

CH4 – CHEMICAL KINETICS

4.1. For the reaction $R \rightarrow P$, the concentration of reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

Ans.

$$\begin{aligned}\text{Average rate} &= \frac{-\Delta[R]}{\Delta t} = \frac{-(R_2 - R_1)}{t_2 - t_1} \\ &= \frac{(0.02 - 0.03)}{25} = \frac{-(-0.01)}{25} \\ &= 4 \times 10^{-4} \text{ M min}^{-1} \\ &= 6.66 \times 10^{-6} \text{ M s}^{-1}\end{aligned}$$

4.2. In a reaction, $2A \rightarrow \text{Products}$, the concentration of A decreases from 0.5 mol L⁻¹ to 0.4 mol L⁻¹ in 10 minutes. Calculate the rate during this interval?

Ans.

$$\begin{aligned}\text{Average Rate} &= \frac{-1 \Delta[A]}{2 \Delta t} = \frac{-1 [A]_2 - [A]_1}{2 t_2 - t_1} \\ &= \frac{-1 (0.4 - 0.5)}{2 \cdot 10} = \frac{-1 (-0.1)}{2 \cdot 10} \\ &= 5 \times 10^{-3} \text{ M min}^{-1}\end{aligned}$$

4.3. For a reaction, $A + B \rightarrow \text{Products}$, the rate law is given by : $r = k [A]^{1/2}[B]^2$. What is the order of reaction?

Ans. Rate law (r) = $k [A]^{1/2}[B]^2$

order of reaction = $1/2 + 2 = 2.5$ or 2.5

4.4. The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y ?

Ans. The reaction is : $X \rightarrow Y$

According to rate law,

$$\text{rate} = k[X]^2$$

If $[X]$ is increased to 3 times, then the new rate is

$$\text{rate}' = k[3X]^2$$

$$\text{rate}' = 9 k [X]^2 = 9 \text{ rate}$$

Thus, rate of reaction becomes 9 times and hence rate of formation of Y increases 9-times.

4.5. A first order reaction has a rate constant $1.15 \times 10^{-3} \text{ s}^{-1}$. How long will 5 g of this reactant take to reduce to 3 g?

Ans.

$$[A]_0 = 5 \text{ g}; [A] = 3 \text{ g}; k = 1.15 \times 10^{-3} \text{ s}^{-1}$$

For 1st order reaction,

$$\begin{aligned} t &= \frac{2.303}{k} \log \frac{[A]_0}{[A]} \\ &= \frac{2.303}{1.15 \times 10^{-3} \text{ s}^{-1}} \log \frac{5}{3} \\ &= 2.00 \times 10^3 (\log 1.667) \\ &= 443.8 \text{ s} \approx 444 \text{ s} \end{aligned}$$

4.6. Time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Ans. For 1st order reaction,

$$\begin{aligned} k &= \frac{0.693}{t_{1/2}} = \frac{0.693}{60} \\ &= 1.155 \times 10^{-2} \text{ min}^{-1} \\ &= 1.925 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

4.7. What will be the effect of temperature on rate constant?

Ans. In general, the rate constant for a reaction nearly becomes double with about 10° rise in temperature because of the fact that the effective collisions become almost double. The exact dependence of the reaction rate on temperature is given by Arrhenius equation; $k = A e^{-E_a/RT}$.

Where A is the Arrhenius factor or the frequency factor. It is also called pre exponential factor. It is a constant specific to a particular reaction. R is gas constant and E_a is activation energy measured in joules/mole (J mol^{-1}).

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

Ans.

Here, $T_1 = 298 \text{ K}$, $T_2 = 308 \text{ K}$, $k_1 = k$, $k_2 = 2k$
We know,

$$\begin{aligned}\log \frac{k_2}{k_1} &= \frac{E_a}{2.303k} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \\ \log \frac{2k}{k} &= \frac{E_a}{2.303 \times 8.314} \left(\frac{308 - 298}{308 \times 298} \right) \\ \log 2 &= \frac{E_a}{2.303 \times 8.314} \times \frac{10}{308 \times 298} \\ \Rightarrow E_a &= \frac{(\log 2)(2.303 \times 8.314)(308 \times 298)}{10} \\ &= 52897.7 \text{ J mol}^{-1} = 52.8 \text{ kJ mol}^{-1}\end{aligned}$$

