

CBSE Class 12 physics
Important Questions
Chapter 4
Chemical Kinetics

4 Marks Questions

1. The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate E_a .

Ans. It is given that $T_1 = 298$ K

Therefore, $T_2 = (298 + 10)$ K

= 308 K

We also know that the rate of the reaction doubles when temperature is increased by 10° .

Therefore, let us take the value of $k_1 = k$ and that of $k_2 = 2k$

Also, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Now, substituting these values in the equation:

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

We get:

$$\log \frac{2k}{k} = \frac{E_a}{2.303 \times 8.314} \left[\frac{10}{298 \times 308} \right]$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \left[\frac{10}{298 \times 308} \right]$$

$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2}{10}$$

$$= 52897.78 \text{ J mol}^{-1}$$

$$= 52.9 \text{ kJ mol}^{-1}$$

2. The activation energy for the reaction $2\text{HI}_{(\text{g})} \rightarrow \text{H}_2 + \text{I}_{2(\text{g})}$ is $209.5 \text{ kJ mol}^{-1}$ at 581K . Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Ans. In the given case:

$$E_a = 209.5 \text{ kJ mol}^{-1} = 209500 \text{ J mol}^{-1}$$

$$T = 581 \text{ K}$$

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

Now, the fraction of molecules of reactants having energy equal to or greater than activation energy is given as:

$$x = e^{-E_a/RT}$$

$$\ln x = -E_a / RT$$

$$\log x = -\frac{E_a}{2.303 RT}$$

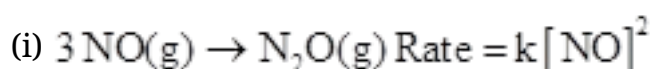
$$\log x = \frac{209500 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 581} = -18.8323$$

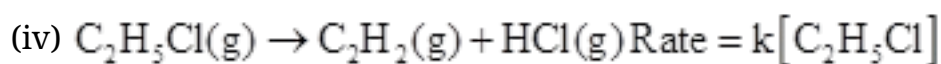
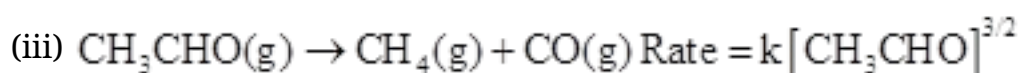
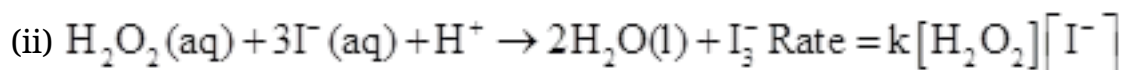
$$\text{Now, } x = \text{Anti log } (18.8323)$$

$$= \text{Anti log } \overline{19.1677}$$

$$1.471 \times 10^{-19}$$

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





Ans. (i) Given rate = $k[\text{NO}]^2$

Therefore, order of the reaction = 2

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

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

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

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

(ii) Given rate = $k[\text{H}_2\text{O}_2][\text{I}^-]$

Therefore, order of the reaction = 2

Dimension of $k = \frac{\text{Rate}}{[\text{H}_2\text{O}_2][\text{I}^-]}$

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

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

(iii) Given rate = $k[\text{CH}_3\text{CHO}]^{3/2}$

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

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

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

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

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

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

Therefore, order of the reaction = 1

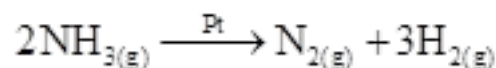
$$\text{Dimension of } k = \frac{\text{Rate}}{[\text{C}_2\text{H}_5\text{Cl}]}$$

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

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

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

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



$$\text{Therefore, Rate} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

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

$$-\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = k$$

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

Therefore, the rate of production of N_2 is

$$\frac{d[\text{N}_2]}{dt} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

And, the rate of production of H_2 is

$$\begin{aligned} \frac{d[\text{H}_2]}{dt} &= 3 \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \\ &= 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

5. The decomposition of dimethyl ether leads to the formation of CH_4 , H_2 and CO and the reaction rate is given by $\text{Rate} = k[\text{CH}_3\text{OCH}_3]^{3/2}$. 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., $\text{Rate} = k(P_{\text{CH}_3\text{OCH}_3})^{3/2}$. 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

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

$$\text{Rate} = k(P_{\text{CH}_3\text{OCH}_3})^{3/2}$$

$$k = \frac{\text{Rate}}{(P_{\text{CH}_3\text{OCH}_3})^{3/2}}$$

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

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

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

Ans. 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,

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

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

7. 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.

