

NCERT Solutions for Class 12 Chemistry

Chapter 4 Chemical Kinetics

Class 12 Chemistry chapter 4 Chemical Kinetics is an important chapter and is often asked in the examination. Chemical kinetics helps to understand the chemical reactions. This chapter explains all about the rate of reaction and the factors determining the rate of reaction.

NCERT IN-TEXT QUESTIONS

Question 1.

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

Answer:

For a reaction, $R \rightarrow P$

$$\begin{aligned} \text{Average Rate} &= -\frac{\Delta[R]}{\Delta t} = -\frac{(0.02 - 0.03)\text{M}}{(25 \times 60\text{s})} \\ &= -\frac{-(0.01\text{M})}{(1500\text{s})} = 6.66 \times 10^{-6} \text{ Ms}^{-1}. \end{aligned}$$

Question 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 minute. Calculate the rate during this interval.

Answer:

For the reaction: $2A \rightarrow \text{Products}$

$$\begin{aligned} \text{Average rate} &= -\frac{1}{2} \frac{\Delta[A]}{dt} = -\frac{1}{2} \frac{(0.4 - 0.5)\text{mol}^{-1}}{(10 \text{ min})} \\ &= \frac{(0.1)\text{mol L}^{-1}}{(20 \text{ min})} = 0.005 \text{ mol L}^{-1} \text{ min}^{-1} \end{aligned}$$

Question 4.

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

Answer:

Order of reaction. = $1/2 + 2 = 2^{1/2}$ or 2.5

Question 4.

The conversion of the 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 ?

Answer:

For the reaction $X \rightarrow Y$

Reaction rate (r) = $k[X]^2$

If the concentration be increased to three times, then

Reaction rate (r') = $k [3X]^2$

$r'r = k[3X]^2 k[X]^2 = 9$

Eduranka.com/chemistry

Question 5.

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

Answer:

For the first order reaction,

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

$$a = 5 \text{ g} ; (a-x) = 3 \text{ g} ; k = 1.15 \times 10^{-3} \text{ s}^{-1}$$

$$\begin{aligned} \therefore t &= \frac{2.303}{(1.15 \times 10^{-3} \text{ s}^{-1})} \log \frac{(5\text{g})}{(3\text{g})} = \frac{2.303}{(1.15 \times 10^{-3} \text{ s}^{-1})} (\log 5 - \log 3) \\ &= \frac{2.303}{(1.15 \times 10^{-3} \text{ s}^{-1})} (0.6990 - 0.4771) \\ &= \frac{2.303}{(1.15 \times 10^{-3} \text{ s}^{-1})} \times 0.2219 = \mathbf{444 \text{ s}} \end{aligned}$$

Question 6.

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

Answer:

For the first order reaction ;

$$\text{Rate constant (k)} = 0.693/t_{1/2} = 0.693/(60\text{min})$$

$$= 0.693/(60 \times 60\text{s}) = \mathbf{1.925 \times 10^{-4} \text{ s}^{-1}}$$

Question 7.

What will be the effect of temperature on rate constant?

Answer:

With the rise in temperature by 10° , the rate constant of a reaction is nearly doubled. The dependence of rate constant on temperature is given the Arrhenius equation, $k = A e^{-E_a/RT}$ where A is the Arrhenius constant and E_a is activation energy of the reaction.

Question 8.

In general, it is observed that the rate of a chemical reaction doubles with every 10° rise in temperature. If the generalisation holds for a reaction in the temperature range 295 K to 305 K, what would be the value of activation energy for the reaction? (C.B.S.E. Delhi2005 Supp., Pb. Board2007)

Answer:

According to Arrhenius equation,

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

$$k_2/k_1 = 2 ; T_1 = 295 \text{ K} ; T_2 = 305 \text{ K} ; R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\therefore \log 2 = \frac{E_a}{2.303 \times (8.314 \text{ JK}^{-1} \text{ mol}^{-1})} \left[\frac{1}{295 \text{ K}} - \frac{1}{305 \text{ K}} \right]$$

$$\text{or } 0.3010 = \frac{E_a}{2.303 \times (8.314 \text{ J mol}^{-1})} \times \frac{(10)}{295 \times 305}$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 295 \times 305}{10} \text{ (J mol}^{-1}\text{)} = 51855 \text{ J mol}^{-1}$$

$$= 51.855 \text{ kJ mol}^{-1}$$

Question 9.

The activation energy for the reaction, $2\text{HI(g)} \rightarrow \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$ is $208.5 \text{ kJ mol}^{-1}$. Calculate fraction of molecules of reactants having energy equal to or greater than activation energy.

Answer:

The fraction of the molecules (x) having energy equal to or more than activation energy may be calculated as follows :

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

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

$$\log x = -\frac{(209.5 \times 10^3 \text{ J mol}^{-1})}{2.303 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times 581 \text{ K}} = -18.8323$$

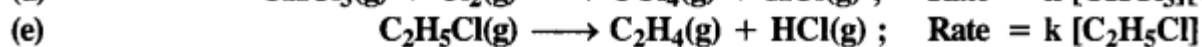
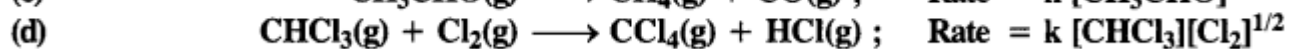
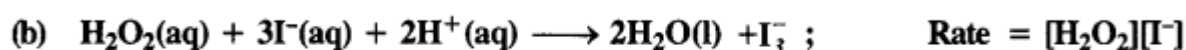
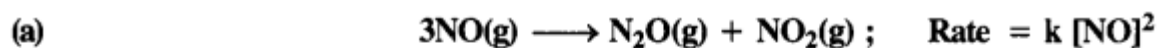
$$x = \text{Antilog}(-18.8324) = \text{Antilog } \overline{19}.1677$$

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

NCERT Exercise

Question 1.

