10^{-2} = k[0.4]^x[0.1]^y$ L L L (iv)

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

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

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

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

Therefore, $x = 1$

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

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

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

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

$$= 4 = 2^y$$

$$= 2^2 = 2^y$$

$$y = 2$$

Thus, the order of the reaction according to A is 1 and according to B is 2 .
So, the rate law is:

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

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

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

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

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

From experiment II:

$$k = \frac{7.3\times10^{-2}}{[0.3][0.2]^2}$$

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

From experiment III:

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

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

From experiment IV:

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

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

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

12. The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

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

12. The given reaction is of the first order with respect to A and of zero order with respect to B.
Therefore, the rate of the reaction is given by,

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

$\Rightarrow$ Rate $= k[A]$

From experiment I, we obtain

$2.0\times10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1} = k\left(0.1\ \text{mol L}^{-1}\right)$

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

From experiment II, we obtain

$4.0\times10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1} = 0.2\ \text{min}^{-1}[A]$

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

From experiment III, we obtain Rate

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

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

From experiment IV, we obtain

$2.0\times10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1} = 0.2\ \text{min}^{-1}[A]$

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

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 $years^{-1}$

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

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

Putting the value of time, we get:

$$k = \frac{0.693}{200} = 3.46\times10^{-3}\ \text{s}$$

So, the rate of the reaction is 3.46×10^{-3} s

(ii) 2min^{-1}

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

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

Putting the value of time, we get:

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

So, the rate of the reaction is 0.346 min .

(iii) 4 years $^{-1}$

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

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

Putting the value of time, we get:

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

So, the rate of the reaction is 0.173 years.

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

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

Here,

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

It is known 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.

15. The experimental data for decomposition of N_2O_5

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

in gas phase at 318K are given below:

t(s)	0	400	800	1200	1600	2000	2400	2800	3
$10^{2\times}\left[N_2O_5\right]$ molL^{-1}	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	(

(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.

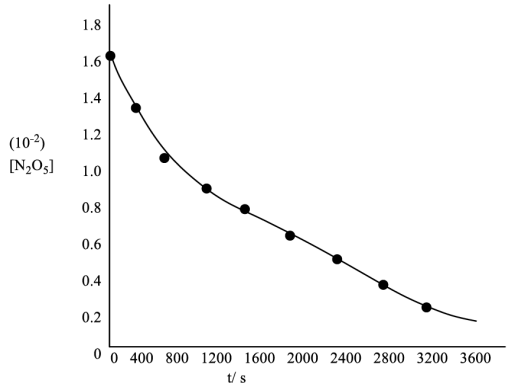
(iv) What is the rate law?

(v) Calculate the rate constant.

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

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

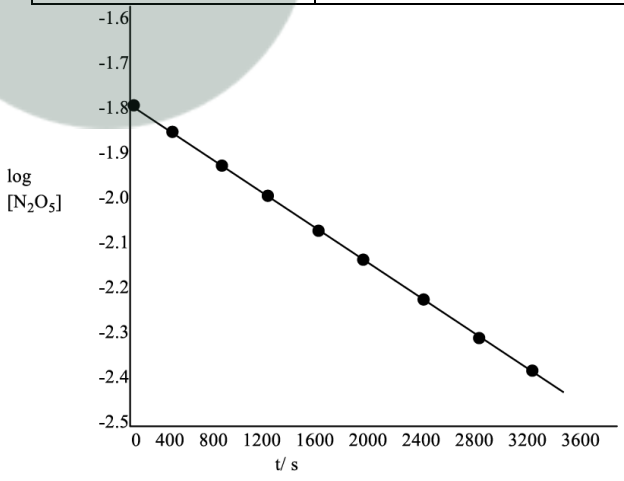
The graph is given below:



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

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

T(s)	$10^{-2} \times [N_2O_5]$/mol L^{-1}	log$[N_2O_5]$
0	1.63	-1.79
400	1.36	-1.87
800	1.14	-1.94
1200	0.93	-2.03
1600	0.78	-2.11
2000	0.64	-2.19
2400	0.53	-2.28
2800	0.43	-2.37
3200	0.35	-2.46



(iv) What is the rate law?

Ans: The rate law of the reaction will be:

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

(v) Calculate the rate constant.

Ans: From the plot $\left[N_2O_5\right] v/s$, is given by: $=-\frac{k}{2.303}$

Therefore, we obtain:

$=-\frac{k}{2.303}=\frac{0.67}{3200}=4.82\times10^{4}\ mol\ L^{-1}\ s^{-1}$

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

Ans: Half-life is given by:

$t_{1/2}=\frac{0.693}{k}=\frac{0.693}{4.82\times10^{-4}}\ s$

$=1438$ seconds.