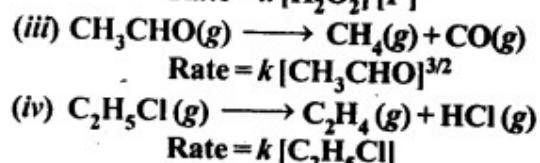
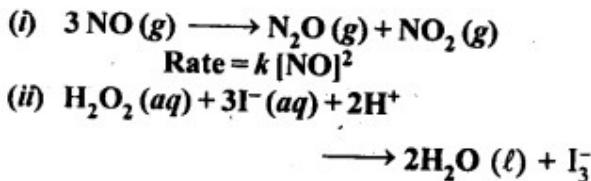
4.9. The activation energy for the reaction, $2 \text{ HI(g)} \rightarrow \text{H}_2 + \text{I}_2 \text{ (g)}$ is $209.5 \text{ kJ mol}^{-1}$ at 581 K . Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Ans. Fraction of molecules having energy equal to or greater than activation energy is given by:

$$\begin{aligned}x &= \frac{n}{N} = e^{-E_a/RT} \\ \therefore \ln x &= \frac{-E_a}{RT} \Rightarrow \log x = \frac{-E_a}{2.303RT} \\ \therefore \log x &= -\frac{209.5 \times 10^3}{2.303 \times 8.314 \times 581} = -18.8323 \\ \therefore x &= \text{antilog}(-18.8323) \\ &= 1.471 \times 10^{-19}\end{aligned}$$

NCERT EXERCISES

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



Sol:

(i) Order = 2, dimension of

$$k = \frac{\text{Rate}}{[\text{NO}]^2} = \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})^2} = \text{L mol}^{-1} \text{s}^{-1}$$

(ii) Order = 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) Order = $\frac{3}{2}$, dimension of

$$k = \frac{\text{Rate}}{[\text{CH}_3\text{CHO}]^{3/2}} = \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})(\text{mol L}^{-1})^{1/2}} = \text{L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$$

(iv) Order = 1, dimension of

$$k = \frac{\text{Rate}}{[\text{C}_2\text{H}_5\text{Cl}]} = \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})} = \text{s}^{-1}$$

4.2. For the reaction ; $2\text{A} + \text{B} \rightarrow \text{A}_2\text{B}$, the reaction rate = $k [\text{A}][\text{B}]^2$ with $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$. Calculate the initial rate of the reaction when $[\text{A}] = 0.1 \text{ mol L}^{-1}$; $[\text{B}] = 0.2 \text{ mol L}^{-1}$. Also calculate the reaction rate when $[\text{A}]$ is reduced to 0.06 mol L^{-1} .

Sol:

First case :

$$\begin{aligned} \text{Rate} &= k [\text{A}][\text{B}]^2 \\ &= (2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}) \times (0.1 \text{ mol L}^{-1}) \times (0.2 \text{ mol L}^{-1})^2 \\ &= 8 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1} = 8 \times 10^{-9} \text{ Ms}^{-1}. \end{aligned}$$

Second case :

The concentration of A after taking part in the reaction = 0.06 mol L^{-1} .

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

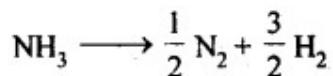
$$\text{Amount of B reacted} = \frac{1}{2} \times 0.04 \text{ mol L}^{-1} = 0.02 \text{ mol L}^{-1}.$$

The concentration of B after taking part in the reaction = $(0.2 - 0.02) = 0.18 \text{ mol L}^{-1}$

$$\begin{aligned} \text{Rate} &= k [\text{A}][\text{B}]^2 \\ &= (2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}) \times (0.06 \text{ mol L}^{-1}) \times (0.18 \text{ mol L}^{-1})^2 \\ &= 3.89 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1} = 3.89 \times 10^{-9} \text{ Ms}^{-1}. \end{aligned}$$

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

Sol:



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

For a zero order reaction, rate of reaction = k

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

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

 \therefore Rate of production of

$$\text{N}_2 = \frac{d[\text{N}_2]}{dt} = \frac{k}{2} = \frac{2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}}{2}$$

$$= 1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

 \therefore Rate of production of

$$\text{H}_2 = \frac{d[\text{H}_2]}{dt} = \frac{3k}{2} = \frac{3 \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}}{2}$$

$$= 3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

4.4. The decomposition of dimethyl ether leads to the formation of CH_4 , H_2 and CO and die 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?

Sol: As the concentration in the rate law equation is given in terms of pressure,

\therefore unit of rate = bar min^{-1}

$$\therefore \text{Unit of } k = \frac{\text{Rate}}{[P_{\text{CH}_3\text{OCH}_3}]^{3/2}} = \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}}$$

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

4.5. Mention the factors which affect the rate of a chemical reaction.

Sol: The rates of chemical reactions are influenced by a number of factors. These are :

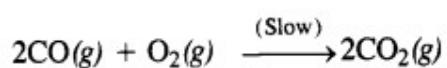
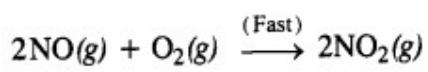
(i) **Concentration of reactants.** The rate of a chemical reaction is proportional to the concentration of the reacting species taking part in the reaction. It is

maximum to start with and slowly decreases since the concentration of the reacting species decreases accordingly. In case of reversible chemical reactions, the rate of chemical reaction can be studied separately for both the forward and backward reactions. In case of gaseous reactions, the increase in pressure increases the reaction rate.