The rate expression for the following reactions determine the order of reaction and the dimensions of the rate constant.



Answer:

(a) 2

(b) 2

- (c) 3/2
(d) 1

Question 2.

For the reaction, $2A + B \rightarrow A_2B$, the rate = $k [A][B]^2$ with $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$. Calculate the initial rate of the reaction when $[A] = 0.1 \text{ mol L}^{-1}$, $[B] = 0.2 \text{ mol L}^{-1}$. Calculate the rate of reaction after $[A]$ is reduced to 0.06 mol L^{-1} .

Answer:

Initial rate of reaction = $k [A] [B]^2$

$$= (2.0 \times 10^{-6} \text{ mol}^{-2} \text{ s}^{-1}) (0.1 \text{ mol L}^{-1}) (0.2 \text{ mol L}^{-1})^2 = 8 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$$

When $[A]$ is reduced from 0.10 mol L^{-1} to 0.06 mol L^{-1} , i.e., 0.04 mol L^{-1} of A has reacted, the concentration of B reacted, is $= 1/2 \times 0.04 \text{ mol L}^{-1} = 0.02 \text{ mol L}^{-1}$

Concentration of B, remained after reaction with A = $0.2 - 0.02 = 0.18 \text{ mol L}^{-1}$

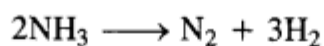
$$\text{Now, rate} = (2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}) (0.06 \text{ mol L}^{-1}) (0.18 \text{ mol L}^{-1})^2$$

$$= 3.89 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$$

Question 3.

The rate of decomposition of NH_3 on the platinum surface is zero order. What is the rate of production of N_2 and H_2 if $k = 2.5 \times 10^{-4} \text{ Ms}^{-1}$? (C.B.S.E. Delhi 2008)

Answer:



The reaction rate may be given as :

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

According to available data,

$$\frac{d[\text{NH}_3]}{dt} = k = 2.5 \times 10^{-4} \text{ Ms}^{-1}$$

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

$$\frac{d[\text{H}_2]}{dt} = 3 \times 2.5 \times 10^{-4} \text{ Ms}^{-1} = 7.5 \times 10^{-4} \text{ Ms}^{-1}$$

Question 4.

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

$$\text{rate} = k [\text{CH}_3\text{OCH}_3]^{3/2}$$

The rate of reaction is followed by increase in pressure in a close vessel and the rate can also be expressed in terms of partial pressure of dimethyl ether :

$$\text{rate} = k [\text{pCH}_3\text{OCH}_3]^{3/2}$$

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

Answer:

$$\text{Units of rate } (r) = \frac{\text{Pressure}}{\text{time}} = \frac{\text{bar}}{\text{min}} = \text{bar min}^{-1}$$

$$\begin{aligned} \text{Units of rate constant } (k) &= (\text{atm})^{1-n} \text{ min}^{-1} = (\text{bar})^{(1-n)} \text{ min}^{-1} \\ &= (\text{bar})^{(1-3/2)} \text{ min}^{-1} = \text{bar}^{-1/2} \text{ min}^{-1} \end{aligned}$$

Question 5.

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

Answer:

- Concentration of reactants
- Temperature
- Nature of reactants and products
- Exposure to light (Radiation)
- Presence of catalysts.

Question 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 1/2? (C.B.S.E. Outside Delhi 2008, 2009)

Answer:

Let the reaction be; $A \rightarrow \text{Products}$

Reaction rate $(r) = k [A]^2$ (for second order reaction)

(i) When concentration is doubled, the rate of reaction may be expressed as :

Reaction rate $(r') = k [2A]^2$

$$\therefore \frac{r'}{r} = \frac{k[2A]^2}{k[A]^2} = 4 \text{ or } r' = 4r$$

reaction rate becomes four times.

(ii) When concentration is reduced to half, the rate of reaction may be expressed as :

Reaction rate $(r'') = k [1/2 A]^2$

$$\frac{r''}{r} = \frac{k[A/2]^2}{k[A]^2} = 1/4 \text{ or } r'' = 1/4 r$$

reaction rate will be reduced to 1/4.

Question 7.

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

Answer:

Increasing the temperature on decreasing the activation energy will result in an increase in the rate of reaction and an exponential increase in the rate constant. On increasing the temperature the fraction of molecules which collide with energy greater than E_a increases and hence the rate constant (exponentially)

$K = A^{-e_a/RT}$, quantitative representation of temperature effect on rate constant.

Question 8.

In pseudo-first-order hydrolysis of ester in water, the following results were obtained.