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

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

16. It is known that,

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

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

$=\frac{2.303}{60\ s^{-1}}\log16$

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

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

17. During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1μg of ^{90}μr 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.

17. As radioactive disintegration follows first order kinetics. Decay constant of

$^{90}Sr(k)=\frac{0.693}{t_{1/2}}=\frac{0.693}{28.1}=2.466\times10^{-2}\ y^{-1}$

$a=1\mu g$

$t=10$ years

$k=2.466\times10^{-2}\ y^{-1}$

$(a-x)=?$

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

$$2.466\times10^{-2} = \frac{2.303}{10}\log\frac{1}{a-x}$$

$$\log(a-x) = -0.1071$$

$$(a-x) = \text{Antilog} - 0.1071 = 0.7814\mu g$$

To calculate the amount left after 10 years.

To calculate the amount left after 60 years.

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

$$2.466\times10^{-2} = \frac{2.303}{60}\log\frac{1}{a-x}$$

$$\log(a-x) = -0.6425$$

$$(a-x) = \text{Antilog} - 0.6425 = 0.2278\mu g$$

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.

18. 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.

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

19. 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 40 min. 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 $7.77\ \text{min}$.

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

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

Calculate the rate constant.

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

$$\left(CH_3\right)_2 CHN = NCH\left(CH_3\right)_{2(g)} \rightarrow N_{2(g)} + C_6H_{1+(g)}$$

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

After time, t, total pressure, $P_t = \left(P_0 - p\right) + p + p$

$$\Rightarrow P_t = P_0 + p$$

$$\Rightarrow p = P_t - P_0$$

Therefore, $P_0 - p = P_0 - \left(P_t - P_o\right)$

$$= 2P_0 - P_t$$

For a first order reaction,

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

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

When $t = 360\ \text{s}$, $= 2.175 \times 10^{-3}\ \text{s}^{-1}$

When $t = 720\ s,\ k = \frac{2.303}{720\ s}\log\frac{35.0}{2\times35.0-63.0} = 2.235\times10^{-3}\ s^{-1}$

Hence, the average value of rate constant is

$$k = \frac{\left(2.175\times10^{-3}\right)+\left(2.235\times10^{-3}\right)}{2}\ s^{-1} = 2.21\times10^{-3}\ s^{-1}$$

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

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.

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

SO_2Cl_2	$\rightarrow$	SO_2	+	Cl_2
At $t = 0$ P_0		0		0
At $t = t$ $P_0 - P$		P		P

Total pressure after time t, we will be:

$P_t = \left(P_o - p\right) + p + p$

$P_t = P_o + p$

$p = P_t - P_\circ$

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

$= P_o - p$

$= P_o - \left(P_t - P_o\right)$

$= 2P_o - P_t$

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

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

When the $t = 100\ s$

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

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

When $P_t = 0.65$ atm

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

$P_{SO_2Cl_2} = 2P_o - P_t$

$= 2 \times 0.50 - 0.65$

$= 0.35$ atm

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

Rate $= k\left(P_{SO_2C_2}\right)$

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

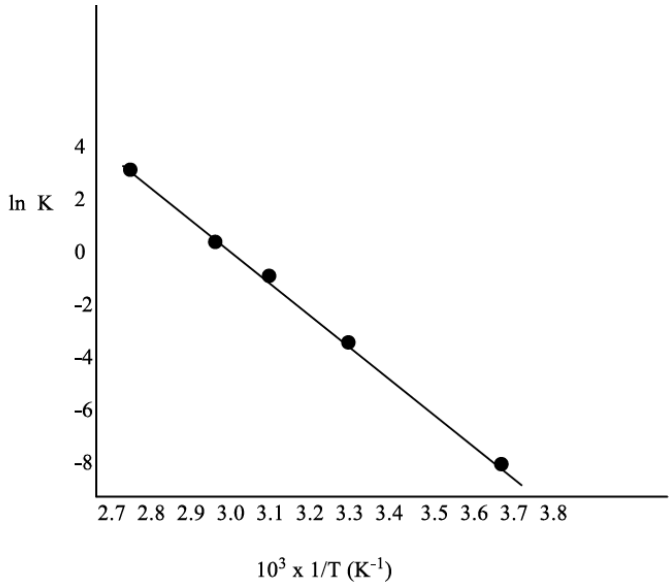
22. The rate constant for the decomposition of N_2O_5 at various temperatures is given below:

T/°c	0	20	40	60	80
10^5 × k/s	0.0787	1.70	25.7	178	2140

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

22. From the given data, we obtain

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



Slope of the line,

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

According to Arrhenius equation,

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

$$\Rightarrow E_a = -\text{Slope} \times R$$

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

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

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

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

When $T = 273\ \text{K}$

$\ln k = -7.147$

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

$= 37.911$

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

When $T = 30 + 273\ \text{K} = 303\ \text{K}$, $\frac{1}{T} = 0.0033\ \text{K} = 3.3 \times 10^{-3}\ \text{K}$

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

$\ln k = -2.8$

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

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

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

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

In $k = -0.5$

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

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.