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

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

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

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

(ii) For a pseudo first order reaction,

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

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

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

$$\text{For } t = 60 \text{ s, } k_2 = \frac{2.303}{60} \log \frac{0.55}{0.17}$$

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

For $t = 90 \text{ s}$,

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

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

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

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

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

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

A / mol L ⁻¹	0.20	0.20	0.40
B / mol L ⁻¹	0.30	0.10	0.05
r_0 / mol L ⁻¹ s ⁻¹	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

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

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

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

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

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

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

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

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

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

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

$$y = 0$$

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

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

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

$$2.821 = 2^x$$

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

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

$$= 1.496$$

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

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

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



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.

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,

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

According to the question,

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

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

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

$$2.40 \times 10^{-2} = k[0.4]^x [0.1]^y \dots\dots\dots(iv)$$

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

$$\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k[0.4]^x [0.1]^y}{k[0.1]^x [0.1]^y}$$

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

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

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

$$x = 1$$

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

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \frac{k[0.3]^x [0.4]^y}{k[0.3]^x [0.2]^y}$$

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

$$4 = 2^y$$

$$2^2 = 2^y$$

$$y = 2$$

Therefore, the rate law is

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

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

From experiment I, we obtain

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

From experiment II, we obtain,

$$\begin{aligned} k &= \frac{7.2 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.3 \text{ mol L}^{-1})(0.2 \text{ mol L}^{-1})^2} \\ &= 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1} \end{aligned}$$

From experiment III, we obtain

$$\begin{aligned} k &= \frac{2.88 \times 10^{-1} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.3 \text{ mol L}^{-1})(0.4 \text{ mol L}^{-1})^2} \\ &= 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1} \end{aligned}$$

From experiment IV, we obtain

$$\begin{aligned} k &= \frac{2.40 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.4 \text{ mol L}^{-1})(0.1 \text{ mol L}^{-1})^2} \\ &= 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1} \end{aligned}$$

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

11. 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}

Ans. 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,

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

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

From experiment I, we obtain

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

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

From experiment II, we obtain

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

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

From experiment III, we obtain

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

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

From experiment IV, we obtain

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

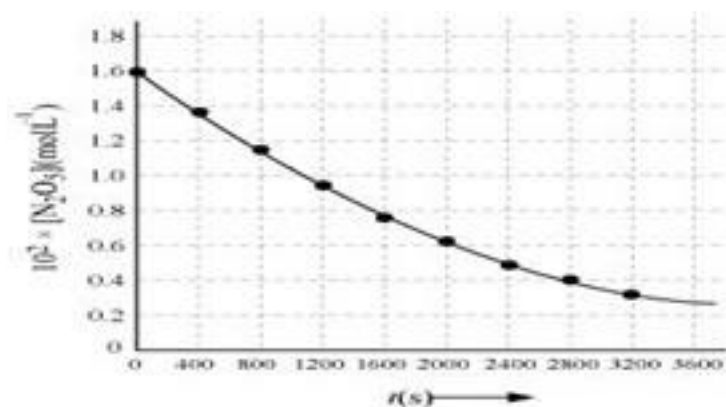
$$[A] = 0.1 \text{ mol L}^{-1}$$

12. 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
$10^2 \times [N_2O_5] \text{ mol L}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

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

Ans.



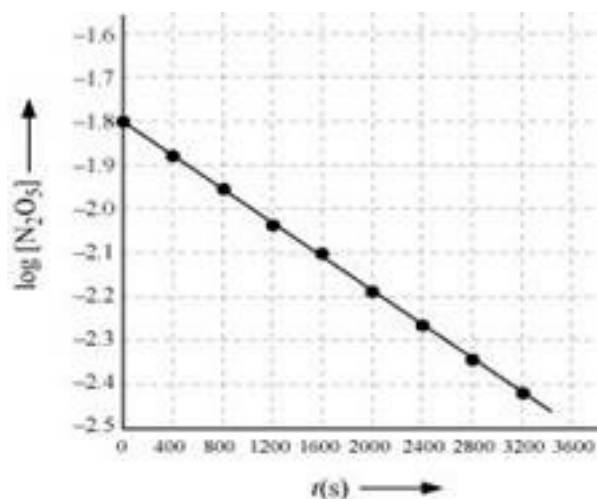
(ii) Time corresponding to the concentration, $\frac{1.630 \times 10^2}{2} \text{ mol L}^{-1} = 81.5 \text{ mol L}^{-1}$ is the half life. From the graph, the half life is obtained as 1450 s.