(ii) Temperature. In general, the increase in temperature increases the reaction rate (there are a few exceptions as well). Actually, the energy of the reactant species increases with the increase in temperature and so will be number of collisions. It has been observed that in most of the cases, about 10° increase in temperature makes reaction rate double. Please note that the effect of temperature is quite independent of the concentration of the reactant species.

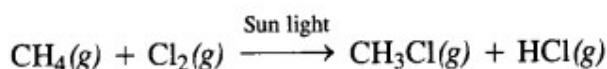
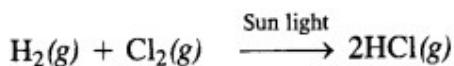
(iii) Presence of catalyst. In many chemical reactions, the reaction rate can be enhanced by certain foreign substances called catalysts. These are actually not consumed in the reactions and also do not undergo any change in chemical characteristics. However, their physical states such as colour, particle size etc., might change. Certain catalysts may have adverse effect as well as the reaction rate. They result in decreasing the reaction rate instead of increasing it. These are called negative catalysts or inhibitors.

(iv) Nature of reactants. The nature of the reacting species may also influence the reaction rate. For example, combustion of nitric oxide (NO) is faster as compared to that of carbon monoxide (CO)



(v) Surface area. Increase in surface area provides more opportunity for the reactants to come in contact or collide resulting in increased reaction rate. For example, in laboratory. We quite often prefer granulated zinc lump of the metal while preparing hydrogen gas on reacting with dilute hydrochloric acid or dilute sulphuric acid. Actually, granulated zinc has greater surface area available for the attack by the acid than lump of zinc. Therefore, it reacts at a faster rate.

(vi) Exposure to radiations. Many chemical reactions known as photochemical reactions are carried in the presence of sun light. For example,



In these reactions, the photons of light are the source of energy which helps in breaking the bonds in the reacting molecules so that may react and form molecules of products.

4.6. 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?

Sol:

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

(i) If $[\text{A}] = 2a$, rate = $k(2a)^2 = 4ka^2 = 4$ times.

(ii) If $[\text{A}] = a/2$, rate = $k\left(\frac{a}{2}\right)^2 = \frac{1}{4}ka^2 = \frac{1}{4}$ th.

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

Sol: The rate constant (k) for a reaction increases with rise in temperature and becomes nearly double with about every 10° rise in temperature. The effect is expressed with Arrhenius equation.

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

$$\log \frac{k_2}{k_1} = \frac{E_a}{2 \cdot 303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] = \frac{0}{2 \cdot 303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] = 0$$

$$\frac{k_2}{k_1} = \text{Antilog } 0 = 1 \text{ or } k_2 = k_1 = 1.6 \times 10^6 \text{ s}^{-1}$$

4.8. In 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.

Sol:

(i) Average rate during the interval 30 – 60 sec

$$= \frac{C_2 - C_1}{t_2 - t_1}$$

$$= \frac{0.31 - 0.17}{60 - 30} = \frac{0.14}{30} = 4.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$(ii) k' = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

where initial concentration of A, $[A_0] = 0.55 \text{ M}$

$$\text{when } t = 30 \text{ sec } k'_1 = \frac{2.303}{30} \log \frac{0.55}{0.31}$$

$$= 1.92 \times 10^{-2} \text{ s}^{-1}$$

$$\text{when } t = 60 \text{ sec } k'_2 = \frac{2.303}{60} \log \frac{0.55}{0.17}$$

$$= 1.96 \times 10^{-2} \text{ s}^{-1}$$

$$\text{when } t = 90 \text{ sec } k'_3 = \frac{2.303}{90} \log \frac{0.55}{0.085}$$

$$= 2.07 \times 10^{-2} \text{ s}^{-1}$$

∴ Average

$$k' = \frac{k'_1 + k'_2 + k'_3}{3} = \frac{(1.91 + 1.96 + 2.07) \times 10^{-2}}{3}$$

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

4.9. 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 is doubled?

Sol:

$$(i) \frac{dx}{dt} = k[A][B]^2$$

$$(ii) \text{Rate} = kab^2$$

$$\text{when } [B] \text{ becomes three times, rate} = ka(3b)^2$$

$$= 9 kab^2 = 9 \text{ times.}$$

$$(iii) \text{When both } [A] \text{ and } [B] \text{ are doubled, rate}$$

$$= k 2a(2b)^2 = 8 kab^2 = 8 \text{ times.}$$

4.10. 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
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?