Time (s)	0	30	60	90
Ester (M)	0.55	0.31	0.17	0.085

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

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

Answer:

$$\text{Average rate of reaction} = \frac{\text{Change in molar concentration}}{\text{Change in time interval}}$$

$$= \frac{(0.17 - 0.31)}{(60 - 30)} = \frac{(-0.14 \text{ M})}{(30 \text{ s})} = -4.67 \times 10^{-3} \text{ Ms}^{-1}.$$

The rate constant $k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$; $[A_0] = 0.55 \text{ M}$

For $t = 30 \text{ s}$; $k_1 = \frac{2.303}{(30 \text{ s})} \log \frac{[0.55]}{[0.31]} = \frac{2.303}{(30 \text{ s})} \times 0.249 = 1.91 \times 10^{-2} \text{ s}^{-1}.$

For $t = 60 \text{ s}$; $k_2 = \frac{2.303}{(60 \text{ s})} \log \frac{[0.55]}{[0.17]} = \frac{2.303}{(60 \text{ s})} \times 0.5099 = 1.96 \times 10^{-2} \text{ s}^{-1}.$

For $t = 90 \text{ s}$; $k_3 = \frac{2.303}{(90 \text{ s})} \log \frac{[0.55]}{[0.085]} = \frac{2.303}{(90 \text{ s})} \times 0.811 = 2.07 \times 10^{-2} \text{ s}^{-1}.$

Average rate constant $(k) = \frac{k_1 + k_2 + k_3}{3} = \frac{(1.91 + 1.96 + 2.07)}{3} \times 10^{-2} \text{ s}^{-1}$
 $= 1.98 \times 10^{-2} \text{ s}^{-1}.$

Question 9.

A reaction is first order in A and second order in B

(i) Write differential rate equation.

(ii) How is rate affected when the concentration of B is tripled?

(iii) How is rate affected when the concentration of both A and B are doubled? (C.B.S.E. Outside Delhi 2010, 2013)

Answer:

(i) Differential rate equation for the reaction is : rate (r) = $k [A]^1 [B]^2$

(ii) Differential rate equation for the reaction is : rate (r') = $k [A]^1 [3B]^2$

$$r'/r = \frac{k[A]^1[3B]^2}{k[A]^1[B]^2} = 9 \text{ or } r' = 9r$$

The reaction rate will increase to 9 times.

(iii) Differential rate equation for the reaction is :

$$\text{rate } (r'') = k [2A]^1 [2B]^2 ; r''/r = \frac{k[2A]^1[2B]^2}{k[A]^1[B]^2} = 8 \text{ or } r'' = 8r$$

The reaction rate will increase to 8 times.

Question 10.

In a reaction between A and B, the initial rate of reaction was measured for different initial concentration of A and B as given ahead :

Expt. No.	[A] mol L ⁻¹	B mol L ⁻¹	rate (r ₀) mol L ⁻¹ s ⁻¹
1	0.20	0.30	5.07 × 10 ⁻⁵
2	0.20	0.10	5.07 × 10 ⁻⁵
3	0.40	0.05	7.56 × 10 ⁻⁵

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

Answer:

The rate law equation may be expressed as :

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

Comparing experiments 1 and 2,

$$(\text{Rate})_1 = k [0.2]^p [0.3]^q = 5.07 \times 10^{-5} \quad \dots(i)$$

$$(\text{Rate})_2 = k [0.2]^p [0.1]^q = 5.07 \times 10^{-5} \quad \dots(ii)$$

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

$$\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{k[0.2]^p [0.3]^q}{k[0.2]^p [0.1]^q} = \frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}}$$

$$[3]^q = [1]^0 \text{ or } q = 0$$

By comparing experiments 2 and 3,

$$(\text{Rate})_2 = k [0.2]^p [0.1]^q = 5.07 \times 10^{-5} \quad \dots(iii)$$

$$(\text{Rate})_3 = k [0.4]^p [0.05]^q = 7.56 \times 10^{-5} \quad \dots(iv)$$

Dividing eqn. (iv) by eqn. (iii),

$$\frac{(\text{Rate})_3}{(\text{Rate})_2} = \frac{k[0.4]^p [0.05]^q}{k[0.2]^p [0.1]^q} = \frac{7.56 \times 10^{-5}}{5.07 \times 10^{-5}}$$

$$[2]^p = [1.49] = [2]^{3/2} \text{ or } p = 3/2$$

Order with respect to A = 3/2

Order with respect to B = 0

Question 11.

The following data were obtained at 300 K for the reaction 2A + B → C + D:

Expt. No	(A) mol L ⁻¹	(B) mol L ⁻¹	Rate of formation of D mol L ⁻¹ min ⁻¹
1	0.1	0.1	6.0 × 10 ⁻³
2	0.3	0.2	7.2 × 10 ⁻²
3	0.3	0.4	2.88 × 10 ⁻¹
4	0.4	0.1	2.4 × 10 ⁻²

Calculate the rate of formation of D when [A] = 0.5 mol L⁻¹ and [B] = 0.2 mol L⁻¹.

Answer:

The rate law may be expressed as :

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

Comparing experiments 2 and 3,

$$(\text{Rate})_2 = k [0.3]^p [0.2]^q = 7.2 \times 10^{-2} \quad \dots (i)$$

$$(\text{Rate})_3 = k [0.3]^p [0.4]^q = 2.88 \times 10^{-1} \quad \dots (ii)$$

Dividing equation (ii) by (i),

$$\frac{(\text{Rate})_3}{(\text{Rate})_2} = \frac{k[0.3]^p [0.4]^q}{k[0.3]^p [0.2]^q} = \frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \frac{28.8 \times 10^{-2}}{7.2 \times 10^{-2}}$$

$$[2]^q = 4 \text{ or } [2]^q = [2]^2 \text{ or } q = 2$$

Comparing experiments 1 and 4,

$$(\text{Rate})_1 = k [0.1]^p [0.1]^q = 6.0 \times 10^{-3} \quad \dots (iii)$$

$$(\text{Rate})_4 = k [0.4]^p [0.1]^q = 2.4 \times 10^{-2} \quad \dots (iv)$$

Dividing equation (iv) by (iii),

$$\frac{(\text{Rate})_4}{(\text{Rate})_1} = \frac{k[0.4]^p [0.1]^q}{k[0.1]^p [0.1]^q} = \frac{2.4 \times 10^{-2}}{6.0 \times 10^{-3}}$$

$$[4]^p = [4]^1 \text{ or } p = 1$$

By substituting the value of p and q in the equation (iii), the value of the rate constant (k) can be calculated as :

$$k = [0.1]^1 [0.1]^2 = 6.0 \times 10^{-3}; k = \frac{6.0 \times 10^{-3}}{0.1 \times 0.01} = 6.0$$