(iii)

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t(s)	$10^2 \times [\text{N}_2\text{O}_5] / \text{mol L}^{-1}$	$\log[\text{N}_2\text{O}_5]$
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, $\log[\text{N}_2\text{O}_5]$ v/s t , is a straight line. Therefore, the rate law of the reaction is $\text{Rate} = k[\text{N}_2\text{O}_5]$



(v) From the plot, $\log[\text{N}_2\text{O}_5]$ v/s t , we obtain

$$\begin{aligned} \text{Slope} &= \frac{-2.46 - (-1.79)}{3200 - 0} \\ &= \frac{-0.67}{3200} \end{aligned}$$

Again, slope of the line of the plot $\log[\text{N}_2\text{O}_5]$ v/s t is given by $-\frac{k}{2.303}$. Therefore, we obtain,

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

13. During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If $1\mu\text{g}$ of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

Ans. Here, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} \text{ y}^{-1}$

It is known that, $t = \frac{2.303}{k} \log \frac{[\text{R}]_0}{[\text{R}]}$

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

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

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

$$[\text{R}] = \text{anti log}(-0.1071)$$

$$= \text{anti log}(1.8929)$$

$$= 0.7814\mu\text{g}$$

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

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

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

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

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

$$= \text{anti log}(1.3575)$$

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

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

14. 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

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

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

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

Therefore, $t_1 = 2t_2$

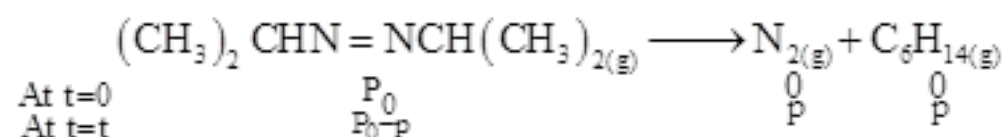
Hence, the time required for 99% completion of a first order reaction is twice the time required for the completion of 90% of the reaction.

15. 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.

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



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

$$P_t = P_0 + p$$

$$p = P_t - P_0$$

$$\text{Therefore, } P_0 - p = P_0 - (P_t - P_0)$$

$$= 2P_0 - P_t$$

For a first order reaction,

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

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

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

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

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

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

Hence, the average value of rate constant is

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

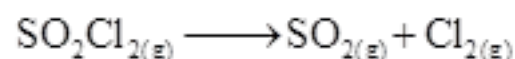
$$= 2.21 \times 10^{-3} \text{ s}^{-1}$$

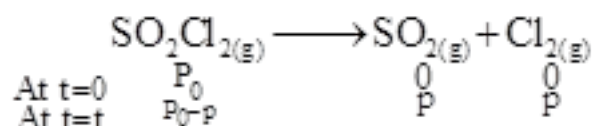
16. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume. $\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$

Experiment	Time / s^{-1}	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.