Sol:

$$\text{Rate} = [A]^\alpha [B]^\beta$$

$$\begin{aligned} r_1 &= 5.07 \times 10^{-5} = (0.20)^\alpha (0.30)^\beta \quad \dots(i) \\ r_2 &= 5.07 \times 10^{-5} = (0.20)^\alpha (0.10)^\beta \quad \dots(ii) \\ r_3 &= 1.43 \times 10^{-4} = (0.40)^\alpha (0.05)^\beta \quad \dots(iii) \end{aligned}$$

$$\frac{r_1}{r_2} = \frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{(0.2)^\alpha}{(0.2)^\alpha} \frac{(0.30)^\beta}{(0.10)^\beta} = 1 = (3)^\beta$$

$$\therefore \beta = 0$$

$$\frac{r_3}{r_2} = \frac{1.43 \times 10^{-4}}{5.06 \times 10^{-5}} = \frac{(0.40)^\alpha}{(0.20)^\alpha} \frac{(0.05)^\beta}{(0.10)^\beta}$$

$$= 2.826 = 2^\alpha \left(\frac{1}{2}\right)^\beta$$

$$2.826 = 2^\alpha \quad (\text{as } \beta = 0)$$

Taking log on both the sides, we get

$$\log 2.826 = \alpha \log 2$$

$$\Rightarrow 0.4511 = \alpha \times 0.3010$$

$$\alpha = \frac{0.4511}{0.3010} = 1.498 \approx 1.5$$

∴ Order with respect to A = 1.5

and order with respect to B = 0

4.11. 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.

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Sol:

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

$$r_1 = k [0.1]^\alpha [0.1]^\beta = 6.0 \times 10^{-3}$$

$$r_2 = k [0.3]^\alpha [0.2]^\beta = 7.2 \times 10^{-2}$$

$$r_3 = k [0.3]^\alpha [0.4]^\beta = 2.88 \times 10^{-1}$$

$$r_4 = k [0.4]^\alpha [0.1]^\beta = 2.40 \times 10^{-2}$$

$$\frac{r_1}{r_4} = \frac{6.0 \times 10^{-3}}{2.40 \times 10^{-2}} = \frac{(0.1)^\alpha}{(0.4)^\alpha} = \left(\frac{1}{4}\right)^\alpha$$

$$\frac{1}{4} = \left(\frac{1}{4}\right)^\alpha$$

$$\therefore \alpha = 1$$

$$\frac{r_2}{r_3} = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{k (0.3)^\alpha (0.2)^\beta}{k (0.3)^\alpha (0.4)^\beta}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^\beta$$

$$\left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^\beta$$

$$\therefore \beta = 2$$

∴ Rate law expression, is, Rate = $k [A] [B]^2$

∴ Order with respect to A = 1 and

Order with respect to B = 2

Overall order of the reaction = $1 + 2 = 3$.

Calculation of rate constant k

Substituting values of experiment I, we get

$$6.0 \times 10^{-3} = k (0.1) (0.1)^2$$

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

$$\therefore k = 6 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

4.12. 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}

Sol:

Rate law expression :

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

$$R_1 = 2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$$

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

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

$$R_2 = 4.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$$

$$= (0.2 \text{ min}^{-1}) [A]$$

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

$$R_3 = \text{Rate} = k [A]$$

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

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

$$R_4 = 2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$$

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

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

4.13. 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}

Sol:

Half life for a first order reaction is, $t_{1/2} = \frac{0.693}{k}$

$$(i) t_{1/2} = \frac{0.693}{200 \text{ s}^{-1}} = 0.346 \times 10^{-2} \text{ s} = 3.46 \times 10^{-3} \text{ s}$$

$$(ii) t_{1/2} = \frac{0.693}{2 \text{ min}^{-1}} = 0.346 \text{ min} = 3.46 \times 10^{-1} \text{ min.}$$

$$(iii) t_{1/2} = \frac{0.693}{4 \text{ year}^{-1}} = 0.173 \text{ year} = 1.73 \times 10^{-1} \text{ year.}$$

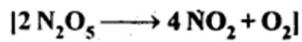
4.14. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

Sol: Radioactive decay follows first order kinetics.

$$\text{Decay constant } (k) = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730} \text{ year}^{-1}$$

$$\begin{aligned} t &= \frac{2.303}{k} \log \frac{[A_0]}{[A]} \\ &= \frac{2.303}{(0.693/5730 \text{ years}^{-1})} \log \frac{100}{80} \\ &= \frac{2.303 \times 5730}{0.693} \times 0.0969 = 1845 \text{ years.} \end{aligned}$$

4.15. The experimental data for decomposition of N_2O_5



in gas phase at 318 K are given below:

t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^{-2} \times [\text{N}_2\text{O}_5]/\text{mol L}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(i) Plot $[\text{N}_2\text{O}_5]$ against t . (ii) Find the half-life period for the reaction.