\therefore Rate of formation D when $[A] = 0.5 \text{ mol L}^{-1}$ and $[B] = 0.2 \text{ mol L}^{-1}$ can be calculated as :

$$\begin{aligned} \text{Rate} &= k [A]^p [B]^q = 6.0 \times [0.5]^1 [0.2]^2 \\ &= 6.0 \times 0.5 \times 0.04 = 1.2 \times 10^{-1} \text{ mol L}^{-1} \text{ min}^{-1} \end{aligned}$$

Question 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:

Expt. No.	[A]/M	[B]/M	Initial Rate/M min ⁻¹
I	0.1	0.1	2.0×10^{-2}
II	-	0.2	4.0×10^{-2}
III	0.4	0.4	-
IV	-	0.2	2.0×10^{-2}

Answer:

The rate equation for the reaction is: $r = k [A]^1 [B]^0$

(i) Comparing experiments I and II,

$$2.0 \times 10^{-2} = k [0.1]^1 [0.1]^0 \quad \dots (i)$$

$$4.0 \times 10^{-2} = k [x]^1 [0.2]^0 \quad \dots (ii)$$

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

$$\frac{4.0 \times 10^{-2}}{2.0 \times 10^{-2}} = \frac{k[x]^1 [0.2]^0}{k[0.1]^1 [0.1]^0}; 2 = \frac{x}{0.1} \text{ or } x = 2 \times 0.1 = 0.2 \text{ M}$$

Thus, the concentration of A in experiment II is 0.2 M

(ii) Comparing experiments II and in.

When the concentration of A is made double, the reaction rate will also become twice.

\therefore Rate of reaction in experiment III is 8.0×10^{-2}

(iii) Comparing experiments I and IV.

Since the reaction rates are the same in both the experiments, the molar concentration of A in experiment IV must be the same as in experiment I i. e., it must be 0.1 M.

Question 13.

Calculate the half-life of the first-order reaction from their rate constants given as

- (a) 200 s^{-1}
- (b) 2 min^{-1}
- (c) 4 year^{-1} .

Answer:

$$(a) \text{ Half life period } (t_{1/2}) = \frac{0.693}{k} = \frac{0.693}{(200 \text{ s}^{-1})} = 3.46 \times 10^{-3} \text{ s}$$

$$(b) \text{ Half life period } (t_{1/2}) = \frac{0.693}{k} = \frac{0.693}{(2 \text{ min}^{-1})} = 0.346 \text{ min} = 3.46 \times 10^{-1} \text{ min}$$

$$(c) \text{ Half life period } (t_{1/2}) = \frac{0.693}{k} = \frac{0.693}{(4 \text{ year}^{-1})} = 1.73 \times 10^{-1} \text{ year}$$

Question 14.

The half-life for the radioactive decay of ^{14}C is 5730 Y. An archaeological artifact contained wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample. (C.B.S.E. Delhi 2008)

Answer:

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

Radioactive decays follow first order kinetics

$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A]} ; k = \frac{0.693}{5730} \text{ yr}^{-1} \quad [A_0] = 100\%; [A] = 80\%$$

$$\begin{aligned} \therefore t &= \left(\frac{2.303 \times 5730}{0.693} \text{ yr} \right) \times \log \frac{100}{80} \\ &= \left(\frac{2.303 \times 5730 \times 0.0969}{0.693} \right) \text{ yr} = 1845 \text{ years.} \end{aligned}$$

Question 15.

The experimental data for decomposition of N_2O_5 [$2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$] in gas phase at 318 K are given below :

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

- (a) Plot $[\text{N}_2\text{O}_5]$ against t
- (b) Find the half-life period for the reaction
- (c) Draw a graph between $\log [\text{N}_2\text{O}_5]$ and t
- (d) What is rate law?
- (e) Calculate the rate constant
- (f) Calculate the half-life period from k and compare it with (b).

Answer:

The available data is:

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

(a) The plot of $[\text{N}_2\text{O}_5]$ versus time is as follows :

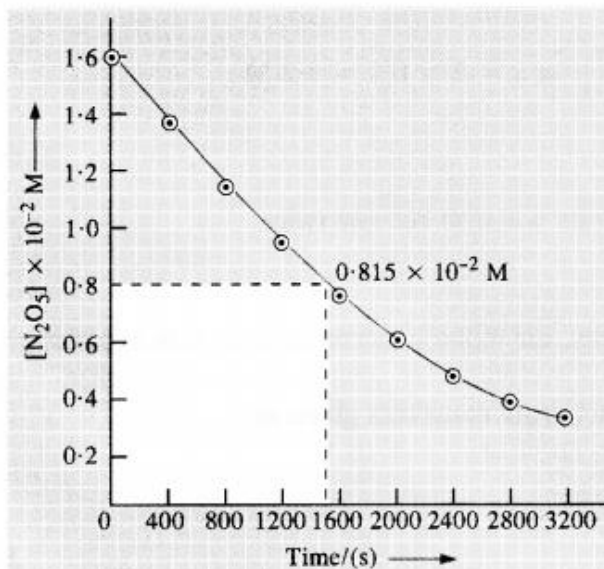


Figure. Plot of $[\text{N}_2\text{O}_5]$ Vs time (a)