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

$$P_t = P_0 + p$$

$$p = P_t - P_0$$

Therefore,

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

$$= 2P_0 - P_t$$

For a first order reaction,

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

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

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

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

When $P_t = 0.65 \text{ atm}$,

$$P_0 + p = 0.65$$

$$p = 0.65 - P_0$$

$$= 0.65 - 0.5$$

$$= 0.15 \text{ atm}$$

Therefore, when the total pressure is 0.65 atm, pressure of SOCl_2 is

$$P_{\text{SOCl}_2} = P_0 - p$$

$$= 0.5 - 0.15$$

$$= 0.35 \text{ atm}$$

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

$$\text{Rate} = k(P_{\text{SOCl}_2})$$

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

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

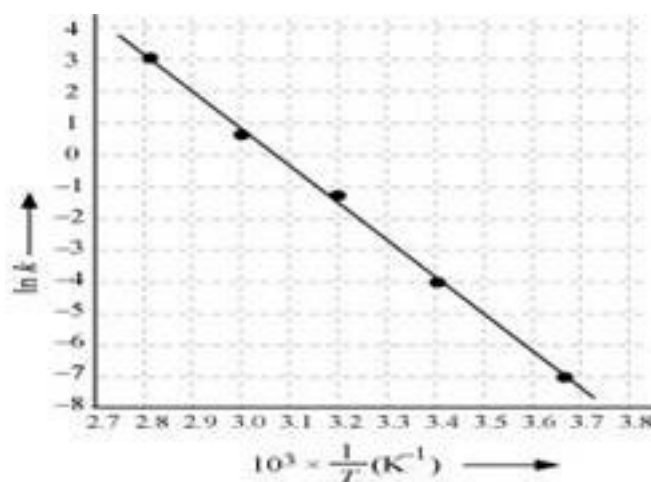
17. The rate constant for the decomposition of N_2O_5 at various temperatures is given below:

T / °C	0	20	40	60	80
$10^5 \times k / \text{s}^{-1}$	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 .

Ans. From the given data, we obtain

T / °C	0	20	40	60	80
T/K	273	293	313	333	353
$\frac{1}{T} / \text{K}^{-1}$	3.66×10^{-3}	3.41×10^{-3}	3.19×10^{-3}	3.0×10^{-3}	2.83×10^{-3}
$10^5 \times k / \text{s}^{-1}$	0.0787	1.70	25.7	178	2140
$\ln k$	-7.147	-4.075	-1.359	-0.577	3.063



Slope of the line,

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

According to Arrhenius equation,

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

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

$$= -(-12.301K) \times (8.134 JK^{-1} mol^{-1})$$

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

Again,

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

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

When $T = 273 K$

$$\ln k = -7.147$$

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

$$= 37.911$$

$$\text{Therefore, } A = 2.91 \times 10^6$$

$$\text{When, } T = 30 + 273\text{K} = 303\text{ K}$$

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

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

$$\ln k = -2.8$$

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

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

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

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

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

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

According to the Arrhenius equation,

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

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

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

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

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

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

$$= 12.5917$$

Therefore, $A = \text{antilog}(12.5917)$

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

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

Ans. For a first order reaction, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

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

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

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

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

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

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

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

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

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

$$= 0.158$$

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

20. The decomposition of hydrocarbon follows the equation

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

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

Arrhenius equation is given by,

$$k = A e^{-E_a / RT} \text{(ii)}$$

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

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

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

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

$$= 232792 \text{ J mol}^{-1}$$

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

21. The rate constant for the first order decomposition of H_2O_2 is given by the following equation: $\log k = 14.34 - 1.25 \times 10^4 \text{ K} / T$ Calculate E_a for this reaction and at what temperature will its half-period be 256 minutes?

Ans. Arrhenius equation is given by,

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

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

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

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

The given equation is

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

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

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

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

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

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

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

Also, when $k_{1/2} = 256 \text{ min}$ utes

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

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

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

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

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

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

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

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

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

$$= 668.95 \text{ K}$$

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

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

Ans. From Arrhenius equation, we obtain $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$

Also, $k_1 = 4.5 \times 10^3 \text{ s}^{-1}$

$$T_1 = 273 + 10 = 283 \text{ K}$$

$$k_2 = 1.5 \times 10^4 \text{ s}^{-1}$$

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

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

$$0.5229 = 3133.6279 \left(\frac{T_2 - 283}{283 T_2} \right)$$

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

$$0.0472 T_2 = T_2 - 283$$

$$0.9528 T_2 = 283$$

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

$$= 297 \text{ K}$$

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

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

23. 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 $4 \times 10^{10} \text{ s}^{-1}$. Calculate k at 318 K and E_a .

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 308 K,

$$t' = \frac{2.303}{k'} \log \frac{100}{75}$$

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

According to the question, $t = t'$

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

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

From Arrhenius equation, we obtain

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

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

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

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

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

To calculate k at 318 K,

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

Again, from Arrhenius equation, we obtain

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

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

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

$$= -1.9855$$

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

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

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

It is given that, $k_2 = 4k_1$

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

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

$$\text{Therefore, } \log \frac{4k_1}{k_1} = \frac{E_a}{2.303 \times 8.314} \left(\frac{313 - 293}{293 \times 313} \right)$$

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

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

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

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

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