(iii) Draw a graph between $\log [\text{N}_2\text{O}_5]$ and t . (iv) What is the rate law?

(v) Calculate the rate constant.

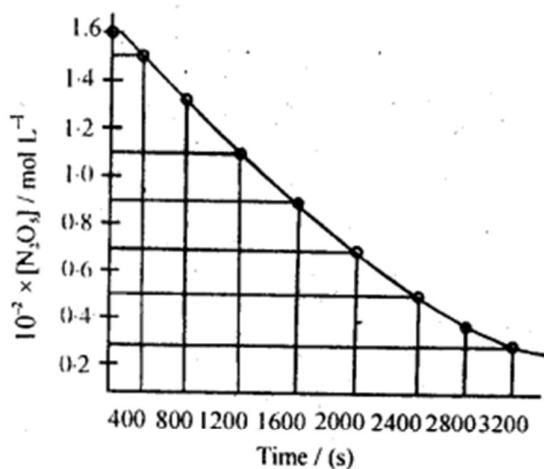
(vi) Calculate the half-life period from k and compare it with (ii).

Sol:

$t(\text{s})$	0	400	800	1200	1600	2000	2400	2800	3200
$10^{-2} \times [\text{N}_2\text{O}_5] (\text{mol L}^{-1})$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35
$\log [\text{N}_2\text{O}_5]$	-1.79	-1.87	-1.94	-2.03	-2.11	-2.19	-2.28	-2.37	-2.46

(i) Plot of $[\text{N}_2\text{O}_5]$ Vs time

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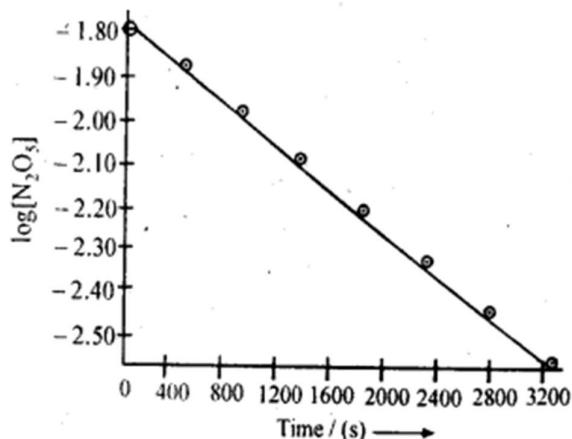


(ii) Initial concentration of N₂O₅ = 1.63×10^{-2} M
 Half of this concentration of

$$N_2O_5 = \frac{1.63 \times 10^{-2}}{2} = 0.815 \times 10^{-2} M$$

From the plot, time corresponding to this half concentration, $t_2 = 1440$ s.

(iii) Plot of log [N₂O₅] Vs time.



(iv) As the plot obtained for $\log [N_2O_5]$ Vs time is a straight line, hence it is a first order reaction.

∴ Rate law expression = rate = $k [N_2O_5]$

(v) Slope of the line

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

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

$$\therefore k = \frac{0.67 \times 2.303}{3200} = 4.82 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$(vi) t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.82 \times 10^{-4}} = 1438 \text{ sec.}$$

Question 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 $1/16$ th value ?

Solution:

$$\text{Given, } k = 60 \text{ s}^{-1}, [R_0] = [R_0], [R] = \frac{[R_0]}{16}, t = ?$$

$$\text{Using formula, } t = \frac{2.303}{k} \log \frac{[R_0]}{[R]} = \frac{2.303}{60} \log 16 \\ = 4.62 \times 10^{-2} \text{ s}$$

Alternatively,

In general, amount of the substance left after

$$n \text{ half lives, } R = \frac{[R_0]}{2^n} = \frac{[R_0]}{16}$$

$$\therefore n = 4 \text{ and } t = n \times t_{1/2}$$

$$t = n \times \frac{0.693}{k} = 4 \times \frac{0.693}{60} = 0.0462 \text{ s}$$

Question 17.

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

Solution:

As radioactive disintegration follows first order kinetics. Hence

$$\text{Decay constant of } {}^{90}\text{Sr, } (\lambda) = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} \\ = 2.466 \times 10^{-2} \text{ yr}^{-1}$$

To calculate the amount left after 10 years

Given, $[R_0] = 1 \mu\text{g}$, $t = 10 \text{ years}$,

$$k = 2.466 \times 10^{-2} \text{ yr}^{-1}, [R] = ?$$

$$\text{Using formula, } \lambda = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

$$\text{or } 2.466 \times 10^{-2} = \frac{2.303}{10} \log \frac{1}{[R]}$$

$$\frac{2.466 \times 10^{-2} \times 10}{2.303} = -\log [R]$$

$$\text{or, } \log [R] = -0.1071$$

$$\text{or, } [R] = \text{Antilog } (-0.1071) = 0.7814 \mu\text{g}$$

To calculate the amount left after 60 years,

$t = 60 \text{ years}$, $[R_0] = 1 \mu\text{g}$, $[R] = ?$

$$\text{or, } 2.466 \times 10^{-2} = \frac{2.303}{60} \log \frac{1}{[R]}$$

$$\text{or, } \frac{2.466 \times 10^{-2} \times 60}{2.303} = -\log [R]$$

$$\text{or, } \log [R] = -0.6425$$

$$\text{or, } [R] = \text{Antilog } (-0.6425) = 0.2278 \mu\text{g}$$

Question 18.