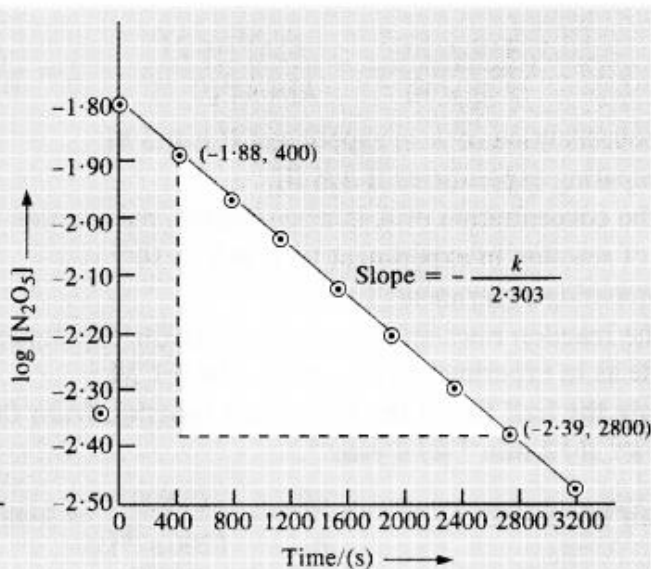


Figure. Plot of log $[\text{N}_2\text{O}_5]$ Vs time (b)

(b) Initial conc. of $\text{N}_2\text{O}_5 = 1.63 \times 10^{-2}\text{M}$. Half of initial conc. = $1/2 \times (1.63 \times 10^{-2}\text{M}) = 0.815 \times 10^{-2}\text{M}$
 Time corresponding to half of initial concentration ($t/2$) from the plot (a) = 1400 (s) approximately

(c) The graph of log $[\text{N}_2\text{O}_5]$ Vs. time has been plotted.

(d) Since the graph between log $[\text{N}_2\text{O}_5]$ and time is a straight line the reaction is of the first order
 The rate equation : rate (r) = $k[\text{N}_2\text{O}_5]$

$$(e) \quad \text{Slope of the line} = \frac{(-2.39) - (-1.88)}{(2800 - 400)} = -\frac{0.51}{2400}$$

$$\text{But slope} = -\frac{k}{2.303} ; \therefore k = -(\text{slope}) \times 2.303 = -\left(\frac{0.51}{2400} \times 2.303\right)$$

$$= 4.89 \times 10^{-4} \text{ s}^{-1}$$

$$(f) \quad \text{Half life period } (t_{1/2}) = \frac{0.693}{k} = \frac{0.693}{(4.89 \times 10^{-4} \text{ s}^{-1})} = 1417 \text{ s}$$

The half life period ($t_{1/2}$) as calculated from the slope is nearly the same as already predicted.

Question 16.

The rate constant for the 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? (C.B.S.E. Delhi 2013)

Answer:

For the first-order reaction

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

Let the initial concentration = a ; Final concentration $(a-x) = a/16$; $k = 60 \text{ s}^{-1}$

$$\begin{aligned} \therefore t &= \frac{2.303}{(60 \text{ s}^{-1})} \log \frac{a}{a/16} = \frac{2.303}{(60 \text{ s}^{-1})} \log 16 \\ &= \frac{2.303 \times 1.2041}{(60 \text{ s}^{-1})} = 0.0462 \text{ s} = \mathbf{4.62 \times 10^{-2} \text{ s}} \end{aligned}$$

Question 17.

During a nuclear explosion, one of the products is ^{90}Sr with a half period of 28.1 Y. 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?

Answer:

$$t_{1/2} = 28.1 \text{ Y} ; k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} \text{ Y}^{-1}$$

All radioactive explosions follow first order kinetics,

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

Ist case. $a = 1 \mu\text{g}$; $t = 10 \text{ Y}$; $k = \frac{0.693}{28.1} \text{ Y}^{-1}$

$$\begin{aligned} \therefore 10 \text{ Y} &= \frac{2.303}{(0.693 / 28.1 \text{ Y}^{-1})} \log \frac{a}{(a-x)} \\ \log \frac{a}{(a-x)} &= \frac{(10 \text{ Y}) \times (0.693 / 28.1 \text{ Y}^{-1})}{2.303} = 0.107 \end{aligned}$$

$$\frac{a}{(a-x)} = \text{Antilog } 0.107 = 1.279$$

$$(a-x) = \frac{a}{1.279} = \frac{(1 \mu\text{g})}{1.279} = \mathbf{0.7819 \mu\text{g}}$$

IInd case. $a = 1 \mu\text{g}$; $t = 60 \text{ Y}$; $k = 0.693/28.1 \text{ Y}^{-1}$

$$60 \text{ Y} = \frac{2.303}{(0.693 / 28.1 \text{ Y}^{-1})} \log \frac{a}{(a-x)}$$

$$\log \frac{a}{(a-x)} = \frac{(60 \text{ Y}) \times (0.693 / 28.1 \text{ Y}^{-1})}{2.303} = 0.642$$

$$\frac{a}{(a-x)} = \text{Antilog } 0.642 = 4.385$$

$$(a-x) = \frac{a}{4.385} = \frac{(1 \mu\text{g})}{4.385} = \mathbf{0.2280 \mu\text{g}}$$

Question 18.

For a first-order reaction, show that the time required for 99% completion is twice the time required for the completion of 90% of the reaction.