23. We are given some values as:

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

$T = 546\ K$

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

We the Arrhenius equation is:

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

In the log form, this can be written as:

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

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

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

$$= \left(0.3835 - 5\right) + 17.2082 = 12.5917$$

Therefore, A = antilog (12.5917)

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

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

24. $k = 2.0 \times 10^{-2}\ s^{-1} T = 100\ s$

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

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

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

$$\Rightarrow 2.0\times10^{-2}\ \text{s}^{-1}=\frac{2.303}{100\ \text{s}}\log\frac{1.0}{[\text{A}]}$$

$$\Rightarrow 2.0\times10^{-2}\ \text{s}^{-1}=\frac{2.303}{100\ \text{s}}\left(-\log[\text{A}]\right)$$

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

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

$$=0.135\ \text{mol L}$$

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

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

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

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

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

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

So, putting the values in this, we get:

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

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

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

$$\log\frac{[R]_0}{[R]}=\frac{0.231\times8}{2.303}$$

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

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

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

Or we can write:

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

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

26. The decomposition of hydrocarbon follows the equation

$$k = \left(4.5 \times 10_{11}\ S - 1\right) e - 28000k / T$$

Calculate E_a.

26. The given equation is $k = (4.5 \times$ $1011\ S - 1\ )$ e-28000 k / T (i)

Arrhenius equation is given by,

$k = Ae^{-E_\alpha / RT}$ (ii)

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

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

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

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

$$= 232792\ Jmol^{-1}$$

$$= 232.792\ kJ\ mol^{-1}$$

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

$\log k = 14.34 - 1.25 \times 104\ K/T$

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

27. 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 given:

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

Comparing these two, we get:

$$\frac{E_a}{2.303RT} = \frac{1.25\times10^4\ K}{T}$$

$$E_a = 2.303R\times1.25\times10^4\ K$$

$$E_a = 2.303\times8.314\times1.25\times10^4\ K$$

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

We are given half-life time as 256 minutes.

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

$$k = \frac{0.693}{256\times60} = 4.51\times10^{-5}\ s^{-1}$$

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

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

$$T = 669\ K$$

28. The decomposition of A into product has value of k as $4.5\times10^3\ s^{-1}$ at 10^oC and energy of activation $60\ kJ\ mol^{-1}$. At what temperature would k be $1.5\times10^4\ s^{-1}$?

28. From Arrhenius equation, we obtain

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

Also, $k_1 = 4.5\times10^3\ s^{-1}$

$T_1 = 273 + 10 = 283\ K$ k_2

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

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

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

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

$$\Rightarrow \frac{0.5229\times283T_2}{3133.627} = T_2 - 283$$

$$\Rightarrow 0.0472T_2 = T_2 - 283$$

$$\Rightarrow 0.9528T_2 = 283$$

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

$= 297\ \text{K}$

$= 24^{\circ}\text{C}$

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

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

29. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of A is 4 × 1010 s^{-1} . Calculate k at 318 K and E_a.

29. 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:

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

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

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

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

For case 2:

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

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

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

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

But $t_1 = t_2$

Hence,

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

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

Now, applying the Arrhenius equation,

$$\log\frac{k_{308R}}{k_{20\,K}}=\frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_1\,T_2}\right)$$

$$\log(2.7289)=\frac{E_a}{2.303\times8.314}\left(\frac{308-298}{298\times308}\right)$$

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

Now, the calculation of k at 318 K

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

$$\log k=\log\left(4\times10^{10}\right)-\frac{7623}{2.303\times8.314\times318}$$

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

$$k=\text{Antilog}(-1.9822)=\text{antilog}\left(\bar{2}.0178\right)=1.042\times10^{-2}\ \text{s}^{-1}$$

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

30. From Arrhenius equation, we obtain

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

It is given that, $k_2=4k_1$

$T_1=293$ K

$T_2=313$ K

Therefore, $\log\frac{4k_1}{k_2}=\frac{E_a}{2.303\times8.314}\left(\frac{313-293}{293\times313}\right)$

$$\Rightarrow0.6021=\frac{20\times E_a}{2.303\times8.314\times293\times313}$$

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

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

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

Hence, the required energy of activation is 52.86kJmol^{-1}.