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Show that for a first order reaction the time required for 99% completion of a reaction is twice the time required to complete 90% of the reaction.

(C.B.S.E.Outside Delhi 2013)

Solution:

$$\text{For a first order reaction ; } t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$\text{Ist case : } a = 100\% \text{ } n = 99\% ; (a-x) = (100-99) = 1\%$$

$$\begin{aligned}
 t_{99\%} &= \frac{2 \cdot 303}{k} \log \frac{100}{1} = \frac{2 \cdot 303}{k} \log 10^2 \\
 &= \frac{2 \cdot 303 \times 2}{k} = \frac{4 \cdot 606}{k} \quad \dots(i)
 \end{aligned}$$

IIInd case : $a = 100\%$; $x = 90\%$ ($a - x$) = $(100 - 90) = 10\%$

$$t_{90\%} = \frac{2 \cdot 303}{k} \log \frac{100}{10} = \frac{2 \cdot 303}{k} \log 10 = \frac{2 \cdot 303}{k} \quad \dots(ii)$$

Dividing eqn. (ii) by eqn. (i),

$$\frac{t_{(99\%)}}{t_{(90\%)}} = \frac{4 \cdot 606}{k} \times \frac{k}{2 \cdot 303} = 2.$$

Question 19.

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

Solution:

30% decomposition means that $x = 30\%$

of $[R_0]$ or, $[R] = [R_0] - 0.3[R_0] = 0.7[R_0]$

For reaction of 1st order,

$$\begin{aligned}
 k &= \frac{2.303}{t} \log \frac{[R_0]}{[R]} = \frac{2.303}{40} \log \frac{[R_0]}{0.7[R_0]} \\
 &= \frac{2.303}{40} \log \frac{10}{7} \text{ min}^{-1} \\
 &= \frac{2.303}{40} \times 0.1549 \text{ min}^{-1} = 8.918 \times 10^{-3} \text{ min}^{-1}
 \end{aligned}$$

For a 1st order reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.918 \times 10^{-3} \text{ min}^{-1}} = 77.7 \text{ min}$$

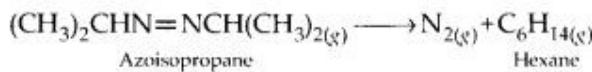
Question 20.

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

Solution:



Initial pressure P_0	0	0
Pressure $P_0 - p$	p	p
after time t		

Total pressure after time t (P_t)

$$= (P_0 - p) + p + p = P_0 + p \text{ or } p = P_t - P_0$$

$$[R]_0 \propto P_0 \text{ and } [R] \propto P_t - P_0$$

On substituting the value of p ,

$$[R] \propto P_0 - (P_t - P_0), \text{ i.e. } [R] \propto 2P_0 - P_t$$

As decomposition of azoisopropane is a first order reaction

$$\therefore k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

When $t = 360$ sec,

$$k = \frac{2.303}{360} \log \frac{35.0}{2 \times 35.0 - 54.0} = \frac{2.303}{360} \log \frac{35.0}{16}$$

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

When $t = 720$ sec,

$$k = \frac{2.303}{720} \log \frac{35.0}{2 \times 35.0 - 63} = \frac{2.303}{720} \log 5$$

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

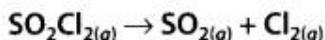
$$\therefore \text{Average value of } k$$

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

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

Question 21.

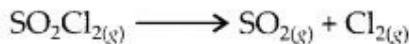
The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.



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.

Solution:



Let initial pressure P_0 0 0

Pressure at time t $P_0 - p$ p p

Let initial pressure $P_0 \propto R_0$

Pressure at time t , $P_t = P_0 - p + p + p = P_0 + p$

∴ Pressure of reactant at time t

$$= P_0 - p = 2P_0 - P_t \propto R$$

Using formula, $k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$

When $t = 100$ s,

$$\begin{aligned} k &= \frac{2.303}{100} \log \frac{0.5}{2 \times 0.5 - 0.6} = \frac{2.303}{100} \log(1.25) \\ &= \frac{2.303}{100} (0.0969) = 2.2316 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

When $P_t = 0.65$ atm,

∴ Pressure of SO_2Cl_2 at time t ($p_{\text{SO}_2\text{Cl}_2}$),

$$R = 2P_0 - p_t = 2 \times 0.50 - 0.65 \text{ atm} = 0.35 \text{ atm}$$

Rate at that time = $k \times p_{\text{SO}_2\text{Cl}_2}$

$$= (2.2316 \times 10^{-3}) \times (0.35)$$

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

Question 22.