Answer:

99% completion means that $x = 99\%$ of $[R_0]$

$$\text{or, } [R] = [R_0] - 0.99[R_0] = 0.01[R_0]$$

$$\text{For first order reaction, } t = \frac{2.303}{k} \log \frac{[R_0]}{[R]}$$

$$\therefore t_{99\%} = \frac{2.303}{k} \log \frac{[R_0]}{0.01[R_0]}$$

$$= \frac{2.303}{k} \log 10^2 = 2 \times \frac{2.303}{k}$$

90% completion means that $[R] = [R_0] - 0.90[R_0]$
 $= 0.1[R_0]$

$$\therefore t_{90\%} = \frac{2.303}{k} \log \frac{[R_0]}{0.1[R_0]} = \frac{2.303}{k} \log 10 = \frac{2.303}{k}$$

$$\therefore \frac{t_{99\%}}{t_{90\%}} = \left(\frac{2 \times 2.303}{k} \right) \div \left(\frac{2.303}{k} \right) = 2$$

$$\text{or, } t_{99\%} = 2 \times t_{90\%}$$

Question 19.

A first-order reaction takes 40 minutes for 30% decomposition. Calculate its half-life period. (C. B. S. E. Outside Delhi 2013)

Answer:

$$\text{For the first order reaction, } k = \frac{2.303}{t} \times \frac{a}{a-x}$$

$$a = 100\% ; x = 30\% ; (a-x) = (100 - 30) = 70\% ; t = 40 \text{ min.}$$

$$k = \frac{2.303}{(40 \text{ min})} \log \frac{100}{70} = \frac{2.303}{(40 \text{ min})} \times 0.1549 = 0.00892 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{(0.00892 \text{ min}^{-1})} = 77.7 \text{ min}$$

Question 20.

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

t (sec)	0	360	720
pressure (atm)	35.0	54.0	63.0

Calculate the rate constant.

Answer:

The decomposition reaction is of gaseous nature and the expression of the rate equation for the

reaction is :

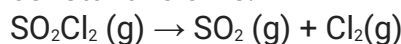
$$k = \frac{2.303}{t} \log \left(\frac{p_i}{2p_i - p_t} \right)$$

$$\begin{aligned} \text{Rate constant after 360 s i.e., } k_{360} &= \frac{2.303}{(360 \text{ s})} \log \frac{(35 \text{ atm})}{(70 - 54) \text{ atm}} = \frac{2.303}{(360 \text{ s})} \log \frac{35}{16} = \frac{2.303}{(360 \text{ s})} (\log 2.1875) \\ &= \frac{(2.303 \times 0.33995)}{(360 \text{ s})} = 2.17 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Rate constant after 720 s i.e. } k_{720} &= \frac{(2.303)}{(720 \text{ s})} \log \frac{(35 \text{ atm})}{(70 - 63) \text{ atm}} \\ &= \frac{(2.303)}{(720 \text{ s})} \log 5 = \frac{(2.303 \times 6990)}{(720 \text{ s})} \log 5 = 2.24 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

Question 21.

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

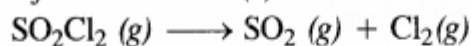


t(s)	0	100
Total pressure (atm)	0.5	0.6

Calculate the rate of the reaction when the total pressure is 0.65 atm. (C.B.S.E. Sample Paper 2011)

Answer:

Step I. Calculation of rate constant (*k*)



At time (*t*) = 0 0.5 atm 0 0

At time (*t*) = 100 (0.5 - *x*) atm *x* atm *x* atm

Total pressure after time *t* (*p_t*) or 100 s = 0.5 - *x* + *x* + *x* = [0.5 + *x*] atm.

$$x = (p_t - 0.5) \text{ atm}; P_{\text{SO}_2\text{Cl}_2} = (0.5 - x) = 0.5 - (p_t - 0.5)$$

$$P_{\text{SO}_2\text{Cl}_2} = 0.5 - (0.6 - 0.5) = 1.0 - 0.6 = 0.4 \text{ atm}$$

For the first order reaction :

$$\begin{aligned} k &= \frac{2.303}{100} \log \frac{p_i}{p_A} = \frac{2.303}{(100 \text{ s})} \log \frac{(0.5 \text{ atm})}{(0.4 \text{ atm})} \\ &= \frac{2.303}{(100 \text{ s})} \log 1.25 = \frac{2.303}{(100 \text{ s})} \times 0.0969 = 2.23 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

Step II. Calculation of reaction rate when total pressure is 0.65 atm

$$\begin{aligned} P_{\text{SO}_2\text{Cl}_2} &= 0.5 - (0.65 - 0.50) = (1 - 0.65) \\ &= 0.35 \text{ atm}; k = 2.23 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Rate (r)} &= k \times P_{\text{SO}_2\text{Cl}_2} = (2.23 \times 10^{-3} \text{ s}^{-1}) \times (0.35 \text{ atm}) \\ &= 7.8 \times 10^{-4} \text{ atm s}^{-1}. \end{aligned}$$

Question 22.

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

T/°C	0	20	40	60	80
$10^5/k/s^{-1}$	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 $50^\circ C$.