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

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

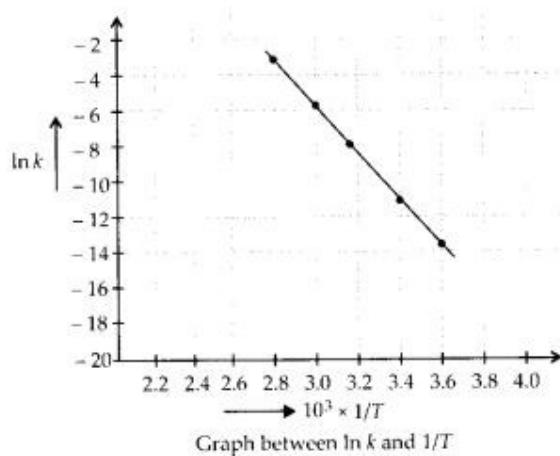
Draw a graph between $\ln k$ and $1/T$ and calculate the value of A and E_a . Predict the rate constant at 30°C and 50°C .

Solution:

The values of rate constants for the decomposition of N_2O_5 at various

temperatures are given below :

T(°C)	T(K)	1/T	k (s ⁻¹)	ln k (= 2.303 log k)
0	273	3.6 × 10 ⁻³	7.87 × 10 ⁻⁷	-14.06
20	293	3.4 × 10 ⁻³	1.70 × 10 ⁻⁵	-10.98
40	313	3.19 × 10 ⁻³	25.7 × 10 ⁻⁵	-8.266
60	333	3.00 × 10 ⁻³	178 × 10 ⁻⁵	-6.332
80	353	2.8 × 10 ⁻³	2140 × 10 ⁻⁵	-3.844



Slope of the line = $\tan \theta$

$$= \frac{y_2 - y_1}{x_2 - x_1} = \frac{-10.98 - (-14.08)}{3.4 - 3.6} \times 10^3$$

$$= -15.5 \times 10^3$$

$$E_a = -\text{slope} \times R = -(-15.5 \times 10^3 \times 8.314)$$

$$= 128.86 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

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

$$= -14.06 + \frac{128.86 \times 10^3 \text{ JK}^{-1} \text{ mol}^{-1}}{8.314 \times 273}$$

$$= -14.06 + 56.77 = 42.71$$

$$\text{or, } \log A = 18.53$$

$$\text{or, } A = \text{antilog } 18.53 = 0.3388 \times 10^{19}$$

$$\text{or, } A = 3.388 \times 10^{18}$$

Value of rate constant k at 303 K and 323 K can be obtained from graph.

First of all $\ln k$ is obtained corresponding to

$$\frac{1}{303 \text{ K}} \text{ and } \frac{1}{323 \text{ K}} \text{ and then } k \text{ is calculated.}$$

Question 23.

The rate constant for the decomposition of a hydrocarbon is $2.418 \times 10^{-5} \text{ s}^{-1}$ at

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546 K. If the energy of activation is $179.9 \text{ kJ mol}^{-1}$, what will be the value of pre-exponential factor?

Solution:

According to Arrhenius equation,

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

$$k = 2.418 \times 10^{-5} \text{ s}^{-1}; E_a = 179900 \text{ J mol}^{-1}; R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}; T = 546 \text{ K}$$

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

$$= \log (2.418 \times 10^{-5} \text{ s}^{-1}) + \frac{(179900 \text{ J mol}^{-1})}{2.303 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times 546 \text{ K}}$$

$$= -4.6184 + 17.21 = 12.5916$$

$$A = \text{Antilog } 12.5916 = 3.9 \times 10^{12} \text{ s}^{-1}.$$

Question 24.

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

Solution:

The units of k show that the reaction is of first order.

$$\text{Hence, } k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

$$\text{or, } 2.0 \times 10^{-2} = \frac{2.303}{100} \log \frac{1.0}{[R]}$$

$$\text{or, } \log [R] = -0.8684$$

$$\therefore [R] = \text{Antilog } (-0.8684) = 0.1354 \text{ mol L}^{-1}$$

Question 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?

Solution:

Sucrose decomposes according to first order rate law, hence

$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}, t_{1/2} = 3 \text{ hrs}, t = 8 \text{ hrs}, \frac{[R]}{[R_0]} = ?$$

$$t_{1/2} = 3.0 \text{ hrs}, \therefore k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3} = 0.231 \text{ hr}^{-1}$$

$$\text{Hence, } 0.231 = \frac{2.303}{8} \log \frac{[R_0]}{[R]}$$

$$\text{or, } \log \frac{[R_0]}{[R]} = 0.8024$$

$$\text{or, } \frac{[R_0]}{[R]} = \text{Antilog}(0.8024) = 6.345$$

$$\text{or, } \frac{[R]}{[R_0]} = \frac{1}{6.345} = 0.158$$

Question 26.

The decomposition of a hydrocarbon follows the equation

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

Solution:

$$\text{Arrhenius equation, } k = A e^{-E_a/RT}$$

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

Comparing both the equations, we get

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

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

Question 27.

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

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

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

Solution:

According to Arrhenius equation,

$$k = A e^{-E_a/RT}$$

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

$$\text{or, } \log k = \log A - \frac{E_a}{2.303RT} \quad \dots(\text{i})$$

Given equation is

$$\log k = 14.34 - 1.25 \times 10^4 \text{ K}^{-1} \quad \dots(\text{ii})$$

$$\text{Comparing (i) with (ii), } \frac{E_a}{2.303RT} = \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\begin{aligned} \text{or, } E_a &= 2.303R \times 1.25 \times 10^4 \text{ K} \\ &= 2.303 \times (8.314) \times 1.25 \times 10^4 \\ &= 239.34 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{When } t_{1/2} = 256 \text{ min, } k = \frac{0.693}{256 \times 60} = 4.51 \times 10^{-5} \text{ s}^{-1}$$

Substituting this value in the given equation,

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

$$\text{i.e., } (-5 + 0.6542) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\text{or, } \frac{1.25 \times 10^4 \text{ K}}{T} = 18.6858 \text{ or, } T = 669 \text{ K}$$

Question 28.

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

Solution:

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

$$T_1 = 10 + 273 \text{ K} = 283 \text{ K}; k_2 = 1.5 \times 10^4 \text{ s}^{-1}, T_2 = ?,$$

$$E_a = 60 \text{ kJ mol}^{-1}$$

Applying Arrhenius equation,

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

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60000}{2.303 \times 8.314} \left(\frac{T_2 - 283}{283 T_2} \right)$$

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

$$\text{or, } \frac{0.5228}{3133.63} = \frac{T_2 - 283}{283 T_2}$$

$$\text{or, } 0.0472 T_2 = T_2 - 283 \text{ or } 0.9528 T_2 = 283$$

$$\text{or, } T_2 = \frac{283}{0.9528} = 297 \text{ K} = 297 - 273 = 24^\circ\text{C}$$

Question 29.

The time required for 10% completion of the first order reaction at 298 K is equal

to that required for its 25% completion at 308 K. If the value of A is $4 \times 10^{10} \text{ s}^{-1}$, calculated at 318 K and E_a .

Solution:

$$t = \frac{2.303}{k_1} \log \frac{[R]_0}{\frac{90}{100}[R]_0},$$

$$t = \frac{2.303}{k_2} \log \frac{[R]_0}{\frac{75}{100}[R]_0}$$

$$t = \frac{2.303}{k_1} \log \frac{10}{9}, t = \frac{2.303}{k_2} \log \frac{4}{3}$$

$$\frac{2.303}{k_1} \log \frac{10}{9} = \frac{2.303}{k_2} \log \frac{4}{3}$$

$$\Rightarrow \frac{k_2}{k_1} = \frac{\log \frac{4}{3}}{\log \frac{10}{9}} = \frac{\log 1.333}{\log 1.111} = \frac{0.1249}{0.0457} = 2.733$$

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

$$\Rightarrow \log 2.733 = \frac{E_a}{2.303 \times 8.314} \left(\frac{308 - 298}{298 \times 308} \right)$$

$$E_a = \frac{2.303 \times 8.314 \times 308 \times 298}{10} \times 0.4367$$

$$= \frac{19.147 \times 308 \times 298}{10} \times 0.4367$$

$$= 76.75 \text{ kJ mol}^{-1}$$

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

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

$$= \log(4 \times 10^{10}) - \frac{76.75 \times 1000}{2.303 \times 8.314 \times 318}$$

$$= 10.6021 - \frac{76750}{6088.746}$$

$$= 10.6021 - 12.6051 = -2.003$$

$$k = \text{Antilog } (-2.003) = 9.93 \times 10^{-3}$$

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Question 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.

Solution:

Given $r_2 = 4r_1$, $T_1 = 293$, $T_2 = 313$ K, $E_a = ?$

$$\text{We know, } \frac{r_2}{r_1} = \frac{k_2}{k_1} = \frac{4}{1}$$

Using Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314} \left(\frac{1}{293} - \frac{1}{313} \right)$$

$$\text{or, } E_a = \log 4 \times \frac{2.303 \times 8.314 \times 293 \times 313}{20}$$

$$\text{or, } E_a = 52.864 \text{ kJ}$$

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