Answer:

To draw the plot of $\log K$ versus $1/T$, we can re-write the given data as follows :

T (K)	273	293	313	333	353
1/T	0.003663	0.003413	0.003413	0.003003	0.002833
$\log k$	-6.1040	-4.7696	-3.5900	-2.7496	-1.6996

Draw the graph as shown on the next page, from the graph, we find that

$$\text{Slope} = \frac{-2.4}{0.00074} = \frac{-E_a}{2.303R}$$

$$\therefore \text{Activation energy, } (E_a) = \frac{2.4 \times 2.303 \times R}{0.00047} = \frac{2.4 \times 2.303 \times 8.314 \text{ J mol}^{-1}}{0.00047}$$

$$= 17,689 \text{ J mol}^{-1} = 17.689 \text{ kJ mol}^{-1}$$

As we know $\log k = \log A - \frac{E_a}{2.303RT}$
 (Compare it with $y = mx + c$ which is equation of line in intercept form)

or $\log k = \left(-\frac{E_a}{2.303RT} \right) \frac{1}{T} + \log A$

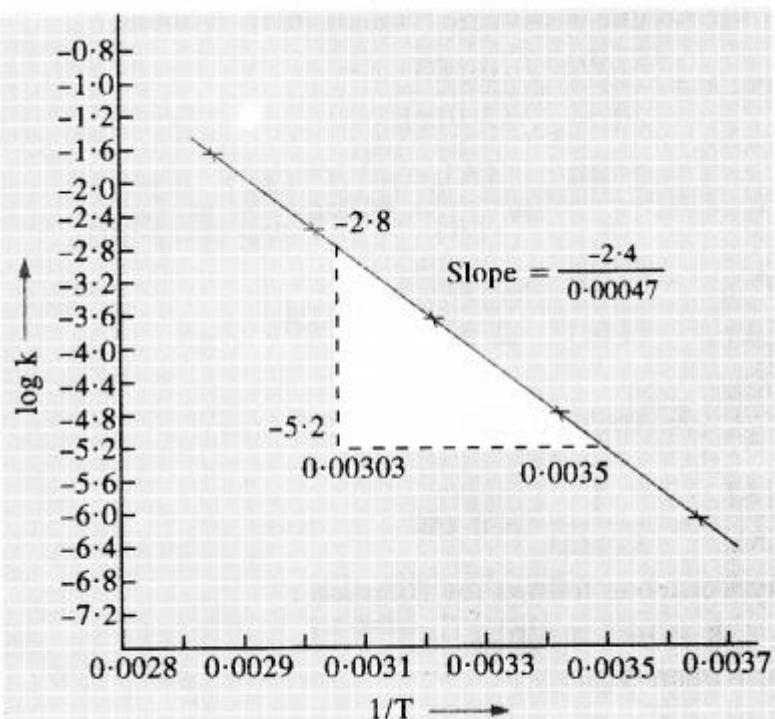


Figure. Graph of log k Vs 1/T

$\log A =$ value of intercept on y-axis *i.e.*, on the k -axis.

$$= (-1 + 7.2) = 6.2$$

$$[y_2 - y_1 = -1 - (-7.2)]$$

Frequency factor,

$$A = \text{antilog } 6.2 = 1585000 = 1.585 \times 10^6 \text{ collisions s}^{-1}$$

The values of rate constant k can be found from the graph as follows :

T	1/T	Values of log k (from graph)	Values of k
303	0.003300	- 5.2	$6.31 \times 10^{-5} \text{ s}^{-1}$
323	0.003096	- 2.8	$1.585 \times 10^{-3} \text{ s}^{-1}$

Question 23.

The rate constant for the decomposition of a hydrocarbon 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 the pre-exponential factor.

Answer:

Here, $k = 2.418 \times 10^{-5} \text{ s}^{-1}$,

$E_a = 179.9 \text{ kJ mol}^{-1}$, $T = 546 \text{ K}$, $A = ?$

According to Arrhenius equation,

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

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

$$= (-5 + 0.3834) + 17.2081 = 12.5924 \text{ s}^{-1}$$

$$\text{or, } A = \text{Antilog } (12.5924) \text{ s}^{-1} = 3.912 \times 10^{12} \text{ s}^{-1}$$

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} .

Answer:

For the first-order reaction :

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]} \quad \text{or} \quad \log \frac{[A]_0}{[A]} = \frac{k \times t}{2.303}$$

$$k = 2.0 \times 10^{-2} \text{ s}^{-1}; t = 100 \text{ s}, [A]_0 = 1.0 \text{ mol L}^{-1} = 1.0 \text{ M}$$

$$\log \frac{[A]_0}{[A]} = \frac{(2.0 \times 10^{-2} \text{ s}^{-1}) \times (100 \text{ s})}{2.303} = 0.8684.$$

$$\frac{[A]_0}{[A]} = \text{Antilog } 0.8684 = 7.3858 ; [A] = \frac{[A]_0}{7.3858} = \frac{(1 \text{ M})}{7.3858} = \mathbf{0.135 \text{ M}}$$

Question 25.

Sucrose decomposes in acid solution into glucose and fructose according to the first-order rate law with $t_{1/2} = 3.0$ hrs. What fraction of the sample of sucrose remains after 8 hours? (C.B.S.E. Sample Paper 2011)

Answer:

$$\text{For the first order reaction ; } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{(3.0 \text{ hr})}$$

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]} \quad \text{or} \quad \log \frac{[A]_0}{[A]} = \frac{k \times t}{2.303}$$

$$\log \frac{[A]_0}{[A]} = \frac{0.693}{(3 \text{ hr})} \times \frac{(8 \text{ hr})}{2.303} = 0.8024$$

$$\frac{[A]_0}{[A]} = \text{Antilog } 0.8024 = 6.3445$$

$$\text{or} \quad \frac{[A]}{[A]_0} = \frac{1}{6.3445} = \mathbf{0.158}$$

Question 26.

The decomposition of a hydrocarbon follows the equation :

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

Calculate the energy of activation (E_a).

Answer:

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

$$\text{According to given data ; } k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000 \text{ K}/T}$$

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

$$\text{or} \quad E_a = (28000 \text{ K}) \times (R) = (28000 \text{ K}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = \mathbf{232.792 \text{ kJ mol}^{-1}}.$$

Question 27.

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

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

Calculate the E_a for the reaction. At what temperature will the half-life period be 256 minutes?

Eduranka.com/chemistry

Answer:

Step I. Calculation of activation energy (E_a)

According to Arrhenius equation ; $k = Ae^{-E_a/RT}$.

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

The given eqn. is $\log k = 14.34 - \frac{1.25 \times 10^4 (\text{K})}{T}$

On comparison : $\frac{E_a}{2.303RT} = \frac{1.25 \times 10^4 (\text{K})}{T}$

$$E_a = 1.25 \times 10^4 \times 2.303 \times 8.314 (\text{J mol}^{-1})$$

$$= 239,339 \text{ J mol}^{-1} = \mathbf{239.339 \text{ kJ mol}^{-1}}$$

Step II. Calculation of desired temperature

For first order reaction ; $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{(256 \text{ min})} = \frac{0.693}{(256 \times 60\text{s})} = 4.51 \times 10^{-5} \text{ s}^{-1}$.

According to Arrhenius theory, $\log k = 14.34 - \frac{1.25 \times 10^4}{T}$

$$\log (4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^4}{T} ; -4.35 = 14.34 - \frac{1.25 \times 10^4}{T}$$

$$\frac{1.25 \times 10^4}{T} = 14.34 + 4.35 = 18.69 \text{ or } T = \frac{1.25 \times 10^4}{18.69} = \mathbf{669 \text{ K}}$$

Question 28.

The decomposition of A into the product has a 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 $1.5 \times 10^4 \text{ s}^{-1}$? (C.B.S.E. Sample Paper 2011)

Answer:

According to Arrhenius equation,

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

$$k_1 = 4.5 \times 10^3 \text{ s}^{-1}; k_2 = 1.5 \times 10^4 \text{ s}^{-1}; T_1 = 10^\circ\text{C} = 283 \text{ K.}$$

$$E_a = 60 \text{ kJ mol}^{-1} = 60000 \text{ J mol}^{-1}.$$

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{(60000 \text{ J mol}^{-1})}{2.303 \times (8.314 \text{ J mol}^{-1})} \left(\frac{T_2 - 283}{283 T_2} \right)$$

$$\log 3.333 = 3133.62 \left(\frac{T_2 - 283}{283 T_2} \right)$$

$$\frac{0.5288}{3133.62} = \frac{T_2 - 283}{283 T_2} \quad \text{or} \quad \frac{0.5288 \times 283}{3133.62} = \frac{T_2 - 283}{T_2}$$

$$1 - \frac{283}{T_2} = 0.04776 \quad \text{or} \quad T_2 = \frac{283}{1 - 0.04776} = \frac{283}{0.95224}$$

$$T_2 = 297.19 \text{ K} = (297.19 - 273.0) = \mathbf{24.19^\circ\text{C.}}$$

Question 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 $4 \times 10^{10} \text{ s}^{-1}$, calculate k at 318 K and E_a .

Answer:

Step I. Calculation of activation energy

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

At 298 K ; $k_{(298K)} = \frac{2.303}{t} \log \frac{100}{90}$

At 308 K ; $k_{(308K)} = \frac{2.303}{t} \log \frac{100}{75}$; $\frac{k_{(308K)}}{k_{(298K)}}$

$$= \frac{\log \frac{100}{75}}{\log \frac{100}{90}} = \frac{0.1249}{0.0458} = 2.73$$

According to Arrhenius theory, $\log \frac{k_{(308K)}}{k_{(298K)}} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

$$\log 2.73 = \frac{E_a}{2.303R} \left[\frac{308 - 298}{298 \times 308} \right]$$

$$E_a = \frac{0.4361 \times 2.303 \times (8.314 \text{ J mol}^{-1}) \times 298 \times 308}{10}$$

$$= 76640 \text{ J mol}^{-1} = \mathbf{76.640 \text{ kJ mol}^{-1}}.$$

Step II. Calculation of rate constant

According to Arrhenius equation, $\log k = \log A - \frac{E_a}{2.303 RT}$

$$\log k = \log(4 \times 10^{10}) - \frac{(76640 \text{ J mol}^{-1})}{2.303 \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times (318 \text{ K})}$$

$$\log k = 10.6021 - 12.5870 = -1.9849$$

$$k = \text{Antilog}(-1.9849) = \text{Antilog}(\bar{2}.0151) = \mathbf{1.035 \times 10^{-2} \text{ s}^{-1}}.$$

Question 30.

The rate of a particular reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$). (C.B.S.E. Outside Delhi 2013)

Answer:

According to Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]; T_1 = 293 \text{ K}, T_2 = 313 \text{ K}$$

$$\log \frac{4}{1} = \frac{E_a}{2.303 \times (8.314 \text{ J mol}^{-1} \text{K}^{-1})} \left[\frac{1}{293 \text{ K}} - \frac{1}{313 \text{ K}} \right]$$

$$\log 4 = \frac{E_a}{2.303 \times (8.314 \text{ J mol}^{-1})} \times \frac{20}{293 \times 313}$$

$$0.6021 = \frac{E_a}{2.303 \times (8.314 \text{ J mol}^{-1})} \times \frac{20}{293 \times 313}$$

$$E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313 (\text{J mol}^{-1})}{20}$$

$$E_a = 5.2863 \times 10^4 \text{ J mol}^{-1} = \mathbf{52.863 \text{ kJ mol}^{-1}}$$

We hope the NCERT Solutions for Class 12 Chemistry Chapter 4 Chemical Kinetics help you. If you have any query regarding NCERT Solutions for Class 12 Chemistry Chapter 4 Chemical Kinetics, drop a comment below and we will get back to you at the earliest.